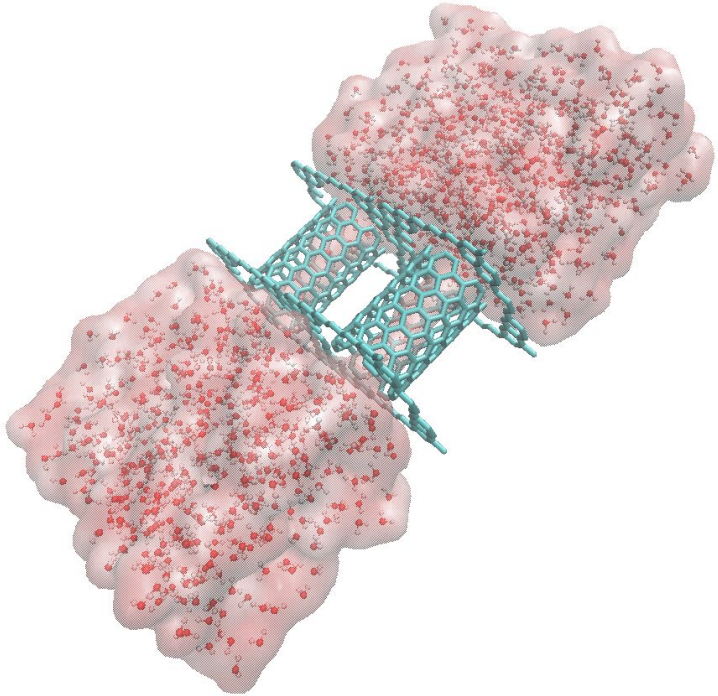
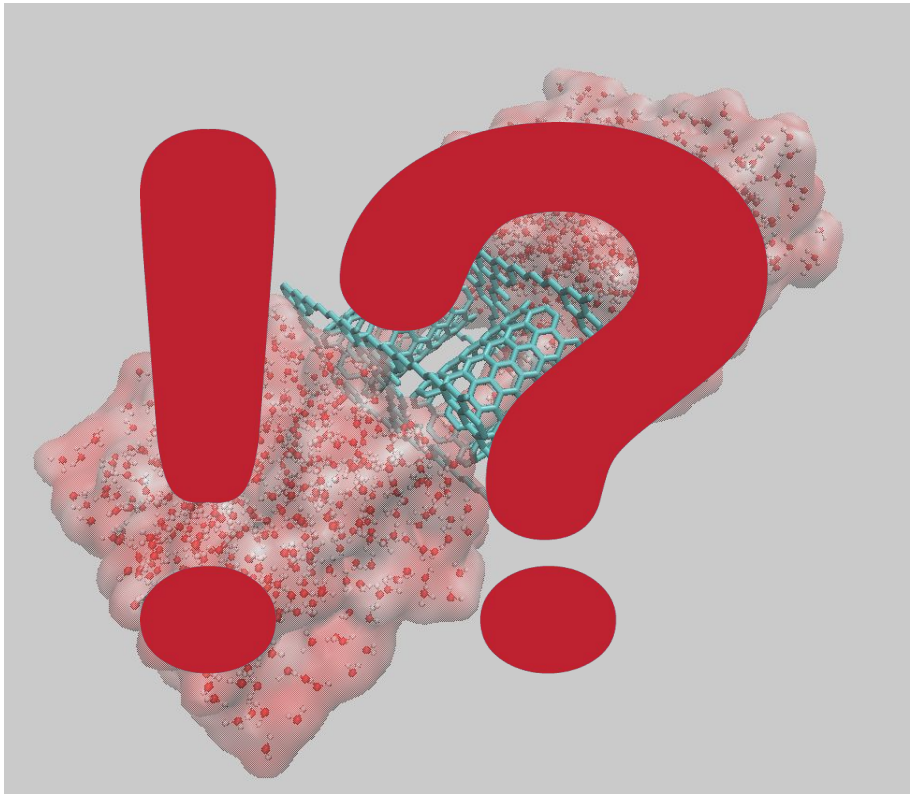
Estudi del transport d'aigua en situacions de no equilibir a través de CNTs



