

# Nanocomposite Tutorial

Gonzalo J. Villegas-Rodríguez<sup>†</sup> and Eduardo R. Cruz-Chú<sup>\*,†,‡</sup>

*\*Laboratorios de Investigación y Desarrollo, Facultad de Ciencias y Filosofía, Universidad Peruana Cayetano Heredia, Lima, Perú.*

*†Computational Science and Engineering Laboratory, ETH-Zürich, Zürich, Switzerland.*

E-mail: [eduardo.cruz@upch.pe](mailto:eduardo.cruz@upch.pe)

# Contents

<b>1 Installation</b>	<b>4</b>
<b>2 Usage</b>	<b>5</b>
<b>3 Random Grid</b>	<b>8</b>
<b>4 geoCollapse</b>	<b>9</b>
<b>5 Phantom Volume</b>	<b>11</b>
<b>6 Simulations</b>	<b>13</b>
6.1 Force Collapse . . . . .	14
6.2 Equilibration 1 . . . . .	16
6.3 Annealing 1 . . . . .	17
6.4 Opening . . . . .	19
6.5 Equilibration 2 . . . . .	21
6.6 Annealing 2 . . . . .	22
6.7 Expand/Contract . . . . .	23
6.7.1 Expand . . . . .	24
6.7.2 Contract . . . . .	25
<b>7 Appendix</b>	<b>27</b>
7.1 Equilibration/A annealing . . . . .	27
7.2 Force Collapse . . . . .	30
7.3 Expand . . . . .	33
7.4 Contract . . . . .	36
7.5 Grid . . . . .	38

One of the most challenging tasks in materials science research is the development of novel nano-composites; that is, new materials that combine different components and phases, their dimensions being within the nanoscale range. An accurate description of the molecular interactions within nano-composites is central to foster the development of nano-composite applications. In this regard, computer simulations play an important role, as they reveal most details about nano-systems and their interactions in equilibrium and mechanically-stressed conditions.

Here, we present the basic operations of **nanocomposite**, a computational tool to model high molecular weight polymers as well as the insertion of different components. **nanocomposite** provides a set of commands to build all-atom nanocomposite models to be used in molecular dynamics (MD) simulations. Below we present a brief description of the **nanocomposite** tool. To test the commands, we provide two sets of examples in the compressed files **nncTest.zip** and **nncBuild.zip**.

This tutorial accompanies an article<sup>7</sup> in which two nano-composites were built. Thus, it is highly recommended to read the article. Figure 1 provides a workflow of the sequence of commands of **nanocomposite**. It may look a bit convoluted, but we will go through each step in this tutorial.

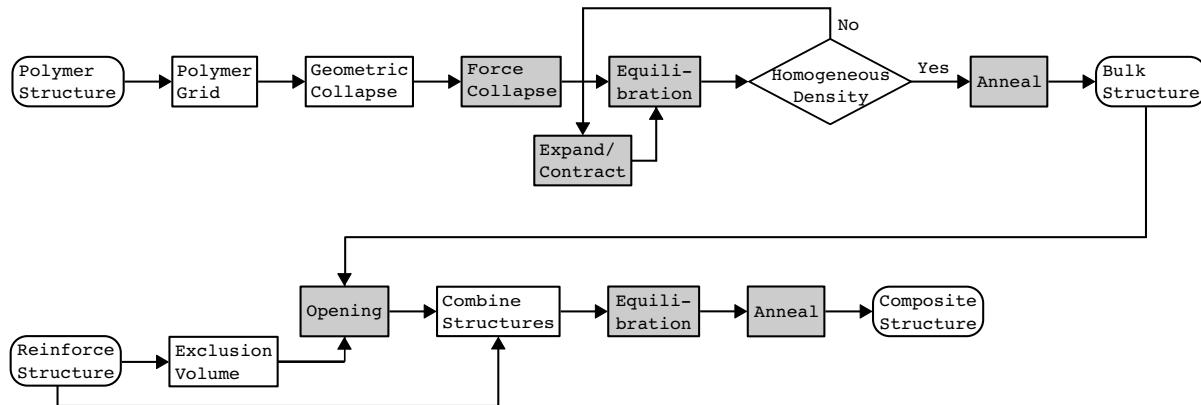


Figure 1: Workflow to build a the model of a nano-composite with the tools described in this tutorial which are part of the plug-in **nanocomposite**. The grey boxes mean the step involves running a MD simulation with NAMD.

# 1 Installation

The **nanocomposite** tool is integrated into a TCL-package in VMD<sup>?</sup> and sets up configuration files to carry out molecular dynamics (MD) simulations in NAMD.<sup>?</sup> Therefore, before starting this tutorial, you are required to have a working knowledge of VMD and NAMD. For details about VMD and NAMD, you can follow:

- <https://www.ks.uiuc.edu/Research/vmd/>
- <https://www.ks.uiuc.edu/Research/namd/>

The installation of **nanocomposite** proceeds as follows:

1. Download **nanocomposite** into your local computer:

```
git clone https://github.com/cruzchue/nanocomposite
```

2. Open VMD, select **Extensions → Tk Console** (Figure 2) and specify the location of **nanocomposite**:

```
lappend :: auto_path $DIR
```

where \$DIR is the path to the **nanocomposite** directory in your computer

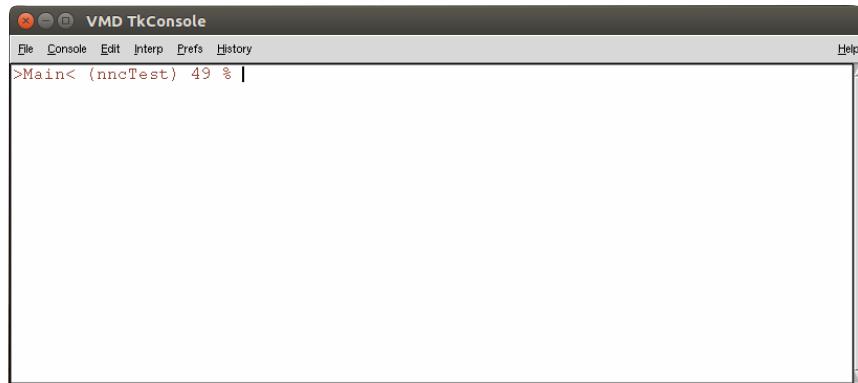


Figure 2: Tk console. To open it on VMD select **Extensions → Tk Console**. Here you will be able to type the commands of this tutorial.

### 3. Load the **nanocomposite**:

```
package require nanocomposite
```

That is it. To avoid specifying the path of **nanocomposite** every time you use it, you can also add the line “`lappend :: auto_path $DIR`” in your `.vmrdrc` file, which is located in your home directory.

## 2 Usage

Once loaded, the different routines can be called using the prefix **nnc** as follows:

```
nnc command [ options ]
```

Currently, **nanocomposite** provides four commands:

- *randomGrid* : builds a spaced grid of randomly oriented structures.
- *geoCollapse* : collapses structures by using translations and rotations.
- *phantomVolume* : delineates an exclusion grid.
- *namdConfiguration* : creates NAMD configuration files to perform MD simulations.

Each **nanocomposite** command provides different options. For example, the command *geoCollapse* can be performed using only translations (Figure 3a) or translations and rotations (Figure 3b); the latter option results in a more compact system but it also requires more calculations; thus, the user can choose the aggregation algorithm, either a “quick” scan (20 minutes) using only translations or a “long” calculation (2 hour) using translations and rotations. All benchmark times reported in this tutorial were performed with a Lenovo laptop with an Intel® Core i7 - 2.10 GHz processor, 8 GB of RAM, and Linux Ubuntu 18.02.

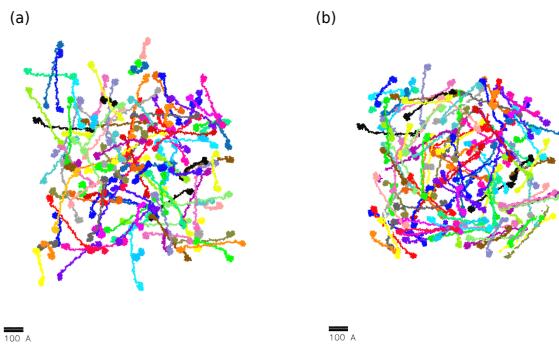
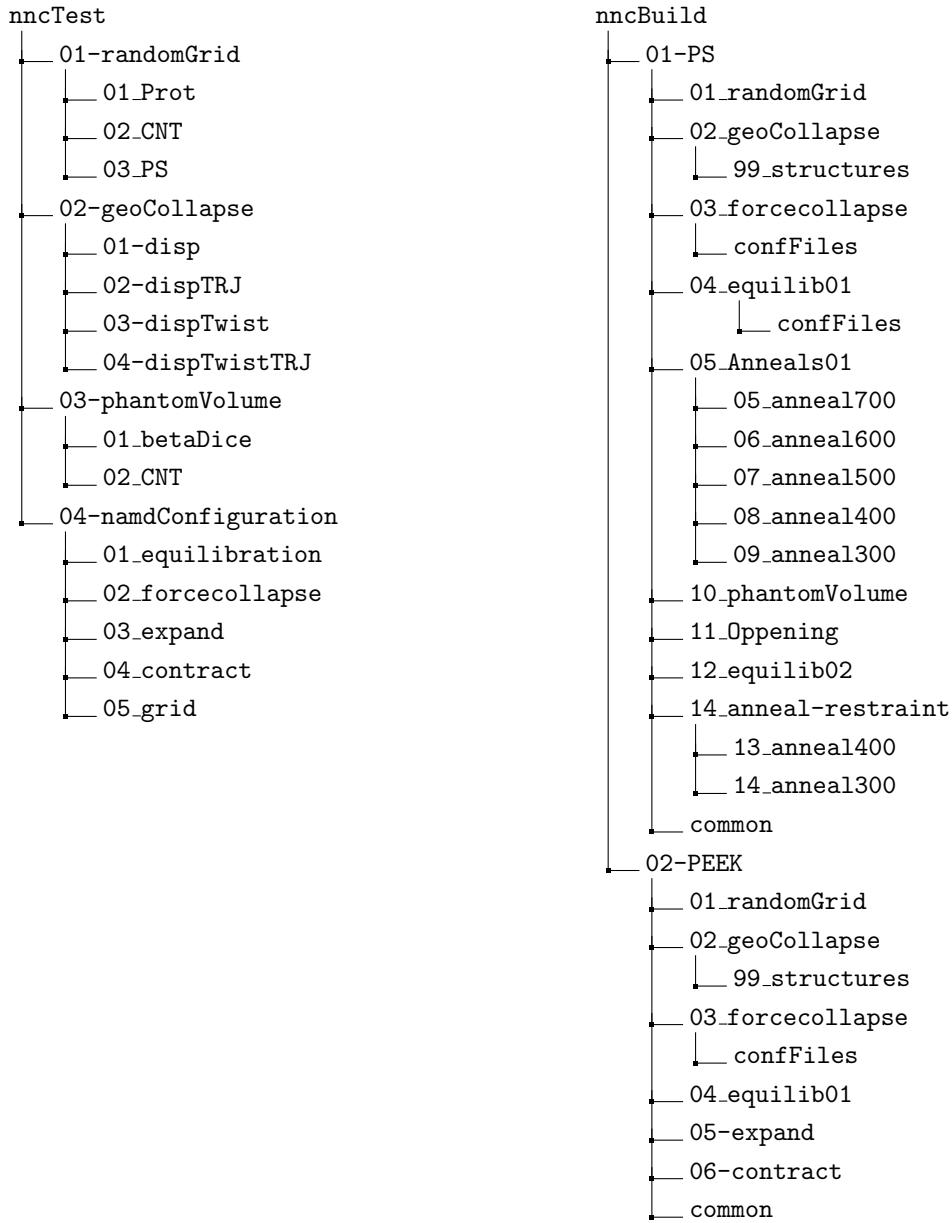


Figure 3: Results of *geoCollapse* algorithm with translations (a) and translations and rotations (b). In both aggregates, there is at least 10 Å of empty space among molecules. Rotations in (b) are activated with the option `-scanAngle`, which allows polymers to aggregate into a more compact structure. Scale bars measure 100 Å.