Daniel Bedmar

Justificació



Procediment

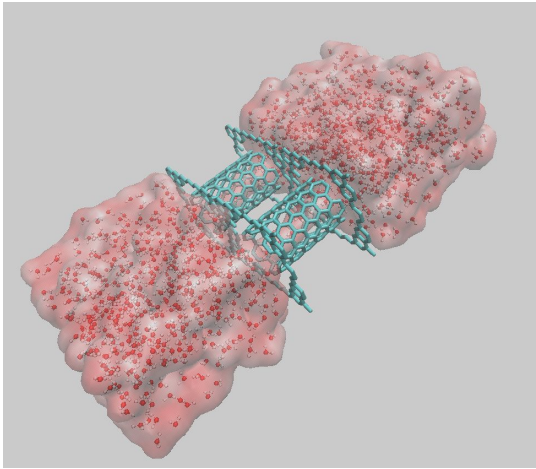
.pdb

.psf

.inp

.namd

NAMD
Scalable Molecular Dynamics



Justificació

NAMD
Scalable Molecular Dynamics

- Simplificacions raonables
- Estudi del fenòmen ✓
- Sistemes amb molts àtoms ✓
- Cost computacional asumible ✓

Procediment

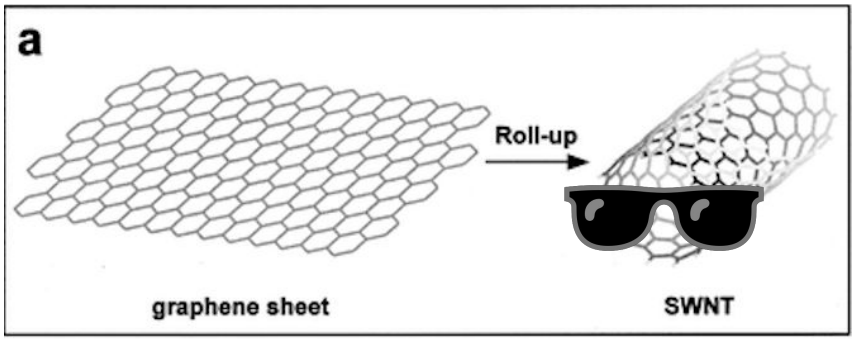
.pdb

· Coordenades
· Noms àtoms i segments
· Beta factor i occupancy

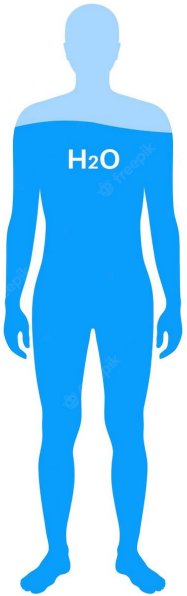
.psf

· Massa i càrrega
· enllaçcos, angles i dièdres

Justificació

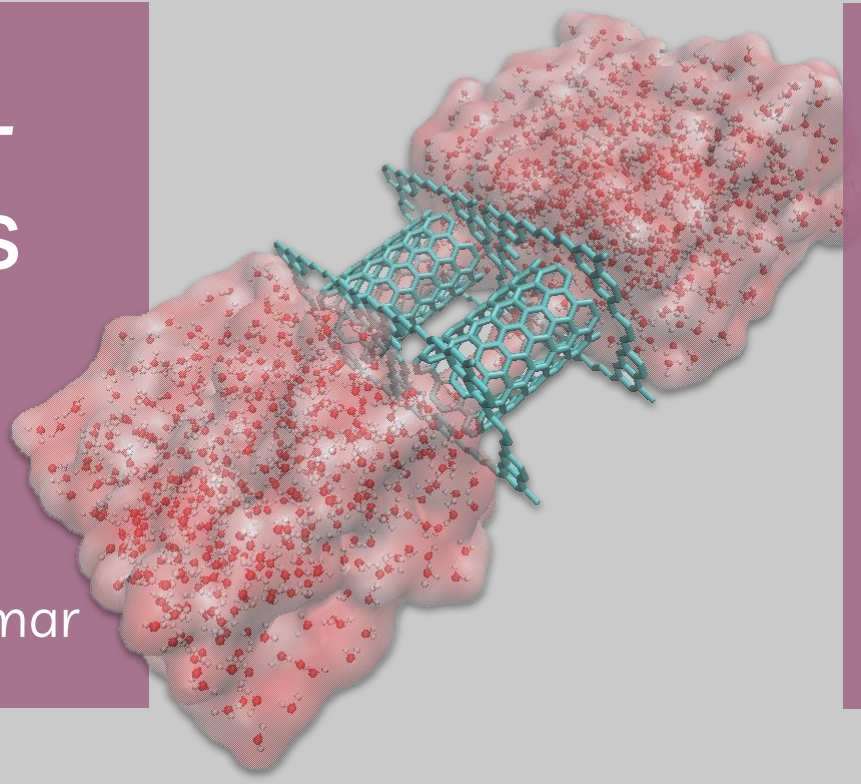


Justificació



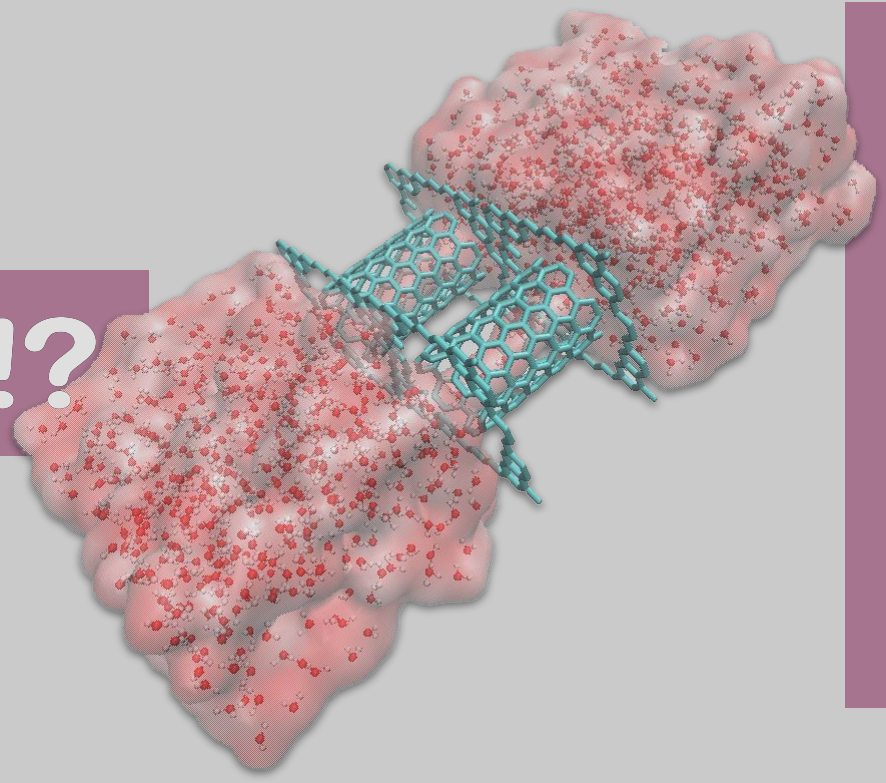
ESTUDI DEL TRANSPORT D'AIGUA EN SITUACIONS DE NO EQUILIBRI A TRAVÉS DE CNTs

Daniel Bedmar

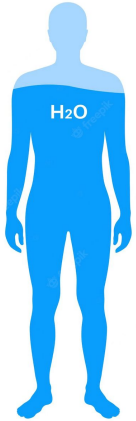


JUSTIFICACIÓ

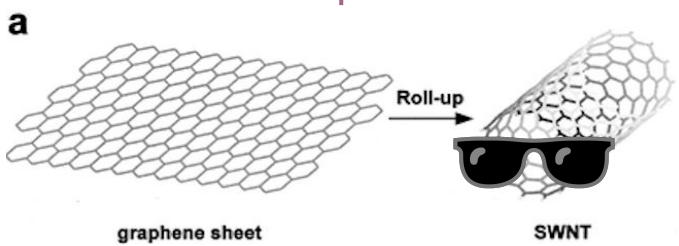
!?