The following sections present examples of the **nanocomposite** commands. First, you have to unzip the compressed files NNCTEST.ZIP and NNCBUILD.ZIP, each one contains several sub-directories with specific examples, which are explained throughout the tutorial. For each exercise, we also provide a tcl-file named `run[COMMAND].tcl`, which contains all the **nanocomposite** commands used.



You can execute the `run[COMMAND].tcl` scripts by moving to the directory and typing:

```
vmd -dispdev text -e ./run[COMMAND].tcl
```

in a linux terminal. Alternatively, you can also execute them from the Tk console in VMD by typing:

```
source ./run[COMMAND].tcl
```

In the following sections we are going to describe these examples. First, the directory `nncTest` contains examples of **nanocomposite** commands using a silk protein from the *Nephila clavipes* spider. Then, the directory `nncBuild` guide us to build a two-phase nanocomposites using Polystyrene (PS), Polyether Ether Ketone (PEEK), and Carbon Nanotubes (CNT). The polymer models of PS and PEEK are shown in Figure 4. The exercises in `nncBuild` require MD simulations, which may be time consuming, depending on the computer you are using.

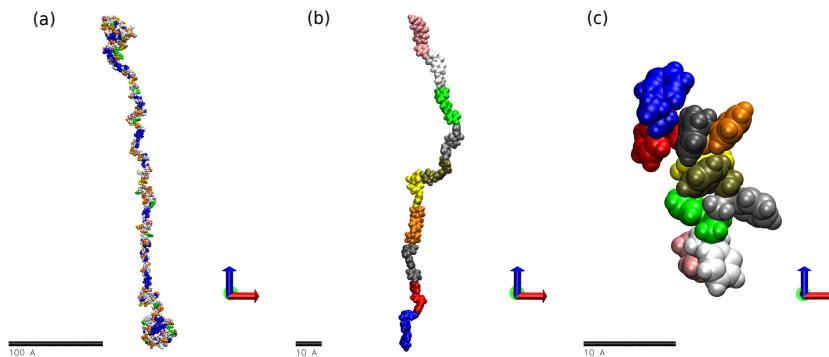


Figure 4: Polymers used in this tutorial. All the polymers are origin centered and aligned with the z-axis (blue arrow). Each color represents a polymer residue. **(a)** Spider silk protein (Sp1) has 593 aminoacids and is  $\approx 350 \text{ \AA}$  long. This is the reason why a  $400 \text{ \AA}$  spacing is used when the grid in section 3 is built. Scale bar measures  $100 \text{ \AA}$ . **(b)** The PEEK we use has 10 residues and is  $\approx 127 \text{ \AA}$  long. Scale bar measures  $10 \text{ \AA}$ . **(c)** The PS we use has 10 residues and is  $\approx 23 \text{ \AA}$  long. Scale bar measures  $10 \text{ \AA}$ .

### 3 Random Grid

Command:

```
nnc randomGrid [ options ]
```

Options:

- psf : structure PSF file
- coor : coordinate PDB or COOR file
- lengthGrid : distance between grid points (in angstrom)
- iGrid : number of polymer repeats in the X direction (integer)
- jGrid : number of polymer repeats in the Y direction (integer)
- kGrid : number of polymer repeats in the Z direction (integer)
- seed : seed value to generate random angles used in the polymer distribution. Default value: current process number (pid)
- outName : name of the output files.

This command creates a cubic grid of randomly oriented structures. The distance between adjacent polymers is stated by the option **-lengthgrid**. The number of polymer repeats in the X, Y and Z directions is defined in **-iGrid**, **-jGrid** and **-kGrid**; respectively. The value in **-seed** initializes a random number generator for the rotations.

As example to generate a grid, we use the spider silk protein from Nephilia clavipes (Sp1, Figure 4a). Move to the directory **nncTest/01-randomGrid**, here you will find three directories. Each directory has PDB and PSF files for spider silk, nanotubes, and polystyrene.

Move to directory **nncTest/01\_randomGrid/01\_Prot**. Open **Sp1.300K.pdb** with VMD, you will find a single protein chain. This structure is centered at the origin and aligned with the Z-axis. This is important for the command to work properly (Figure 4a). Open the Tk console and type the following commands:

```
package require nanocomposite

nnc randomGrid -psf Sp1.300K.psf -coor Sp1.300K.pdb -lengthGrid 400 -iGrid 5 -jGrid 5
-kGrid 5 -outName grid5x5x5
```

Three files are going to be generated: **grid5x5x5.psf**, **grid5x5x5.coor** and **grid5x5x5.rp**. The first two files are the structure and coordinate files for the grid (Figure 5a). The options **-psf** and **-coor** are used to select the structure and coordinates files of the spider silk. The distance

between every adjacent polymer is 400 Å (option `-lengthGrid`). Sp1 is about 350 Å long, the grid spacing must be larger value than the polymer's length to avoid collisions when they are rotated. As we chose 5 repeats in each direction, you should be able to see 125 polymers chains.

`grid5x5x5.rp` is the reference point file, this file will be necessary in following steps. The `randomGrid` command uses euler angles for the rotations, the reference is changed every time the polymers are rotated. You can also run the script `runRandomGrid.tcl`, make sure to change the directory directions in the script before running it.

#### IMPORTANT:

- a) If you are not sure when to run this command check Figure 1.
- b) Your polymer should be centered at {0 0 0} and aligned with the Z-axis for the command to work properly.
- c) It is not needed to add suffix names. For example, instead of typing `-outName output.pdb` you should type `-outName output`, because other files will be created with such name besides the COOR file.
- d) For the every command in this tutorial the input distance is in Å.

## 4 geoCollapse

Command:

```
nnc geoCollapse [ options ]
```

Options:

- `-psf` : structure PSF file.
- `-coor` : coordinate PDB or COOR file.
- `-outName` : name of the output files.
- `-rp` : reference point file, used for rotations. Generated with `randomGrid` in section 3.
- `-gapLength` : minimum distance to maintain between polymers during aggregation. Default value: 10 Å.
- `-scanAngle` : rotating angle step to find best orientation for next move. Angles in degrees. Default value : -1 (no rotations).
- `-vortexPoint` : point to aggregate molecules. Default value : “0 0 0”.

**-trj** : write trajectory. If not stated, no trajectory will be saved, only the last frame is saved (Figure 5e).

To generate a polymer melt, all the polymers from our previously generated grid (see section 3) must come together. Use the `geoCollapse` command works by (1) calculating the empty space surrounding each polymer, (2) moving the polymer within that empty space towards the aggregation point, and (3) rotating the polymer if it were blocked and repeating (1) and (2). `-scanAngle` is set to calculate rotations. Once the polymer can no longer move to the center (because there are atoms within the distance stated with `-gapLength`), the polymer will be rotated. If no rotation in a total turn meets the condition, then the polymer is no longer moved. Figure 5 shows snapshots of `geoCollapse` working.

`geoCollapse` starts moving the polymers that are closer to the aggregation point, defined with the option `-vortexPoint`. Our grid is centered at  $\{0\ 0\ 0\}$ , thus we can use the default value. The minimum distance between polymers is set with `-gapLength`. If this value is too

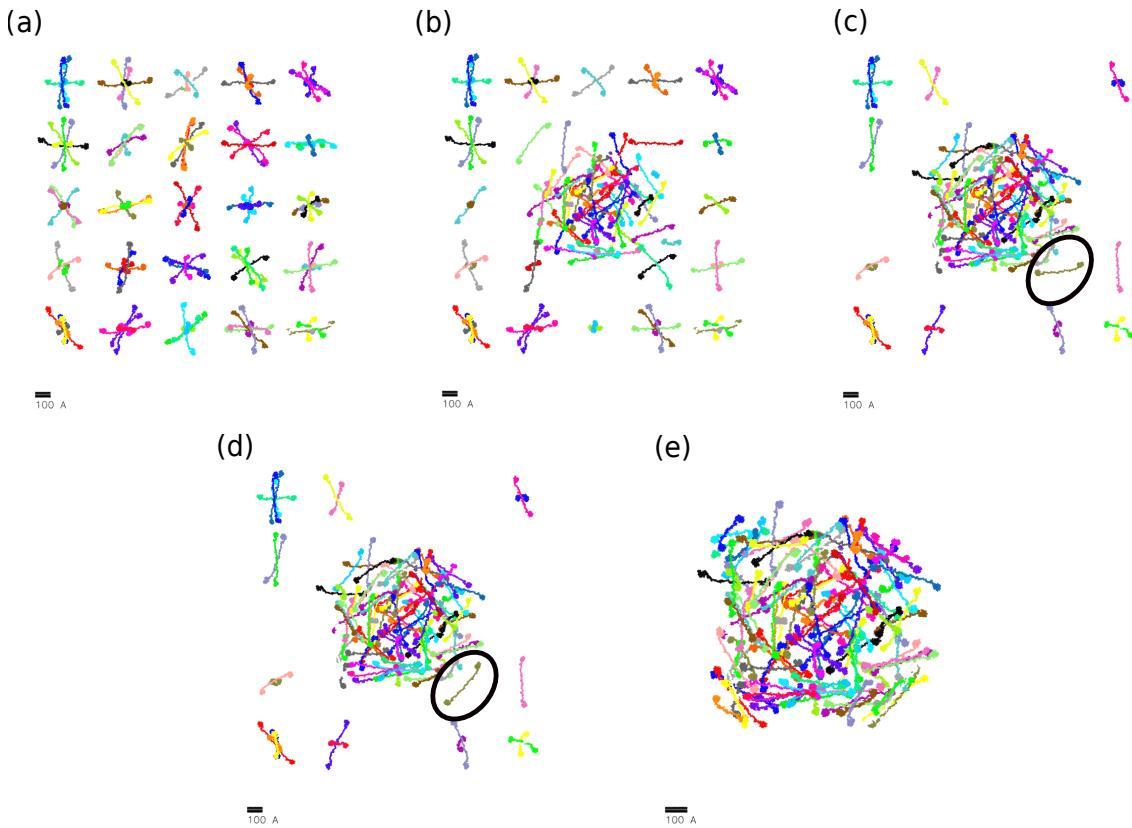


Figure 5: Polymer aggregation with `geoCollapse`. (a) 5x5x5 grid of spider silk proteins which was created with `randomGrid`. (b), (c) and (d) are snapshots of `geoCollapse` in action and (e) is the final result. As explained in section 4, the aggregation starts with the polymers that are closer to the center. If the option `-scanAngle` is selected the polymers will rotate and further approach the center if possible. Rotation of the black-circled polymer can be observed in (c) and (d). In (e) the distance between every polymer should be of at least 10 Å, as stated with `-gapLength`. All scale bars measure 100 Å.

large the polymers might not get near at all.

Move to the directory `nncTest/02-geoCollapse`, here you will find five directories. Copy the generated files in the previous section to `nncTest/02-geoCollapse/99-structures`. We can aggregate our polymer chains with or without rotation and save a trajectory. If “Twist” and “TRJ” appear in the names it means with rotations and saving the trajectory, respectively.

Move to directory `nncTest/02-geoCollapse/04-dispTwist`. Open VMD, open the Tk console and type

```
package require nanocomposite

set psfFile "../99-structures/grid5x5x5.psf"
set pdbFile "../99-structures/grid5x5x5.pdb"
set rpFile "../99-structures/grid5x5x5.rp"

nnc geoCollapse -psf $psfFile -coor $pdbFile -rp $rpFile -gapLength 10
-scanAngle 30 -outName aggregateGRID
```

A COOR file should have been generated. The minimum distance between every polymer chain should be at least 10 Å, your result should be similar to Figure 5e. From Figure 3 you can notice that the aggregation is more effective when you allow rotations with `-scanAngle`. Rotations with a small step angle should lead to a better aggregation, but it is computationally costly and you might get a similar result by using a larger step angle like 30°. To obtain these results you can run the script `runGeoCollapse.tcl`, make sure to change the directory directions in the script before running it.

The structure that is generated with this command should undergo the Force Collapse step which involves running MD simulations. Force Collapse simulations are described in subsection 6.1.

#### IMPORTANT:

1. If you are not sure when to perform a *geoCollapse* step check Figure 1.
2. 02-dispTRJ and 04-dispTwistTRJ examples have the `-trj` flag active; thus trajectory files are generated. To save the trajectory files make sure to type the flag `-trj` at the end. The generated DCD files are large, about 6 GB in size. Before executing the command, make sure your harddrive has available space.