JUSTIFICACIÓ



JUSTIFICACIÓ



NAMD
Scalable Molecular Dynamics

JUSTIFICACIÓ

SIMPLIFICACIONS RAONABLES

ESTUDI DEL FENÒMEN

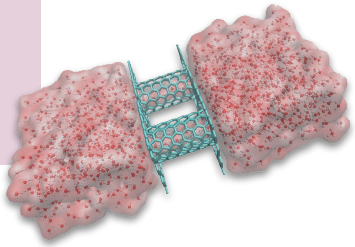
SISTEMES AMB MOLTS ÀTOMS

COST COMPUTACIONAL ASUMIBLE

PROCEDIMENT

NAMD
Scalable Molecular Dynamics

.pdb
.psf
.inp
.namd



PROCEDIMENT

.pdb

Coordenades

Noms àtoms i segments

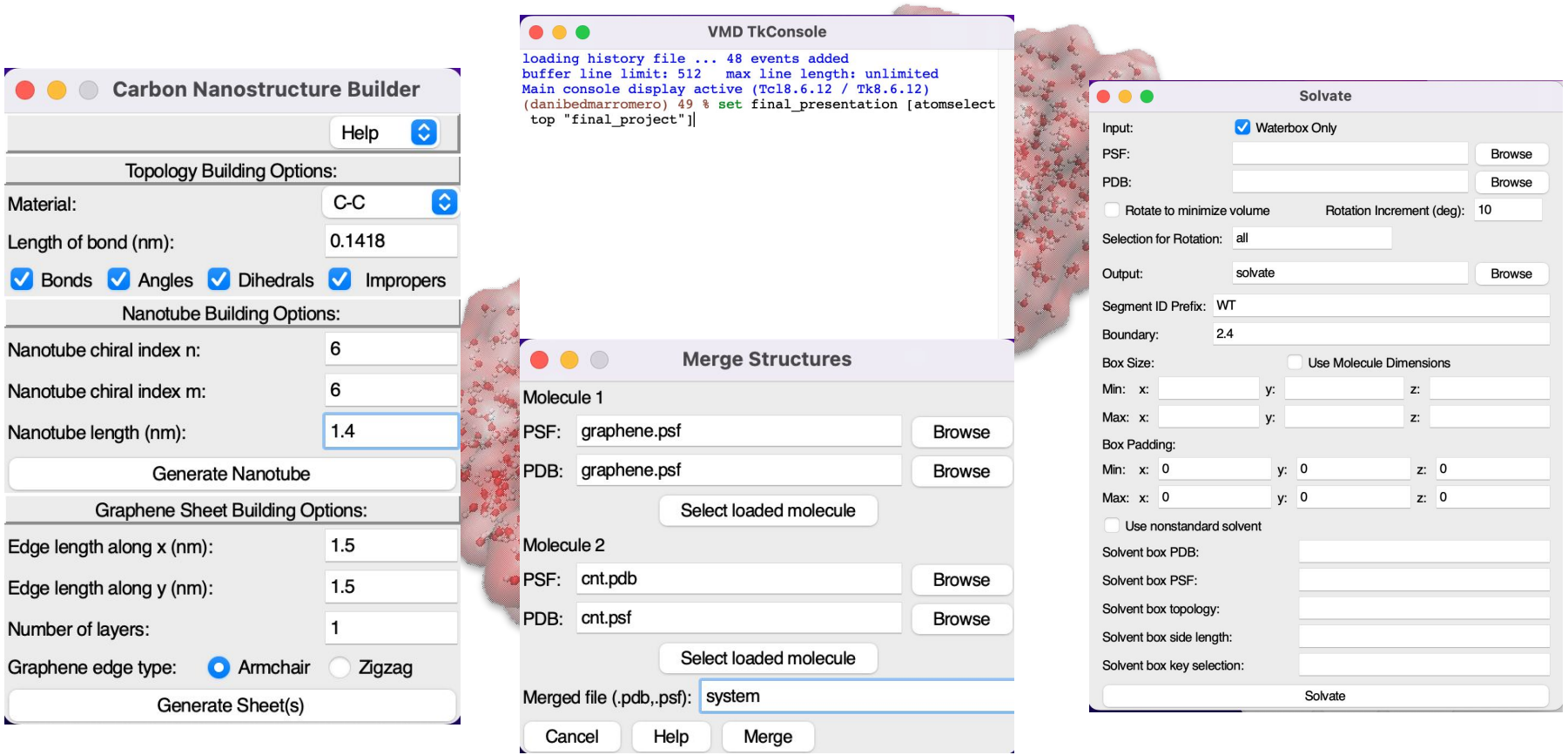
Beta factor i occupancy

.psf

Massa i càrrega

Enllaçcos, angles i dièdres

PROCEDIMENT



PROCEDIMENT

PROCEDIMENT

par_nanotubes.inp

```
* This is a reduced version of the CHARMM22 parameter file for
* a nanotube simulation in water
*

BONDS
!V(bond) = Kb(b - b0)**2
!
!atom type Kb          b0
CA   CA    305.000     1.3750

ANGLES
!V(angle) = Ktheta(Theta - Theta0)**2
!V(Urey-Bradley) = Kub(S - S0)**2
!
!atom types     Ktheta    Theta0   Kub     S0
CA   CA   CA    40.000    120.00   35.00   2.41620

DIHEDRALS
!V(dihedral) = Kchi(1 + cos(n(chi) - delta))
!
!atom types             Kchi    n   delta
CA   CA   CA   CA       3.1000  2   180.00


NONBONDED nbxmod  5 atom cdiel shift vatom vdistance vswitch -
cutnb 14.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5
!V(Lennard-Jones) = Eps,i,j[(Rmin,i,j/ri,j)**12 - 2(Rmin,i,j/ri,j)**6]
!
!atom  ignored    epsilon      Rmin/2
CA     0.000000  -0.070000     1.992400

HBOND CUTHB 0.5

END
```

par_water.inp

```
!
! TIP3P MODEL OF WATER
! ForceField for simulation with NAMD
!
BONDS
!
!V(bond) = Kb(b - b0)**2
!
!Kb: kcal/mole/A**2
!b0: A
!
!atom type Kb          b0
!
HT    HT      0.0       1.5139  ! from TIPS3P geometry (for SHAKE w/PARAM)
HT    OT    450.0       0.9572  ! from TIPS3P geometry

ANGLES
!
!V(angle) = Ktheta(Theta - Theta0)**2
!
!Ktheta: kcal/mole/rad**2
!Theta0: degrees
!
!atom types     Ktheta    Theta0
!
HT   OT   HT     55.0      104.52   ! FROM TIPS3P GEOMETRY

NONBONDED nbxmod  5 atom cdiel fshift vatom vdistance vfswitch -
cutnb 14.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5

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!
!atom  ignored    epsilon      Rmin/2
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OT       0.0       -0.1521    1.7682

END
```

PROCEDIMENT

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PROCEDIMENT