## 5 Phantom Volume

Command:

```
nnc phantomVolume [ options ]
```

Options:

-psf : structure PSF file.

-coor : coordinate PDB or COOR file.

-outName : name of the output files.

-within : distance covering the molecule. Default value: 5 Å.

-dxRes : resolution of exclusion grid. Default value : 2 Å

phantomVolume creates a DX file which contains an exclusion grid with the contour of a structure. The DX file is used in the Opening step (Figure 1), to create a cavity in an amorphous melt. This step is further described in subsections 6.4 and 7.5.

For this example, we will create a exclusion grid using a carbon nanotube. Move to the directory `nncTest/03-phantomVolume/02_CNT`, open VMD, open the Tk console and type

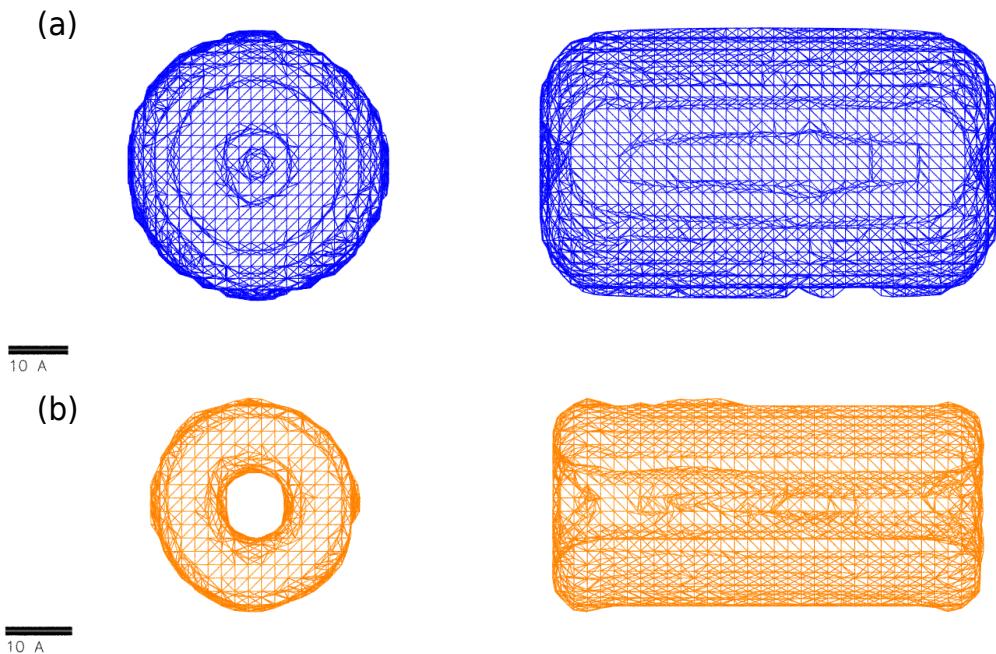


Figure 6: Force grids generated with phantomVolume. Visualization with VMD. Front view on the left and side view on the right. The grids fill a volume of (a) 10 Å and (b) 5 Å within the CNT. That is why you are able to see a hole in (b). When GRID-SMD simulations are run with these grids the forces will point outwards, this is because the isovalue are larger near the structure contour. Distance between every grid adjacent point is 2 Å. Scale bars measure 10 Å.

```

package require nanocomposite

nnc phantomVolume -psf CNT.psf -coor CNT.pdb -within 10.0 -outName CNT

```

This generates the file `CNT.dx` (Figure 6a). The isovalue of the grid are higher at the center of the nanotube compared to the extremes. Verify this by creating representations with different isovalue with *Graphical Representations* in VMD.

We use the options `-psf` and `-coor` to specify the input structure for the grid. The borders of the grid are determined with the option `-within`. For this example, the grid in Figure 6a comprises a volume within 10 Å of the carbon nanotube. The grid resolution is 2 Å, which is the default value, modifiable with option `-dxRes`).

The hole of the CNT is covered by the grid. Now we will obtain a hollow grid by using a lower value for `-within`. Type in the Tk console:

```
nnc phantomVolume -psf CNT.psf -coor CNT.pdb -within 2.0 -outName CNT-2
```

When you visualize `CNT-2.dx` with VMD and change the isovalue in *Draw Style* you will observe the hollow contour (Figure 6b). You may wonder which of both grids is better. There is less risk of collision between the polymer melt and the inserted structure if the grid is larger. Also it is expected that in experiments the polymer enters the CNT hole. Therefore, we suggest to use the larger value for `-within`.

You can run the script `runPhantomVolume.tcl` instead of typing the commands, just make sure to change the directory directions in the script. Alternatively, an example to create a grid for a parallel sheet of polyalanines is available in `nncTest/03-phantomVolume/01_betaDice`.

For more information about force grids you can check the User-Defined Forces tutorial in the NAMD webpage.

## IMPORTANT

- a) This command has to be run whenever you wish to combine two structures. A grid created with `phantomVolume` is used in MD simulations in subsection 6.4.
- b) The grid we mention in this subsection is an exclusion grid, different from the grid we mentioned in section 3.
- c) For every command in this tutorial the input distance has to be in Å.

## 6 Simulations

In this section we are going to run MD simulations. The `namdConfiguration` is used to create the configuration files. The simulations will follow the order to build the nano-composite

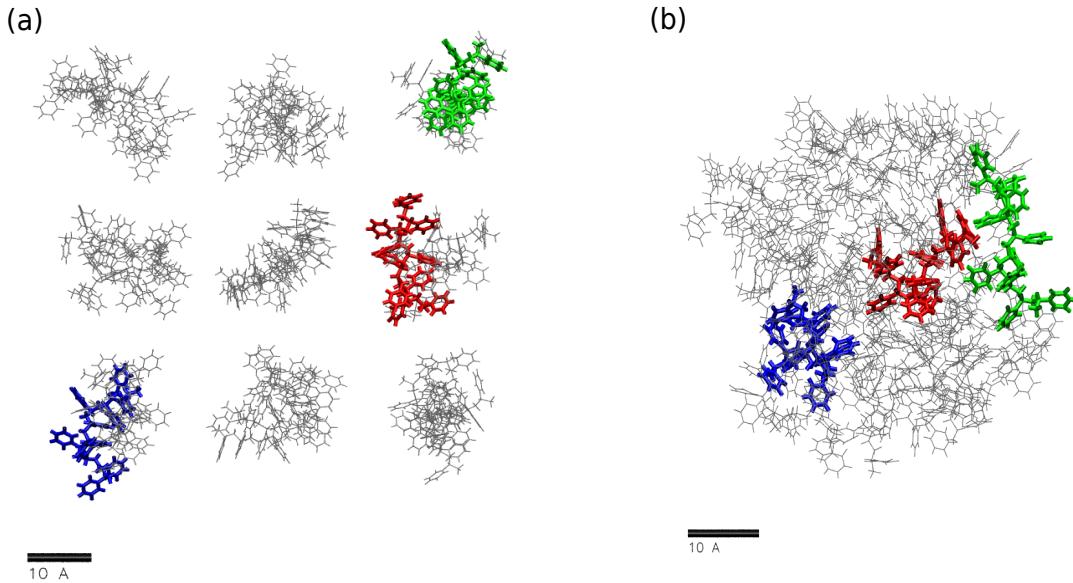


Figure 7: Force Collapse step for PS. The colored polymers are the same in each frame. **(a)** Initial frame, this is the result of geoCollapse. **(b)** Final frame, as the polymer is short there is no significant interwinding. This will be evident in the following equilibration step, and is the main reason why no Expand/Contract step is required. Scale bars measure 10 Å.

(Figure 1). Keep in mind that the chosen system is small so that simulations do not require much run time.

Before you start this section you can apply what you have learned so far. Create a 3x3x3 grid (section 3) of a PS 10-mer provided in `02-smallCNT/01-PS/common`, and aggregate the polymers with geoCollapse (section 4). The required files are also included in the directories.

The main purpose of this tutorial is to explain the workflow (Figures 1) and reasoning behind every step to build the nano-composite. Keep in mind that the parameters we have used work well for our small system, you may need to adjust the parameters for a larger system.

## 6.1 Force Collapse

After the Geometric Collapse, we will further aggregate the polymers by running a Force Collapse (FC) simulation. Move to the directory `nncBuild/01-PS/03_forcecollapse`, there you will find the directory `confFiles`. Move to this directory and you will find an script which creates configuration files. Run the script with VMD or type in the Tk console:

```
package require nanocomposite

nnc namdConfiguration -type forcecollapse -coor ../../common/aggregateGRID.pdb
-psf ../../common/PS3x3x3.psf -par ../../common/par_PNC.prm -outName forcecol -temp 700
```

```
-minsteps 10000 -runsteps 400000 -cteForce 0.072 -numConfFiles 10
```

For a more in-depth explanation of this code check subsection 7.2. Now, we will run a non-periodic MD simulation for 0.4 ns at 700 K which will be started from the geoCollapse output. And the generated files will have the name “forcecol”. The files required to run the simulations are found in the directory `nncBuild/01-PS/common`.

Create the directory `nncBuild/01-PS/03-forcecollapse/00/`. Copy `forcecol.000.namd` and move to the created directory. Now run the simulation with:

```
namd2 forcecol.000.namd > forcecol.000.log &
```

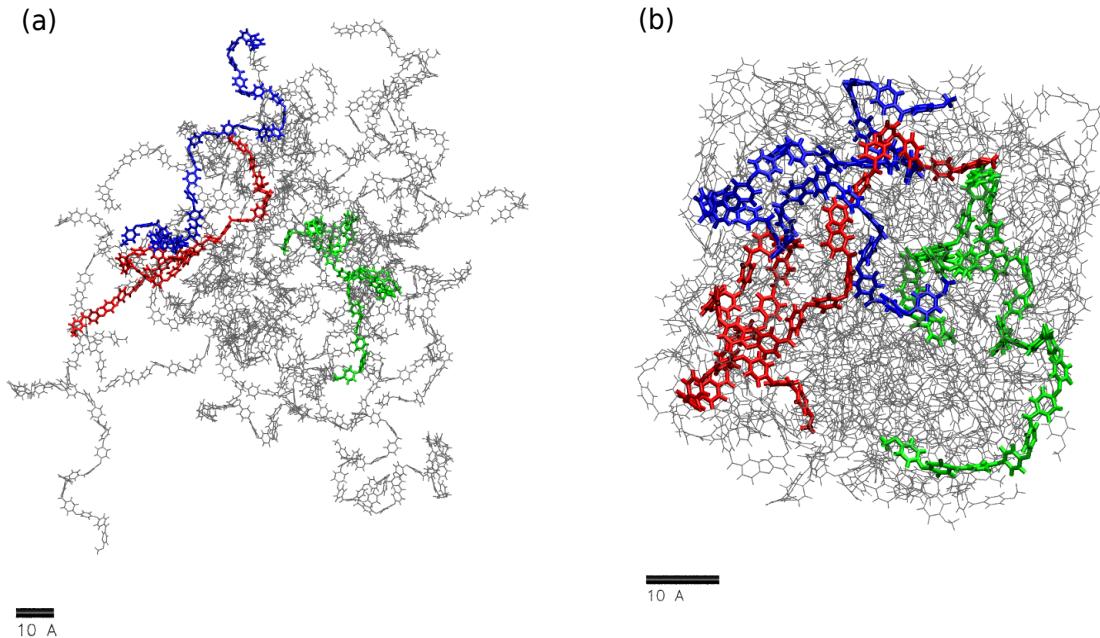


Figure 8: Force Collapse step for PEEK. The colored polymers are the same in each frame. **(a)** Initial frame, this is the result of geoCollapse. **(b)** Final frame, there is polymer interwinding, this was not seen for PS bulk because PS polymer is shorter (Figure 7). Common polymers have more than 10 residues, when you try to build your nanocomposite you might encounter something similar to **(b)** after the Force Collapse step. We do not try to build the nanocomposite with this polymer in this tutorial as the simulations need more computational power than PS simulations. Scale bars measure 10 Å.

You may use the suitable amount of cores to run the simulation, we used four cores with a benchmark time of 16 ns/day. The last frame of the simulation are provided, we run 0.4 ns. In case you need to restart the simulation just create the next directory (for example `nncBuild/01-PS/03-forcecollapse/01/`), copy the suitable NAMD configuration file to it and also the restart files (copy `forcecol.001.restart*` and `forcecol.001.namd` to `nncBuild/01-PS/03-forcecollapse/01/`); and run the simulation. The configuration files can be restarted from the previous one (see section 7).

We stopped the simulation when there was no major change in the volume for about 0.1 ns (Figure 7). In the simulation a force 5 pN force is applied to all carbon atoms outside a 36 Å edge box towards the box center. By default, the defined box has a volume that would give a density of  $1 \text{ g cm}^{-3}$  for your system. The main reason why the polymers did not enter the defined box is the high temperature, which is used to keep the polymer fluid. You might need to run the FC simulation at higher temperatures for long polymers. With short polymers, you can run the FC simulation at 700 K as it is easier to keep them fluid (Figure 7), 1000K is suggested for long polymers. In Figure 8, we observe interwinding for the PEEK Force Collapse step.

Next we should run an NVT Equilibration to probe if the system reaches homogeneous density (Figure 1).

## 6.2 Equilibration 1

After the Force Collapse step we will equilibrate our system. For this, we will simulate result of the Force Collapse step as an NVT ensemble. After that, we will decide whether we perform an Expand/Contract step or an Annealing step (Figure 1). Move to directory `nncBuild/01-PS/04_equilib01`, there you will find the directory `confFiles`, inside it there is a script to create NAMD configuration files. Make sure to copy the last restart files from the Force Collapse step to `confFiles`.

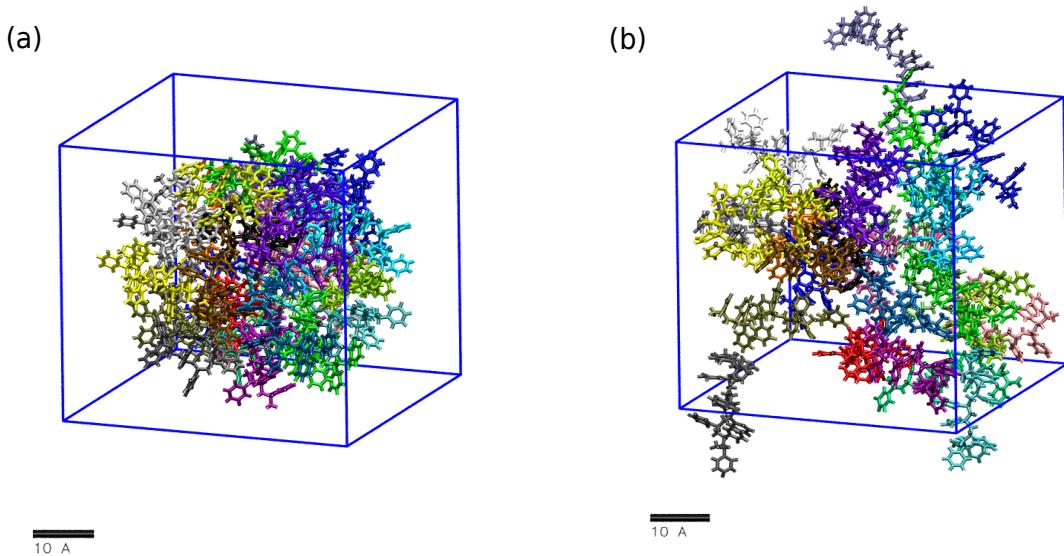


Figure 9: NVT Equilibration for PS. The blue cube is the 50x50x50 periodic box. **(a)** Initial frame, this is the result of FC. **(b)** Final frame. It is evident that the PS chains can fill the entire periodic box without restraint. Because of this we will go on with the Annealing step (subsection 6.3) and will not perform an Expand/Contract step. Scale bars measure 10 Å.

To create the configuration files type in the Tk console:

```
package require nanocomposite

nnc namdConfiguration -type equilibration -coor ../../common/aggregateGRID.pdb
-psf ../../common/PS3x3x3.psf -outName equilibrate -temp 1000 -runsteps 300000
-par ../../common/par_PNC.prm -minsteps 10000 -prevConf forcecol.004.restart
-numConfFiles 10 -ensemble NVT -a calculate
```

Ten files are created. Check file `equilibrate.000.namd`, you would run an NVT ensemble at 1000 K for 0.3 ns which is started from the restart files `forcecol.004.restart.coor`, `forcecol.004.restart.vel` and `forcecol.004.restart.dcd`. You should change `-prevConf forcecol.004.restart` for your suitable restart files from Force Collapse. Force Collapse was not a periodic simulation, in other words, there is no periodic box. As we want to run a periodic simulation we have to define the periodic box dimensions, for this we use the option `-a calculate` which opens `../../common/PS3x3x3.psf` and `forcecol.004.restart.coor`, and outputs the dimensions of the periodic box by executing `measure minmax $sel`

Create the directory 00 in `nncBuild/01-PS/04_equilb01` and copy the recently created NAMD configuration file `equilibrate.000.namd` to that directory. Then run the simulation with NAMD. We run 0.3 ns, we obtained constant energy and volume for more than 0.1 ns. From the trajectory it is clear that the polymer can fill the voids in the edges of the periodic box (Figure 9). There is no major interwinding, as expected for a short polymer. Then, we will proceed with the annealing and we will not go through the Expand/Contract step. Another way to find out if your system should go to an Expand/Contract step is to calculate the density of the periodic box and the density of a smaller origin-centered box.

## IMPORTANT

- a) If you are not sure when to run this MD simulation check Figure 1.
- b) In this subsection we run an NVT equilibration. An NPT simulation at high temperature could enlarge the periodic cell as they were not intertwined.
- c) We also provide the script `get-den.tcl` which calculates the density of a cubic region for a trajectory. One can use this script to decide if an Expand/Contract step is required.

### 6.3 Annealing 1

In this step we run NPT simulations at various decreasing temperatures. Once our system equilibrates at one temperature we will restart the simulation 100 K lower. At the end of the Annealing step we should have an equilibrated Polymer melt. Move to directory `nncBuild/01-PS/05_Anneals01/05_anneal700`, there you will find the directory `confFiles`. Move to this directory and run the script `runNamdConfiguration_1.tcl` with VMD or type in the Tk console:

```

package require nanocomposite

nnc namdConfiguration -type equilibration -coor ../../common/aggregateGRID.pdb
-psf ../../common/PS3x3x3.psf -outName ann700 -par ../../common/par_PNC.prm -temp 700
-minsteps 10000 -runsteps 2000000 -prevConf equilibrate.000.restart -numConfFiles 10
ensemble NPT -wrap 1

```

Ten files are created. With file `ann700.000.namd` you would run an NPT ensemble at 700 K for 0.3 ns which is started from the restart files `equilibrate.000.restart.coor`, `equilibrate.000.restart.vel` and `equilibrate.000.restart.xsc`. NAMD configuration files can be restarted sequentially, see subsection 7.1.

Create the directory 00 in `nncBuild/01-PS/05_anneal700` and copy the recently created NAMD file `equilibrate.000.namd` to it. Then run the simulation with NAMD. The results of a 2 ns simulation are provided. Total energy and volume converged. We performed annealing simulations at 600 K, 500 K, 400 K and 300 K for 0.5 ns each. For all simulations we reached constant volume and constant total energy. At 300 K we also reached constant RMSD. In the end we obtained a density of  $0.98 \text{ g cm}^{-3}$ , the density of the half-volume inner cube is  $0.97 \text{ g cm}^{-3}$ . This confirms that we did not need an Expand/Contract step to reach homogeneous density. You can see the final structure in Figure 10, this is what we call the **Polymer melt** or **Polymer bulk** (Figure 1). We provide an script (`get-den.tcl`) that calculates density within a cubic region which can be useful to tell if a system reaches homogeneous density.

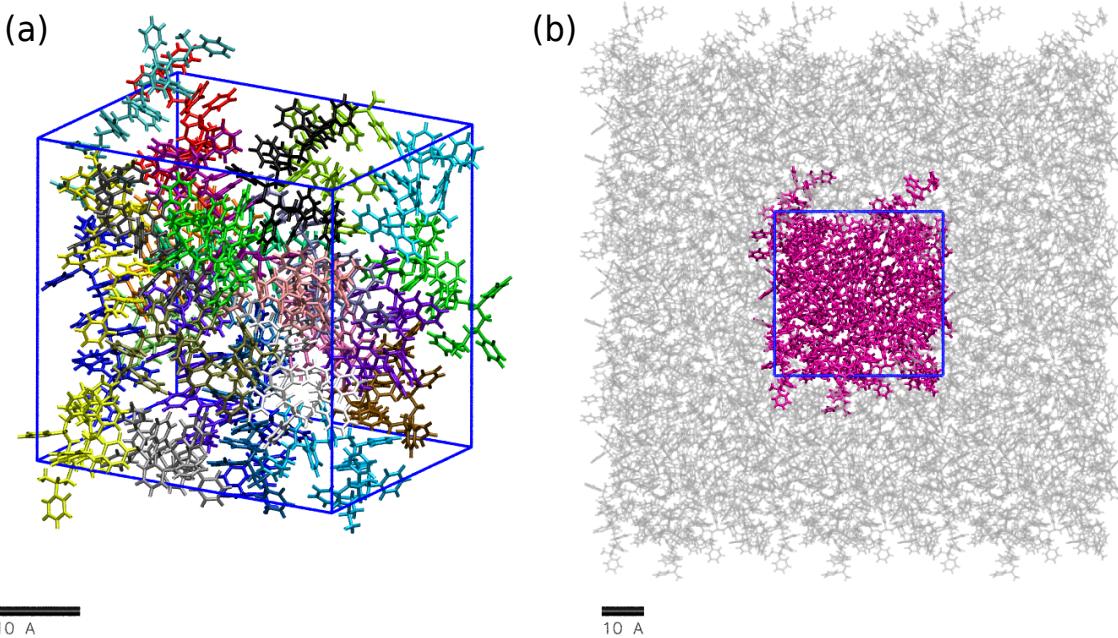


Figure 10: PS Polymer melt or Polymer bulk. This is the system we get after the Annealing step. The blue box is the periodic cell. (a) Each polymer is colored differently, they fill the periodic cell. (b) The system is shown (in purple) with the  $\pm x$  and  $\pm y$  periodic images (in gray). Scale bars measure 10 Å.

## 6.4 Opening

This step involves creating a grid of the reinforcement structure to insert in the polymer melt and opening a hole in the polymer melt. Practice what you learned in section 5 and create the grid for the CNT (CNT-inner.psf and CNT-inner.pdb) provided in the directory `nncBuild/01-PS/common`, leave the DX file in the same directory and name it CNT-inner.dx.

With the grid, we are going to run a GRID-SMD (GSMD) simulation. In this simulation a CNT-shaped hole will open in the polymer melt. First we need to create the NAMD configuration files. Move to directory `nncBuild/01-PS/11_opening`, there you will find the sub-directory `confFiles`. Run the following commands in the Tk console:

```
package require nanocomposite

nnc namdConfiguration -type grid -coor ../../common/aggregateGRID.pdb
-psf
../../common/PS3x3x3.psf -par ../../common/par_PNC.prm -outName opening -temp 600
-prevConf ann300.001.restart -minsteps 0 -runsteps 2000000 -gridforcefile
../../common/PSgrid.gforce -gridforcepotfile ../../10_phantomVolume/CNT-inner.dx
-numConfFiles 10
```

Ten files are created. You can check the configuration file `opening.000.namd`: a NPT ensem-

ble at 600 K for 1 ns. The simulation is started from the restart files `ann300.001.restart.xsc`, `ann300.001.restart.vel` and `ann300.001.restart.coor`. You should change `-prevConf ann300.001.restart` for your suitable restart files from the Annealing step. All NAMD configuration files are restarted from the previous configuration file. Forces will be applied to all the backbone carbons (defined with `-gridforcefile ..../common/PSgrid.gforce`) in order to take them out of the grid defined with `-gridforcepotfile ..../10_phantomVolume/CNT-inner.dx`. `..../common/PSgrid.gforce` is a pdb file in which the “beta” and “Occupancy” columns have a value of 1.0 (see subsection 7.5).