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```

PROCEDIMENT

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CA     0.000000  -0.070000     1.992400

HBOND CUTHB 0.5

END
```

par_water.inp

```
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! ForceField for simulation with NAMD
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BONDS
!
!V(bond) = Kb(b - b0)**2
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!b0: A
!
!atom type Kb          b0
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HT    OT    450.0       0.9572  ! from TIPS3P geometry

ANGLES
!
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!Ktheta: kcal/mole/rad**2
!Theta0: degrees
!
!atom types     Ktheta    Theta0
!
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NONBONDED nbxmod  5 atom cdiel fshift vatom vdistance vfswitch -
cutnb 14.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5

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HT       0.0       -0.046     0.2245
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END
```

PROCEDIMENT

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!
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!V(Lennard-Jones) = Eps,i,j[(Rmin,i,j/ri,j)**12 - 2(Rmin,i,j/ri,j)**6]
!
!atom  ignored    epsilon      Rmin/2
CA     0.000000  -0.070000     1.992400

HBOND CUTHB 0.5

END
```

par_water.inp

```
!
! TIP3P MODEL OF WATER
! ForceField for simulation with NAMD
!
BONDS
!
!V(bond) = Kb(b - b0)**2
!
!Kb: kcal/mole/A**2
!b0: A
!
!atom type Kb          b0
!
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HT    OT    450.0       0.9572  ! from TIPS3P geometry

ANGLES
!
!V(angle) = Ktheta(Theta - Theta0)**2
!
!Ktheta: kcal/mole/rad**2
!Theta0: degrees
!
!atom types     Ktheta    Theta0
!
HT   OT   HT     55.0      104.52   ! FROM TIPS3P GEOMETRY

NONBONDED nbxmod  5 atom cdiel fshift vatom vdistance vfswitch -
cutnb 14.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5

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!V(Lennard-Jones) = Eps,i,j[(Rmin,i,j/ri,j)**12 - 2(Rmin,i,j/ri,j)**6]
!
!atom  ignored    epsilon      Rmin/2
HT       0.0       -0.046     0.2245
OT       0.0       -0.1521    1.7682

END
```