Run the simulation with NAMD. In the trajectory you will find that a hole opens in the middle of the polymer melt (Figure 11), find the best frame to insert the carbon nanotube. We chose the first frame in which there were not atom collisions when the structures are joined. You can join the structures with `psfgen` and see if there is superposition of atoms, finally save your PSF and PDB files with the names `PS-inNT.psf` and `PS-inNT.pdb` (It will be assumed that they have this names in following steps). After this you have generated a nano-composite. However, it is not equilibrated yet, there are still some steps to go.

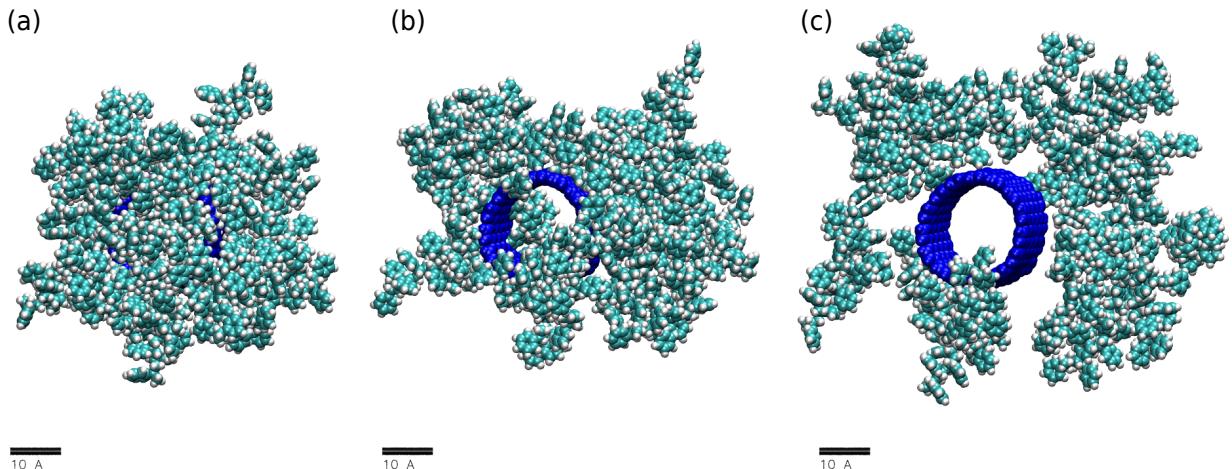


Figure 11: Opening step. Each image shows a frame of the opening simulation combined with the CNT we want to insert. (a) Initial frame. In (b) and (c) we can notice a cavity in the middle of the Polymer bulk. We decided to keep the structure in (c) for following steps as it was the first frame in which there was not atom collisions between the CNT and PS. Scale bars measure 10 Å.

Now, to finish your nanocomposite you have to run an NVT equilibration at 500 K (100 K lower than the Opening step) and perform another Annealing step (Figure 1). This will be done in the following subsections.

## IMPORTANT

- If you are not sure when to run this MD simulation see Figure 1.
- We chose a temperature of 600 K for the opening to prevent the high increase of the periodic cells dimensions. This is suitable for a short chain polymer. For long chain

polymers like Sp1 you might need to run the Opening simulation at 700 K as the interwindinghinders the creation of a cavity.

- c) We suggest that you run the equilibration that comes after the Opening step at 100 K lower.

## 6.5 Equilibration 2

In this subsection we will equilibrate the nano-composite generated in the Opening step (subsection 6.4) at 100 K lower. The main difference between this subsection and subsection 6.2 is that we employ equilibration Harmonic Restraints to fix the position of the carbon nanotube. This keeps the CNT in place so that later other CNTs can be added.

First of all, we have to specify which atoms will be restraint, for this open `nncBuild/01-PS/11_opening/PS-inNT.psf` and `nncBuild/01-PS/11_opening/PS-inNT.pdb` with VMD. Set the “beta” value of all CNT atoms (use *resname ARM* for the selection) to 1.0 and save the structure as a PDB file in the same directory with the name `hrestraint.pdb`.

Move to directory `nncTeest/05-smallCNT/01-PS/12_equilib02`, there you will find the directory `confFiles`. In this directory you will find a script to create NAMD configuration files. Run the script with VMD or type in the Tk console:

```
package require nanocomposite

nnc namdConfiguration -type equilibration -coor ../../11_Opening/PS-inNT.pdb
-psf ../../11_Opening/PS-inNT.psf -outName equi02 -temp 500 -runsteps 1000000
-par ../../common/par_PNC.prm -numConfFiles 10 -ensemble NPT
-xsc opening.000.restart.xsc -hrestraint ../../11_Opening/hrestraint.pdb
```

Ten files are created. The configuration file `equi02.000.namd` runs an NPT ensemble at 500 K for 1 ns. There are not previous files from which you can restart the simulation as the system is the result of joining two structures, you can only use the XSC file form the Opening step (`-xsc opening.000.restart.xsc`). These configuration files have the lines:

```
constraints on
consref ../../11_opening/hrestraint.pdb
conskfile ../../11_opening/hrestraint.pdb
conskcol B
# Harmonic constant of 1 kcal/molA
constraintScaling 1.0
```

which are used to restrain the CNT.

Create the directory `nncTeest/05-smallCNT/01-PS/12_equilib02/00` and copy `equi02.000.namd` to it. Then, run the simulation with NAMD. Your results should be similar to Figure 12.

After 1 ns we obtained a constant volume and constant total energy but the polymers did not enter the CNT center. We think this is because of the high temperature and carried on with the Annealing step (subsection 6.6).

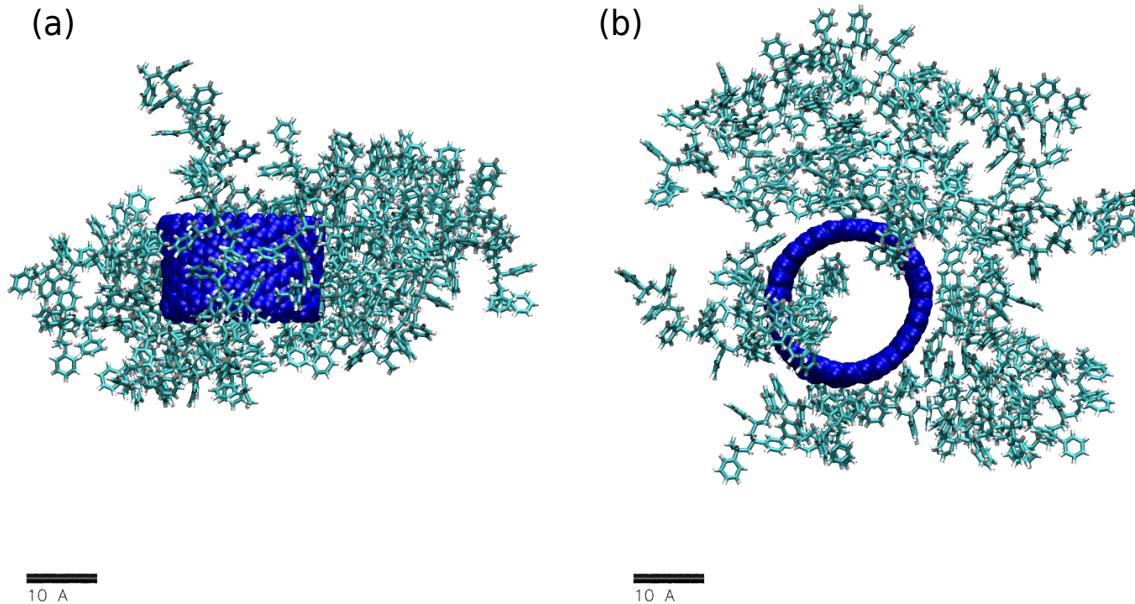


Figure 12: Result of the Equilibration 2. CNT in blue. (a) Side view (y axis) and (b) upper view (z axis). The polymers fill the space that was left due to the Opening step. Even though the polymers do not fill the CNT cavity, ee will go to the Annealing step. All scale bars measure 10 Å.

## IMPORTANT

- a) If you are not sure when to run this MD simulation check Figure 1 after the Opening step.
- b) We suggest that you run this equilibration at 100 K lower than the Opening step.
- c) For more information about Harmonic Restraints you can check the NAMD webpage.

## 6.6 Annealing 2

In this section you should perform the Annealing step as described in subsection 6.3. Starting from the result of the equilibration of the nano-composite (subsection). MD simulations are carried out at 400 K and 300K. At 400 K we used Harmonic Restraints for the CNT and at 300 K we did not use restraints. We provide the scripts to create the NAMD configuration files in the directory `nncBuild/01-PS/14_anneal-restraint/`. Your result should be similar to Figure 13, this is the Equilibrated nano-composite. We obtained a density of  $0.98 \text{ g cm}^{-3}$ .

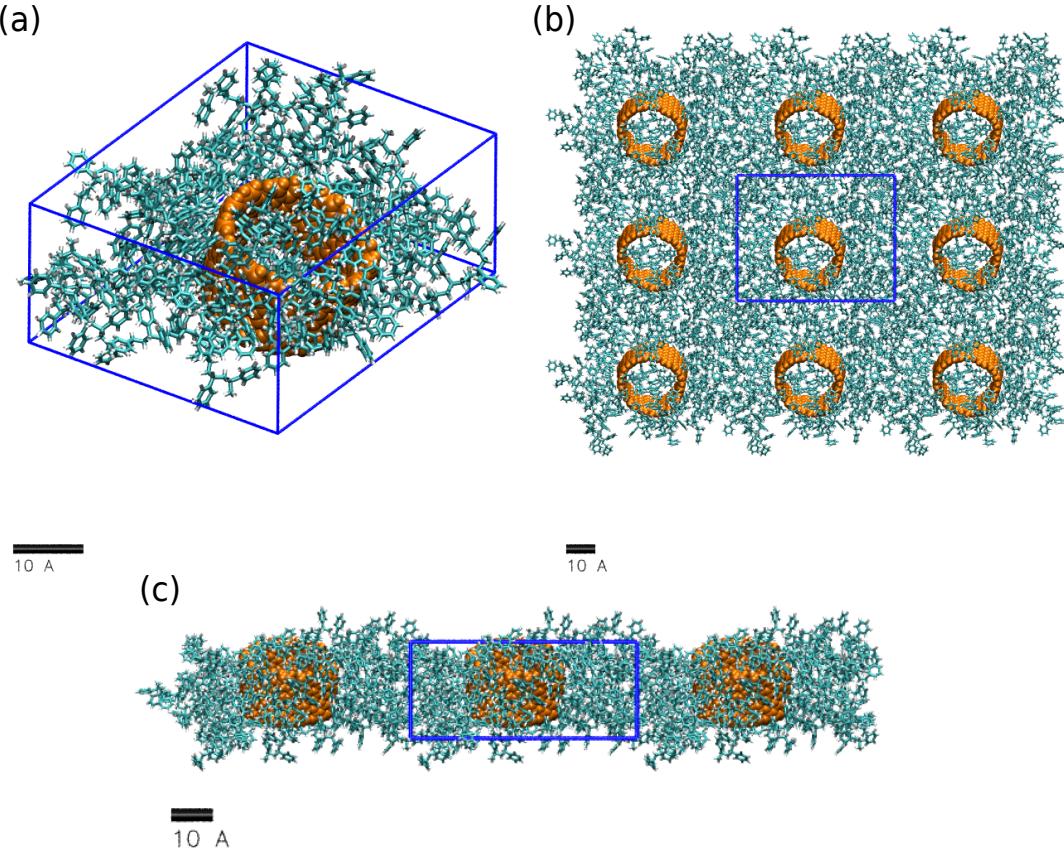


Figure 13: PS-CNT nano-composite (PS-NNC). CNT in orange and periodic box in blue. (a) PS-NNC and the periodic box, we can see that the polymers have made their way into the CNT cavity. (b) Top view (z axis) of the  $\pm x$  and  $\pm y$  periodic images. (c) Side view (y axis) of the  $\pm x$  periodic images. All scale bars measure 10 Å.

## 6.7 Expand/Contract

The PS 10-mer system is small and it does not need large computational resources as it is a short polymer. Since the polymer fills the periodic box we did not use an Expand/Contract step. To exemplify how to perform this step, we will run this simulations for an aggregate of Polyether Ether Ketone (PEEK) 10-mers. After creating the grid, geoCollapsing and equilibrating we obtain the system showed in Figure 14b. After 1 ns equilibration polymers do not fill all the voids in the periodic cell. We can do two things, keep running the equilibration or performing a Expand/Contract step to speed up the filling. The latter uses Tcl forces. In Expand, forces facing outwards are applied to the atoms inside a defined box, these forces are proportional to the distance from the box center (see subsection 7.3). In Contract, forces facing inwards are applied to the polymers inside a defined sphere (see subsection 7.4). Both simulations are part of the Expand/Contract step (Figure 1).

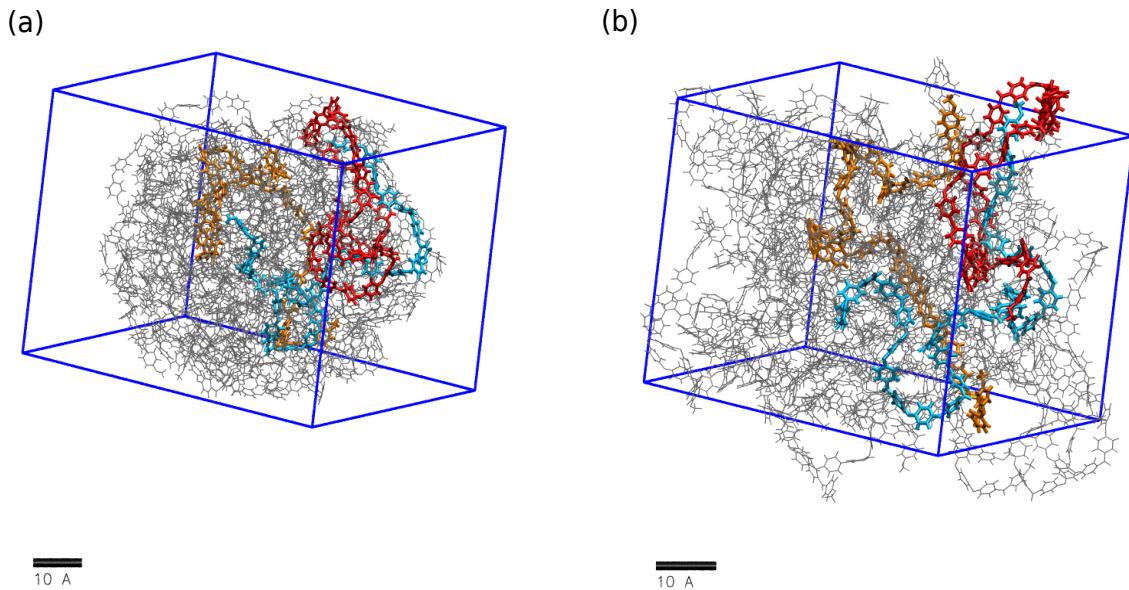


Figure 14: NPT Equilibration for PEEK. The colored polymers are the same in each frame, blue box is the periodic cell. **(a)** Initial frame, this is the result of FC. **(b)** Final frame, corresponds to 1.0 ns. As we mentioned in Figure 8, there is polymer interwinding. Instead of running a longer equilibration, we perform a Expand/Contract step which helps in the empty space filling. This step would eventually lead to homogeneous density after another equilibration (Figure 1). Scale bars measure 10 Å.

### 6.7.1 Expand

We are going to start with the expansion. Move to directory `nncBuild/02-PEEK/05-expand`, there you will find the directory `confFiles`. Move to this directory, you will find an script. Run the script with VMD or type in the Tk console:

```
package require nanocomposite

nnc namdConfiguration -type expand -coor ../../common/aggregateGRID.pdb
-psf ../../common/PEEK3x3x3.psf -par ../../common/par_PNC.prm -outName expand
-prevConf equib01.002.restart -temp 700 -dWall 40 -fe 0.072 -runsteps 200000
-minsteps 10000
```

Ten files are created. The configuration file `expand.000.namd` runs an NVT ensemble at 500 K for 0.5 ns, starting from the restart files `equib01.002.restart.xsc`, `equib01.002.restart.vel` and `equib01.002.restart.coor`. The option `-fe` states the force which will be used to calculate the force proportional to the distance of the atom (subsection 7.3) ( $1 \text{ pN} = 0.0144 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$ ). A box centered at the origin with 40 Å of edge will be defined, this edge is stated with the option `-dWall`. The forces will be applied to all the carbon atoms inside this defined box. To choose the value for `-dWall` we substracted 10 Å to the edge of the periodic cell which is almost cubic.

Run the simulation with NAMD, you should obtain something similar to Figure 15. A cavity was formed in the middle of the system, this makes evident that the density at the borders of the periodic cell will increase. It took about 4 hours to run with the specifications we described in **Usage** (section 2).

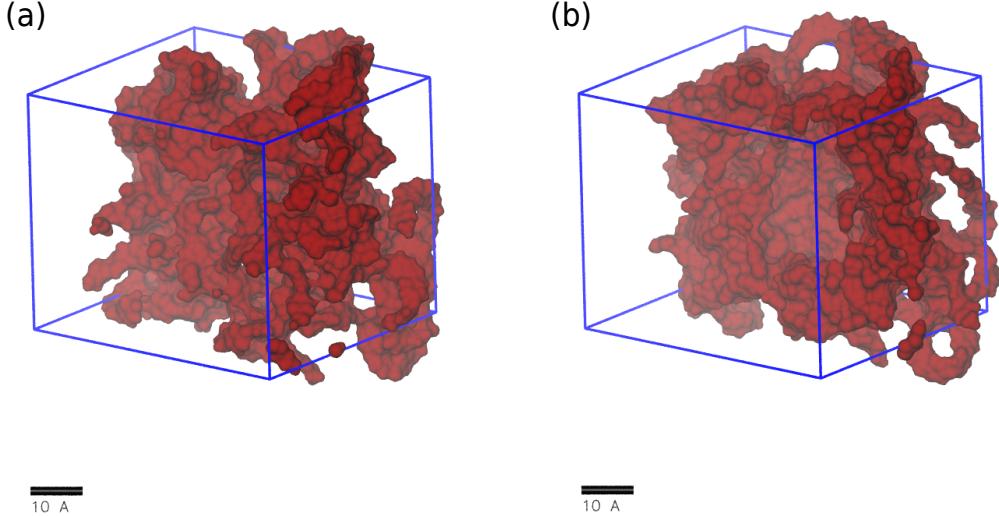


Figure 15: Expansion of PEEK bulk. Half of the bulk is shown. (a) beginning of the expansion step and (b) end. We decided to stop the simulation once we noticed a cavity in the middle of the bulk. In expansion, the polymers are driven towards the boundaries of the periodic cell in an attempt to lower the density in the middle. Here it is clear that the Expansion is working, in cases it is not evident you can calculate the densities of the entire periodic cell and an inner cube (you can use *get-den.tcl*)

### 6.7.2 Contract

Now we will do the Contraction. Move to directory `nncBuild/02-PEEK/06-contract`, there you will find the directory `confFiles`. Move to this directory, you will find an script. Run the script with VMD or type in the Tk console:

```
package require nanocomposite

nc namdConfiguration -type contract -coor ../../common/aggregateGRID.pdb
-psf ../../common/PEEK3x3x3.psf -par ../../common/par_PNC.prm -outName contract
-prevConf expand.002.restart -temp 600 -minsteps 10000 -runsteps 200000
-radSquare 332.0 -cteForce 0.0432 -numConfFiles10
```

The created files would run an NPT ensemble at 600 K for 0.5 ns which starting from the restart files of the Expand simulation. In Contract a constant force (stated with `-cteForce`) will be applied to all the carbon atoms inside an origin-centered sphere (squared radius stated with `-radSquare`). The forces point towards the center of the system.

Run the simulation with NAMD, you should obtain something similar to Figure 14b. To

know if the Expand/Contract step worked you have to run an NPT equilibration (Figure 1).

Well, up to this point we have gone through what **nanocomposite** can do. THanks for reading and hopefully you will find use to what we have done in this tutorial.

#### IMPORTANT

- a) KEEP IN MIND! Expand simulates a NVT ensemble and Contract simulates a NPT ensemble.
- b) Because of how FC works, the initial density in the box center will be higher in comparison to the edges.
- c) When we used the provided script *get-den.tcl* to get the density of the periodic cell and an inner box we that after 1 ns NPT equilibration the densities were almost  $0.92 \text{ g cm}^{-3}$ . We could have gone to the Annealing step, but we went to the Expand/Contract step to show the workflow of this step (Figure 1).
- d) We used 5 pN for the expansion and 3 pN for the contraction. However the suggested values are 2 pN and 1 pN, respectively. We used higher values to avoid long run times.
- e) When you are building your nano-composite you might not be able to observe a cavity in the middle of the bulk in expansion. We suggest 0.5 ns as a runtime. Stop the contraction simulation once a constant volume is achieved.
- f) In contraction simulation, if you observe a rapid aggregation of polymers in the box center, maybe you should lower the pulling force.

## 7 Appendix

This section offers a deeper documentation for the creation of NAMD configuration files.

Command:

```
nnc namdConfiguration [ options ]
```

This command creates NAMD configuration files for simulations that are necessary to build the nanocomposite. We are not going to run any simulations, we will just create the NAMD configuration files. For more information on when to run the NAMD configuration files check Figure 1 and the section **Methods** from the article.

In the Tk console type:

```
package require nanocomposite  
  
nnc namdConfiguration
```

As the output says, we can create 5 type of files: Equilibration, contract, expand, forcecollapse, grid. We will go through each type of file.

### 7.1 Equilibration/Annealing

Command:

```
nnc namdConfiguration -type equilibration [ options ]
```

Options:

**-coor** : The pdb file with the initial coordinates of the simulation.

**-psf** : Structure file of the pdb file.

**-outName** : The name of all the output files.

**-temp** : Temperature of the simulation.

**-runSteps** : Amount of steps for the simulation.

**-inName** : Name of the restart files. DEFAULT: The output name of the previously written file.

**-par** : Parameters file.

**-rfreq** : Frequency in which the restart files will be written.

**-outfreq** : Frequency in which the output files are written.

**-minSteps** : Amount of steps for the minimization. Default value: 10 000 steps.  
**-prevConf** : Name of the .coor, .vel, .xsc files from which the simulation will be started.  
**-numConfFiles** : Amount of namd configuration files to be written.  
**-ensemble** : Available options: NPT, NVT and NVE. DEFAULT: NPT.  
**-a** : x component of the periodic cell, define it when no XSC file is not available and you want to run a Periodic simulation. -a **calculate** opens the PSF file and the COOR file stated with **-prevConf** to calculate the dimensions of the periodic box with *measure minmax \$sel*  
**-b** : y component of the periodic cell, define it when no XSC file is not available and you want to run a Periodic simulation. -b **calculate** opens the PSF file and the COOR file stated with **-prevConf** to calculate the dimensions of the periodic box with *measure minmax \$sel*  
**-c** : z component of the periodic cell, define it when no XSC file is not available and you want to run a Periodic simulation. -c **calculate** opens the PSF file and the COOR file stated with **-prevConf** to calculate the dimensions of the periodic box with *measure minmax \$sel*  
**-wrap** : Input values 1 or 0. If you type **-wrap** 1, “wrapAll on” will be written on the configuration file. Default value: 0, which will lead to “wrapAll off”  
**-hrestraint** : PDB file in which the atoms that have a beta value of 1 will be restraint.  
**-xsc** : inputs the XSC restart file to get the periodic box of a system.

The options can also be visualized if you type in the Tk console:

```
nnc namdConfiguration -type equilibration
```

This command is used to create namd configuration files for equilibration or annealing simulations, which are run after the Force Collapses and the Expand/Contract simulations (Figure 1). This command does not run any simulation, it just creates the configuration files. For further details on when to run this simulation check the section **Methods** from the article.