PROCEDIMENT

Equilibration NpzT

- Sistema en equilibri
- 300 K
- 1 atm
- Carboni fixat

Non equilibrium NVT

- Pressió sobre el sistema
- 300 K
- Carboni fixat

PROCEDIMENT

```
tclForces               on

tclForcesScript {
  set cellLengthZ 30.3962  ;
  set LowerBoundary -12.5
  set UpperBoundary 12.5
  set force {0 0 0.4}
  set watIdList {}
  for {set i 577} {$i<1320} {incr i 3} {
    lappend watIdList $i
    addatom $i
  }
  proc calcforces {} {
    global cellLengthZ LowerBoundary UpperBoundary force watIdList
    loadcoords coorList
    foreach i $watIdList {
      set z [lindex $coorList($i) 2]
      set z [expr $z-round($z/$cellLengthZ)*$cellLengthZ]  ;
      if {$z>$UpperBoundary || $z<$LowerBoundary} {
        addforce $i $force
      }
    }
  }
}
```

ANÀLISI

```
# This script counts the total net water flow through the
# nanutube layer in the trajectory

# Before running it, first load the dcd file in VMD, and make sure
# it's the "top" molecule.

# Specify the upper and lower boundaries of the nanotube layer
# data for practical J Faraudo
set upperEnd 6.754
set lowerEnd -6.754

#Added by J Faraudo
#Save data into file during calculations
set filename "flow.dat"
set fileId [open $filename "w"]

# The following function sets the status for each water molecule
# status 0: Inside the nanotube layer
# status 1: Above the nanotube layer
# status -1: Below the nanotube layer
proc set_status {} {
  global wat statusList upperEnd lowerEnd
  set statusList {}
  foreach z [$wat get z] {
    if {$z < $lowerEnd} {
      lappend statusList -1
    } elseif {$z > $upperEnd} {
      lappend statusList 1
    } else {
      lappend statusList 0
    }
  }
}
```

flow.t

```
set wat [atomselect top "name OH2"]
set numFrame [molinfo top get numframes]
set total 0

molinfo top set frame 0
set_status

# For every frame, the status of each water molecule is
# calculated, and compared with its status in the previous frame.
# If the status changes from 0 to +-1 or vice versa, it means that
# this water molecule has crossed one of the boundaries of the
# nanotube layer. The variable "total" records the total number
# of such crossing events (for each event, either +1 or -1 is
# added to "total", according to the crossing direction). However,
# due to the periodic boundary condition, a change of the status
# from +1 to -1 or vice versa doesn't mean the water molecule has
# crossed the channel.

for {set fr 1} {$fr < $numFrame} {incr fr} {
  molinfo top set frame $fr
  set oldList $statusList
  set_status
  foreach oldSt $oldList newSt $statusList {
    if {$oldSt!=$newSt && $oldSt+$newSt!=0} {
      incr total [expr $newSt - $oldSt]
    }
  }
  set data "[expr $fr] [expr $total/2.0] \n"
  puts -nonewline $fileId $data
}

close $fileId

# The net flow is taken as the average of the numbers of the
# crossing events for the two boundaries, i.e., one half of "total"

if {$total > 0} {
  puts "The net flow is [expr $total/2.0] water molecules along +z"
} elseif {$total < 0} {
  puts "The net flow is [expr -$total/2.0] water molecules along -z"
} else {
  puts "The net flow is 0"
}
puts "Time evolution saved in a .dat file (J Faraudo)"
```