In the Tk console, move to the directory `nncTest/04_namdConfiguration/01_equilibration` and type:

```
nnc namdConfiguration -type equilibration -coor melt.pdb -psf melt.psf
-outName equilibrate -temp 310 -runsteps 100 -par parameter.par -rfreq 100 -outfreq 100
-minsteps 10 -prevConf previousfile -numConfFiles 5 -ensemble NPT
```

In your current directory you will find 5 new files: `equilibrate.000.namd`, `equilibrate.001.namd`, `equilibrate.002.namd`, `equilibrate.003.namd` and `equilibrate.004.namd`. You may open them and check what is written. Let us start with the first file, open `equilibrate.000.namd` with any text editor. As expected, we need to state the name of the PDB, PSF and output files. For this we used the options `-coor`, `-psf` and `-outName`; respectively. You may notice that the only name that is different from the input is the output name. You have the option to create many files, consequently, it is convenient that the command numbers the files by adding three digits to the output name you type.

Next, we state the desired temperature with the option `-temperature`. As the simulation will be restarted from a previous one no “temperature \$temperature” will further appear in the file, it will just appear in the temperature and pressure control if the chosen ensemble includes them. `-runsteps` and `-minsteps` state the amount of run steps and the minimization steps, respectively.

`-inName` and `-prevConf` may look as the same, the first one is to restart the simulation once it has been run at least once and the second one is to start the very first simulation. In this example we have not used the option `inName`. In `equilibrate.000.namd` you will find the simulation will be started from files with the name `previousfile`. In `equilibrate.001.namd` you will find the simulation will be restarted from files with the name `equilibrate.000.namd`, the same will happen with `output.002.namd`, `output.003.namd` and so on. The simulations will be restarted from the previous configuration file. This happens as default when we do not state anything with the option `-inName`. You will find this useful in case the simulation breaks or you have limited run time in a computer cluster. In all the created configuration files, but `equilibrate.000.namd` there is a procedure called `get_first_ts`, which gets the first time step of the previous simulation. Basically, without stating `-inName` you only have to run the next configuration file with NAMD if the simulation stops. If preferred, you can name your restart files with `-inName`.

`-par` states the parameters file, `-rfreq` states the frequency in which the restart files will be written (100 for this example), `-outfreq` states the frequency in which the output files are written (100 for this example) and `-numConfFiles` states the amount of configuration files to be written (5 for this example). The available ensembles are NPT, NVT and NVE; if other words are typed with the `-ensemble` option no file will be generated. If no `-ensemble` option is used, NPT configuration file will be written as default. For the NVE ensemble there is no need to state the temperature with `-temp`.

The Force-field parameters that appear in the configuration files are the ones mentioned in the article. Instead of typing on the Tk console you can run the script `runNamdConfiguration_01.tcl`, just make sure to change the directory direction in the script before running it.

## IMPORTANT

- a) DO NOT forget to type “package require nanocomposite” in the Tk console every time you want to start using nanocomposite commands.

- b) Every file that is named in the options is assumed to be in the same directory of the created configuration file, if not put the direction of the file (e.g `-coor ..\common\polymer.pdb`).
- c) For some options you should not put the last part of the name of the files. Instead of typing `-outName output.dcd` you should type `-outName output`, because other files will be created with the name besides the dcd file.
- d) It is not necessary to type the options in an specific order.
- e) If you are not sure when to run the equilibration or annealing simulations check Firgue 1 and the section **Methods** in the article.

## 7.2 Force Collapse

Command:

```
nnc namdConfiguration -type forcecollapse [ options ]
```

Options:

- coor** : The pdb file with the initial coordinates of the simulation.
- psf** : Structure file of the pdb file.
- outName** : The name of all the output files.
- temp** : Temperature of the simulation.
- runSteps** : Amount of steps for the simulation.
- inName** : Name of the restart files. Default: The output name of the previously written file.
- par** : Parameters file.
- rfreq** : Frequency in which the restart files will be written.
- outfreq** : Frequency in which the output files are written.
- minSteps** : Amount of steps for the minimization. Default value: 10 000 steps.
- atommass** : Mass of the atoms on which the force will be applied. In g/mol. 12 is the default value.
- dWall** : Edge of the cube defined for the selection of atoms. Default: the PDB and PSF files will be opened, the mass of all the atoms will be measured and the edge of the cube that would give you a density of  $1g\ cm^{-3}$  for that mass will be saved.
- cteForce** : Force that will be applied to the selected atoms. The default value is 0.072 in namd units = 5 pN.

**-stride** : Frequency in which the selection of the pulled atoms will be refreshed, in steps. 100 steps is the default value.

**-numConfFiles** : Amount of namd configuration files to be written.

The options can also be visualized if you type in the Tk console:

```
nnc namdConfiguration -type forcecollapse
```

This command creates the NAMD configuration file for the Force Collapse simulation. This step comes after the geometric collapse with *geoCollapse* and its objective is to generate a well-mixed polymeric bulk. As this is the first MD simulation, the option **-prevConf** is not used. With the created configuration files, which is implemented with a TclBC script, a high temperature (we suggest 1000 K) MD simulation will be run in which the atoms outside a defined box will be pulled with a constant force towards the box center {0 0 0}. The objective of the Force Collapse step is to increase the density of the polymer melt by pulling the polymers to the center. A high temperature is used to prevent the folding of the polymers and the formation of a crystal, as our polymer melt should be amorphous. For further information you can check the section **Polymeric melts** of the article.

Move to the directory `nncTest/04_namdConfiguration/02_forcecollapse` open the Tk console in VMD and type:

```
nnc namdConfiguration -type forcecollapse -coor melt.pdb -psf melt.psf  
-par parameters.par -outName forcecol -temp 1000 -rfreq 100 -outfreq 100 -minsteps 10000  
-runsteps 1000000 -atommass 12 -dWall 36 -cteForce 0.072 -stride 100 -numConfFiles 5
```

The options that are not described in depth in the following explanation were described in the subsection 7.1. Now you will find 5 new files, you may open them and check what is written. Let us start with the first file, open `forcecol.000.namd` with any text editor. This simulation will not be started from any other simulation. The Force Collapse simulation is non-periodic, in the created configuration files we have constant temperature control at 1000K. We have used the default option for **-inName**, hence in the other written configuration files the restart files will be the previously written files (check subsection 7.1 for a more in-depth explanation).

The TclBC script, which is found after the “EXTRA PARAMETERS”, is characteristic of this configuration file. In the input values you will find the variables “lowMass” and “highMass” which are calculated by subtracting and adding 0.3 g/mol, respectively, to the mass that was stated for **-atommass**. Hence, only carbon atoms will be selected which have a mass of 12 g mol<sup>-1</sup>. Take into account that generally the backbone of polymers involve carbon atoms. Next, the limits of the box centered at {0 0 0} are defined. Carbon atoms that have coordinates x, y and z within the range defined by the variables “bottomWall” and “topWall” will be selected. “bottomWall” is the half negative of the value stated with the option **-dWall**, “topWall” is equal to half of the value stated with the option **-dWall**.

That is why the range goes from -18 to 18 Å, in other words the defined box will have an edge of 36 Å. The Force Collapse step should be over once you do not appreciate significant change in the volume (you can use *measure minmax \$variable*). You may wonder why we chose 36 Å for the edge of the cube and how to get the right edge for your system. Organic polymers commonly have a density near  $1g\ cm^{-3}$  and you can get the mass of your system with “*measure sumweights \$sel weight mass*”. You can get the ideal volume that your polymers should be confined to and you assume it is cubic (this is the default option if you do not use the option *-dWall*). Anyway, the dimensions of the periodic cell will change in steps following to Force Collapse, then the final density for the polymer melt can differ from the assumed value. If you know the density of your polymer, you can use it for the calculation.

A force of 5 pN (0.072 in namd units) will be applied to the selected atoms towards the box center {0 0 0}. The magnitude of the force was stated with the option *-cteForce* and the selection will be refreshed after a certain amount of steps stated by *-stride*. Lower than 10 pN magnitudes for pulling forces are reasonably used, as they will allow the reaccommodation of the polymers when they come together. In the end of the simulation we expect to get a polymeric ball without voids in which all the polymers are inside the defined box (Figure 1). For more information on the parameters and when to perform the Force Collapse step check the section **Polymeric melts** in the article.

You may think that you can aggregate the polymers from the starting grid without *geoCollapse*, and just with Force Collapse. It could be done but the simulations take too long for high molecular wieght polymers. In fact, there is an approach to build polymer melts from low molecular weight polymers in which only the Force Collapse step is used for the aggregation (a 9-mer was used).<sup>7</sup> The **nanocomposite** tool is based on this approach. Instead of typing on the Tk console you can run the script *runNamdConfiguration\_02.tcl*, just make sure to change the directory direction in the script before running it.

## IMPORTANT

- a) DO NOT forget to type “package require nanocomposite” in the Tk console every time you want to start using nanocomposite commands.
- b) A simulation in NAMD stops when atom speeds exceed a threshold. As we are using a high temperature for the Force Collapse step, you might need to restart the simulation many times. In other words, make sure to create many configuration files with the option *-numConfFiles*.
- c) BE CAREFUL! Check your structure before you restart a simulation. At high temperatures peptide bonds can go from trans to cis form and chiral carbons can switch to its mirror images. Make sure correct your structure before you restart MD the simulation.
- d) A minimization of at least 10 000 steps is suggested every time you restart the MD simulation.
- e) Remember that you can choose another atom by stating a different mass with *-atommass*.

- f) Remember that the length unit in NAMD is Angstroms ( $\text{\AA}$ ) and force units are kcal  $mol^{-1}$   $\text{\AA}$ .

## 7.3 Expand

Command:

```
nnc namdConfiguration -type expand [ options ]
```

Options:

- coor** : The PDB file with the initial coordinates of the simulation.
- psf** : Structure file of the PDB file.
- par** : Parameters file.
- outName** : The name of all the output files.
- inName** : Name of the restart files. DEFAULT: The output name of the previously written file.
- temp** : Temperature of the simulation.
- prevConf** : Name of the COOR, VEL, XSC files from which the simulation will be started.
- rfreq** : Frequency in which the restart files will be written.
- outfreq** : Frequency in which the output files are written.
- minsteps** : Amount of steps for the minimization.
- runsteps** : Amount of steps for the simulation.
- atommass** : Mass of the atoms on which the force will be applied. In g/mol. 12 is the default value.
- dWall** : Edge of the cube defined for the selection of atoms. It is the value of  $L_{expand}$  in equation 1 and 2 of the article. 107  $\text{\AA}$  is the default value. We suggest that you use the edge of the periodic box minus 10  $\text{\AA}$ .
- fe** : Force in NAMD units used to calculate the pulling force over the selected atoms, this final pulling force points outwards and is proportional to the distance of the atom from the origin. It is the value of  $f_e$  in equation 2 of the article.
- stride** : Frequency in which the selection of the pulled atoms will be refreshed, in steps. 100 steps is the default value.
- numConfFiles** : Amount of NAMD configuration files to be written.

The options can also be visualized if you type in the Tk console:

```
nnc namdConfiguration -type expand
```

This command is used to create NAMD configuration files for the expansion in the expansion/contraction step, which is used to redistribute the mass at the boundaries of the periodic box. The simulation is run if a non-homogeneous density is obtained after the equilibration step (Figure ??a). Commonly homogeneous density cannot be obtained due to polymer interwinding. The expansion contraction step helps us to reach homogeneous density after an additional step of equilibration. The expansion comes before the contraction. For more information about when to run the configuration files check the section **Polymeric melts** of the article. The configuration files created with this command are implemented with a TclBC script. With this script, a cubic region (with edge stated with the option `-dWall`) centered at  $\{0\ 0\ 0\}$  is defined, the chosen edge of the cube is the edge of the periodic cell minus 10 Å. All the atoms with certain mass (stated with the option `-atommass`) within the defined box will be selected and a force proportional to the distance of the atom from the box center  $\{0\ 0\ 0\}$  will be applied. The force that is applied to the selected atoms ( $f_{out}$ ) is calculated as follows:

$$\overrightarrow{f_{out}} = f_e \frac{2 \overrightarrow{d_{c2c}}}{L_{expand}}, \quad (1)$$

where  $f_e$  is stated with the option `-fe`, for the polymeric melts described in the article a value of 0.0288 namd units (2 pN) was used.  $L_{expand}$  is defined with `-dWall`.  $\overrightarrow{d_{c2c}}$  is the vector distance from the selected atom to the box center  $\{0\ 0\ 0\}$ .  $\overrightarrow{f_{out}}$  acts stronger at the borders where there is empty space and weaker at the center where atoms are crowded. The atoms selection will be refreshed after a certain amount of steps (stated with the option `-stride`). `-numConfFiles` states the amount of NAMD configuration files to be written.

As example, we are going to create the expansion configuration files. Move to the directory `nncTest/04_namdConfiguration/03_expand` open the Tk console in VMD and type:

```
nnc namdConfiguration -type expand -coor melt.pdb -psf melt.psf -par parameter.par
-outName expand -prevConf previousfile -temp 310 -rfreq 100 -outfreq 100 -minsteps 10
-runsteps 100 -atommass 12 -dWall 107 -fe 0.0288 -stride 100 -numConfFiles 5
```

The options that are not described in depth in the following explanation were described in the subsection 7.1. In your current directory, you will find 5 new files: `expand.000.namd`, `expand.001.namd`, `expand.002.namd`, `expand.003.namd` and `expand.004.namd`. You may open them and check what is written. Let us start with the first file, open `expand.000.namd` with any text editor. The simulation for this configuration file is to be started from a previous simulation. For this example, the simulation would be started from the files with the name `previousfile`, which was stated by `-prevConf`. We have used the default option for `-inName`, hence in the other written configuration files the restart files will be the previously written

files (check subsection 7.1 for a more in-depth explanation). As you may notice, the contraction simulation runs an NVT ensemble. In the created configuration files we have constant temperature control.

The TclBC script, which is found after the comment “EXTRA PARAMETERS”, is characteristic of this configuration file. In the input values you will find the variables “lowMass” and “highMass” which are calculated by subtracting and adding 0.3 g/mol, respectively, to the mass that was stated with the option `-atommass`. Hence, only carbon atoms will be selected which have a mass of 12 g/mol. Take into account that generally the backbone of polymers involve carbon atoms. Next, the limits of the box centered at {0 0 0} are defined. Carbon atoms that have coordinates x, y and z within the range defined the variables “bottomWall” and “topWall”. “bottomWall” is the negative of the value stated with the option `-dWall`, `topWall` is equal to the value stated with the option `-dWall`. That is why the range goes from -107 to 107 Å(remember that the length unit in NAMD is Å). Remember that you can choose another atom by stating a different mass with `-atommass`.

A force will be applied to the selected atoms. First, the variable “dFdR” is defined as two times the value stated with the option `-fe` over the value stated with `-dWall`. The force to be applied to each selected atom, according to equation 1, is the variable “dFdR” multiplied to the position vector of the selected atom (box centered at {0 0 0}). This means the force will be facing outwards and it will be of higher magnitude near the borders of the defined box. As you might guess, overall, the expansion simulation will increase the density in the boundaries of the periodic cell as all the previous steps have aggregated the polymers in the center of the periodic cell. So that the density does not drop near the center a contraction step has also been implemented, how to create the configuration files for the contraction simulation is described in the following subsection. The selection of the atoms will be refreshed every 100 steps, as stated with the option `-stride`.

You can also create the configuration files with the script `runNamdConfiguration_04.tcl`, just make sure to change . For more information regarding TclBC you can check the User-Defined Forces tutorial in the NAMD webpage. All the configuration files have the same Force-Field parameters, which are mentioned in the **Methods** section in the article. For more information about the selected values check the section **Polymeric melts** in the article. Instead of typing on the Tk console you can run the script `runNamdConfiguration_03.tcl`, just make sure to change the directory direction in the script before running it.

## IMPORTANT

- a) The TclBC script assumes your system is centered at {0 0 0} for the selection.
- b) If you realize that the equilibration simulation is taking too long to reach an homogeneous density, you should carry out an Expansion/Contraction step.
- c) If your polymer is not too long you might not need to carry out the Expansion/Contraction step (Figure 1).

## 7.4 Contract

Command:

```
nnc namdConfiguration -type contract [ options ]
```

Options:

**-coor** : The PDB file with the initial coordinates of the simulation.

**-psf** : Structure file of the PDB file.

**-par** : Parameters file.

**-outName** : The name of all the output files.

**-inName** : Name of the restart files. DEFAULT: The output name of the previously written file.

**-temp** : Temperature of the simulation.

**-prevConf** : Name of the COOR, VEL, XSC files from which the simulation will be started.

**-rfreq** : Frequency in which the restart files will be written.

**-outfreq** : Frequency in which the output files are written.

**-minsteps** : Amount of steps for the minimization.

**-runsteps** : Amount of steps for the simulation.

**-atommass** : Mass of the atoms on which the force will be applied. In g/mol. 12 is the default value.

**-radSquare** : The square of the radius of the sphere defined for the selection of atoms.

**-cteForce** : Force that will be applied to the selected atoms. The default value is 0.0144 in namd units = 1 pN.

**-stride** : Frequency in which the selection of the atoms will be refreshed, in steps. 100 steps is the default value.

**-numConfFiles** : Amount of namd configuration files to be written.

The options can also be visualized if you type in the Tk console:

```
nnc namdConfiguration -type contract
```

This command is used to create NAMD configuration files for the contraction in the expansion/contraction step, which is used to redistribute the mass at the boundaries of the periodic

box. The contraction comes after the expansion. For more information about when to run the configuration files check the section **Polymeric melts** of the article. The configuration files created with this command are implemented with a TclBC script. With this script, a spherical region (with squared radius stated with the option **-radSquare**) centered at {0 0 0} is defined. All the atoms with certain mass (stated by **-atommass**) within the defined sphere will be selected and a constant force (stated by **-cteForce**) will be applied to them towards the center of the sphere {0 0 0}. The selection will be refreshed after a certain amount of steps (stated with **-stride**).

As example, we are going to create the contraction configuration files. Move to the directory `nncTest/04_namdConfiguration/04_contract`, open the Tk console in VMD and type:

```
nnc namdConfiguration -type contract -coor melt.pdb -psf melt.psf -par parameter.par
-outName contract -prevConf previousfile -temp 310 -rfreq 100 -outfreq 100 -minsteps 10
-runsteps 100 -atommass 12 -radSquare 6400.0 -cteForce 0.0144 -stride 100 -numConfFiles 5
```

The options that are not described in depth in the following explanation were described in subsection 7.1. Now you will find 5 new files: `contract.000.namd`, `contract.001.namd`, `contract.002.namd`, `contract.003.namd` and `contract.004.namd`. You may open them and check what is written. Let us start with the first file, open `contract.000.namd` with any text editor. As the simulation for this configuration file is to be started from a previous simulation, simulation would be started from the files with the name *previousfile*, which was stated with the option **-prevConf**. As you may notice, the contraction simulation runs an NPT ensemble. In the created configuration files we have constant temperature and constant pressure control.

The TclBC script, which is found after the comment “EXTRA PARAMETERS”, is characteristic of this configuration file. In the input values you will find two values: “lowMass” and “highMass” which are calculated by subtracting and adding 0.3 g/mol, respectively, to the mass that was stated with the option **-atommass**. Hence, only carbon atoms will be selected. Take into account that generally the backbone of polymers involve carbon atoms. Next, the square of the radius of the spherical region is 6400 Å<sup>2</sup>, this means the radius of the spherical region is 80 Å. For the radius, we suggest that the value of 0.35 times the length of the periodic cell is used.

The force that is assigned to every selected atom is 0.0144 in NAMD units (kcal mol<sup>-1</sup> Å), equivalent to 1 pN. The force is directed towards the center {0 0 0}. The selection will be refreshed every 100 steps, as stated with the option **-stride**. For more information regarding TclBC you can check the User-Defined Forces tutorial in the NAMD webpage.

All the configuration files have the same Force-Field parameters, which are mentioned in the **Methods** section in the article. For more information on the selected values check the section **Polymeric melts** in the article. Instead of typing on the Tk console you can run the script `runNamdConfiguration_04.tcl`, just make sure to change the directory direction in the script before running it.

## IMPORTANT

- a) The TclBC script assumes your system is centered at {0 0 0} for the selection.

## 7.5 Grid

Command:

```
nnc namdConfiguration -type grid [ options ]
```

Options:

- coor : The PDB file with the initial coordinates of the simulation.
- psf : Structure file of the pdb file.
- par : Parameters file.
- outName : The name of all the output files.
- inName : Name of the restart files. DEFAULT: The output name of the previously written file.
- temp : Temperature of the simulation.
- prevConf : Name of the .coor, .vel, .xsc files from which the simulation will be started.
- rfreq : Frequency in which the restart files will be written.
- outfreq : Frequency in which the output files are written.
- minsteps : Amount of steps for the minimization.
- runsteps : Amount of steps for the simulation.
- gridforcefile : pdb file specifying atoms to which force will be applied. Default file ./files/PEEK.7H034.gforce.
- gridforcepotfile : dx file defining grid, which is created with Phantom Volume from the previous section. Default file ./files/PEEK10nmCNT.K0.Free.dx
- numConfFiles : Amount of namd configuration files to be written.
- sfactor : scaling factor for the GRID-SMD simulation. Default: 0.10

The options can also be visualized if you type in the Tk console:

```
nnc namdConfiguration -type grid
```

The configuration files created with this command are used in the Opening step (Figure ??a). The files are used to perform GRID-SMD simulations. In this simulation a cavity is created in the polymer melt according to the grid in the dx file (stated with the option `-gridforcepotfile`). The grid has the contour of the structure you want to insert in the polymer melt and it can be created with the command described in section 5. After you create the cavity, you can join the polymer melt with another structure. This is part of the final steps in order to build your nanocomposite. For further information check the section **PNC systems**.

As an example we are going to create the configuration files. Open the Tk console in VMD, go to the directory `nncTest/04_namdConfiguration/05_grid` and type:

```
nnc namdConfiguration -type grid -coor melt.pdb -psf melt.psf
-par parameter.par -outName grid -temp 700K -prevConf bulk -rfreq 100 -outfreq 100
-minsteps 0 -runsteps 100 -gridforcefile ./files/PEEK.7H034.gforce
-gridforcepotfile ./files/PEEK10nmCNT.K0.Free.dx -numConfFiles5
```

The options that are not described in depth in the following explanation were described in subsection 7.1. In the current directory you will find 5 new files: `grid000.namd`, `grid001.namd`, `grid002.namd`, `grid003.namd` and `grid004.namd`. You may open them and check what is written. Let us start with the first file, open `grid.000.namd` with any text editor. The simulation for this configuration file is to be started from a previous simulation in this case the name is “bulk” which was stated with the option `-prevConf`. The created configuration files run a NPT ensemble, we have constant temperature and constant pressure control.

The TclBC script, which is found after the “EXTRA PARAMETERS”, is characteristic of this configuration file. You will find that “gridforce” is activated. The GRID-SMD force will be applied to the atoms according to the values found in the Occupancy column and the charge will be taken from the Beta column in the pdb file `./files/PEEK.7H034.gforce`, stated with the option `-gridforcefile` (You should write this file for your polymer melt). The dx file `./files/PEEK10nmCNT.K0.Free.dx` contains the grid stated with `-gridforcepotfile`. The forces will be pointing outwards (as we explained in section 5), in other words a cavity will be formed (Figure 1). For more information regarding GRID-SMD check the User-Defined Forces tutorial in the NAMD webpage.

We have used the default option for `-inName`, hence in the other written configuration files the restart files will be the previously written files (check the subsection 7.1 for a more in-depth explanation). As you may notice, the contraction simulation runs an NPT ensemble. In the created configuration files we have constant temperature and constant pressure control. Instead of typing on the Tk console you can run the script `runNamdConfiguration_05.tcl`, just make sure to change the directory direction in the script before running it.

You may wonder when to stop running the GRID-SMD simulation. If you insert the structure from which you built the grid in the formed cavity and there are not collisions with the polymers then you do not need to keep running the simulation (you can use the command

*within* available in VMD).

## IMPORTANT

- a) In order to finish building your nanocomposite, after you perform the opening simulation you should join your structures and perform equilibration and annealing simulations. For further information check the sections **Polymer melts** and PNC systems in the article.
- b) The grid we mention in this subsection is a force grid, different from the grid we mentioned in the section **randomGrid**.

aaa