ANÀLISI

permeation.tcl

```
# This script identifies water molecules that permeate through the
# nanotube layer

# Before running it, first load the dcd file in VMD, and make sure
# it's the "top" molecule.
# data for practical J Faraudo
set upperEnd 6.754
set lowerEnd -6.754

# Start counting permeation events after this number of frames
#set skipFrame 500
#no skip (modified J Faraudo)
set skipFrame 0

#Added by J Faraudo
#Save data into file during calculations
set filename "permeation.dat"
set fileId [open $filename "w"]
set data "# frame +z -z \n"
puts -nonewline $fileId $data

puts "Computing permeation events... (please wait)"

set wat [atomselect top "name OH2"]
set segList [$wat get segname]
set ridList [$wat get resid]
set labelList {}
foreach foo $segList {
  lappend labelList 0
}

set num1 0
set num2 0
set numFrame [molinfo top get numframes]


# Each water molecule has a label, which has 5 possible values
#  2: Above the nanotube layer
# -2: Below the nanotube layer
#  1: Inside the nanotube layer, entering from upper surface
# -1: Inside the nanotube layer, entering from lower surface
#  0: Inside the nanotube layer from the beginning

# For every frame, the label of each water molecule is
# determined, and compared with its label in the previous frame.
# If the new label is +2 (or -2), while the old label is -1 (or +1),
# it means the water molecule has traversed the nanotube, thus a
# permeation event is reported and counted. If a water molecule
# is inside the nanotube layer in the current frame, its label
# will be determined by its old label.

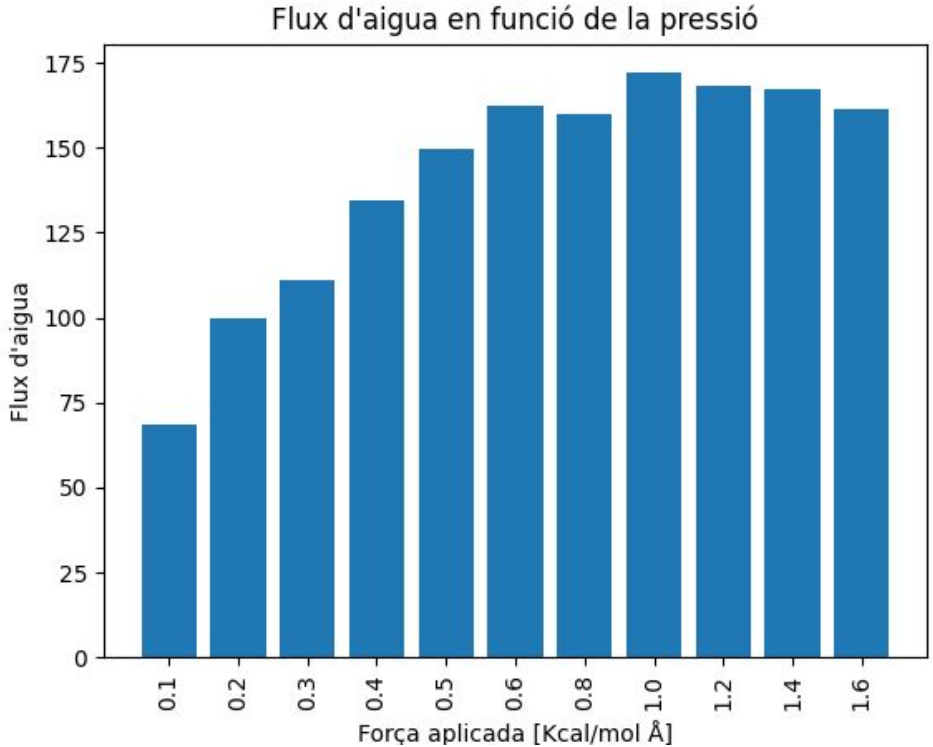
for {set fr 0} {$fr < $numFrame} {incr fr} {
  molinfo top set frame $fr
  set oldList $labelList
  set labelList {}
  foreach z [$wat get z] oldLab $oldList segname $segList resid $ridList {
    if {$z > $upperEnd} {
      set newLab 2
      if {$oldLab == -1} {
        puts "$segname:$resid permeated through the nanotubes along +z direction at frame $fr"
        if {$fr >= $skipFrame} {
          incr num1
        }
      }
    } elseif {$z < $lowerEnd} {
      set newLab -2
      if {$oldLab == 1} {
        puts "$segname:$resid permeated through the nanotubes along -z direction at frame $fr"
        if {$fr >= $skipFrame} {
          incr num2
        }
      }
    } elseif {abs($oldLab) > 1} {
      set newLab [expr $oldLab / 2]
    } else {
      set newLab $oldLab
    }
    lappend labelList $newLab
  }

  #added by J Faraudo: save data
  set data "[expr $fr] [expr $num1] [expr $num2] \n"
  puts -nonewline $fileId $data
}

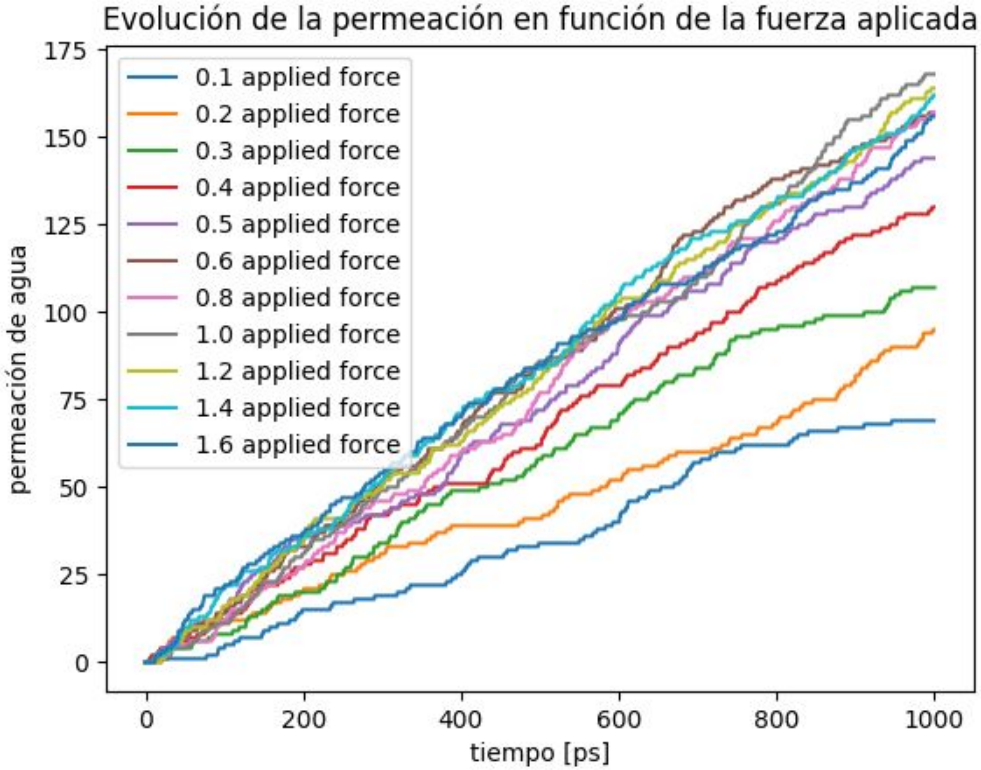
close $fileId

puts ""
set nf [expr $numFrame-$skipFrame]
if {$nf >= 0} {
  puts "The total number of permeation events during $nf frames in +z direction is: $num1"
  puts "The total number of permeation events during $nf frames in -z direction is: $num2"
} else {
  puts "The specified first frame ($skipFrame) is larger than the total number of frames ($numFrame)"
}
puts "Time evolution saved in a .dat file (J Faraudo)"
```

RESULTATS


Flux d'aigua en funció de la pressió
Flux d'aigua
175
150
125
100
75
50
25
0
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0
1.2
1.4
1.6
Força aplicada [Kcal/mol Å]

RESULTATS


Evolución de la permeación en función de la fuerza aplicada
permeación de agua
tiempo [ps]
0.1 applied force
0.2 applied force
0.3 applied force
0.4 applied force
0.5 applied force
0.6 applied force
0.8 applied force
1.0 applied force
1.2 applied force
1.4 applied force
1.6 applied force
0
25
50
75
100
125
150
175
0
200
400
600
800
1000

CONCLUSIONS

Saturació a 10,4 GPa

Velocitat màxima de $8{,}15 \cdot 10^{10}$ molec/seg

12,5 litres/min si omplim una aixeta de CNTs