

LAMMPS: A Powerful Tool for Large-scale Molecular Dynamics Simulations- Part II

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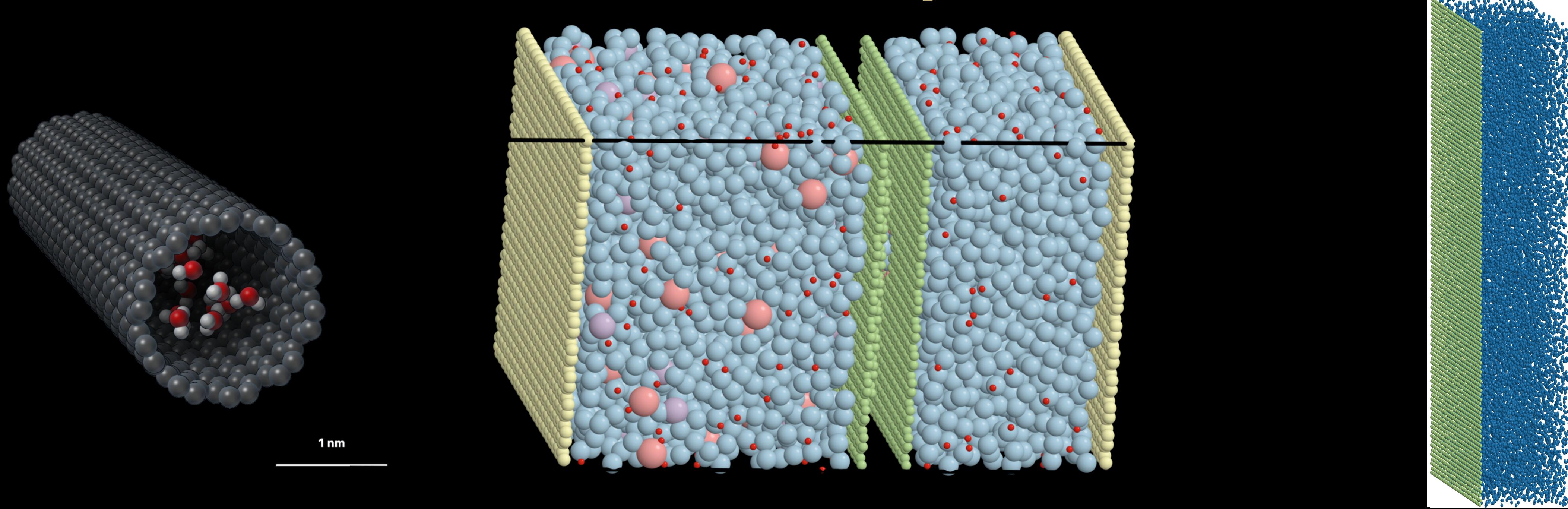
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Confinement

How to Characterize Position-
Dependence of Physical
Properties in Confined Systems

What is Confinement?

Characterized by interfaces



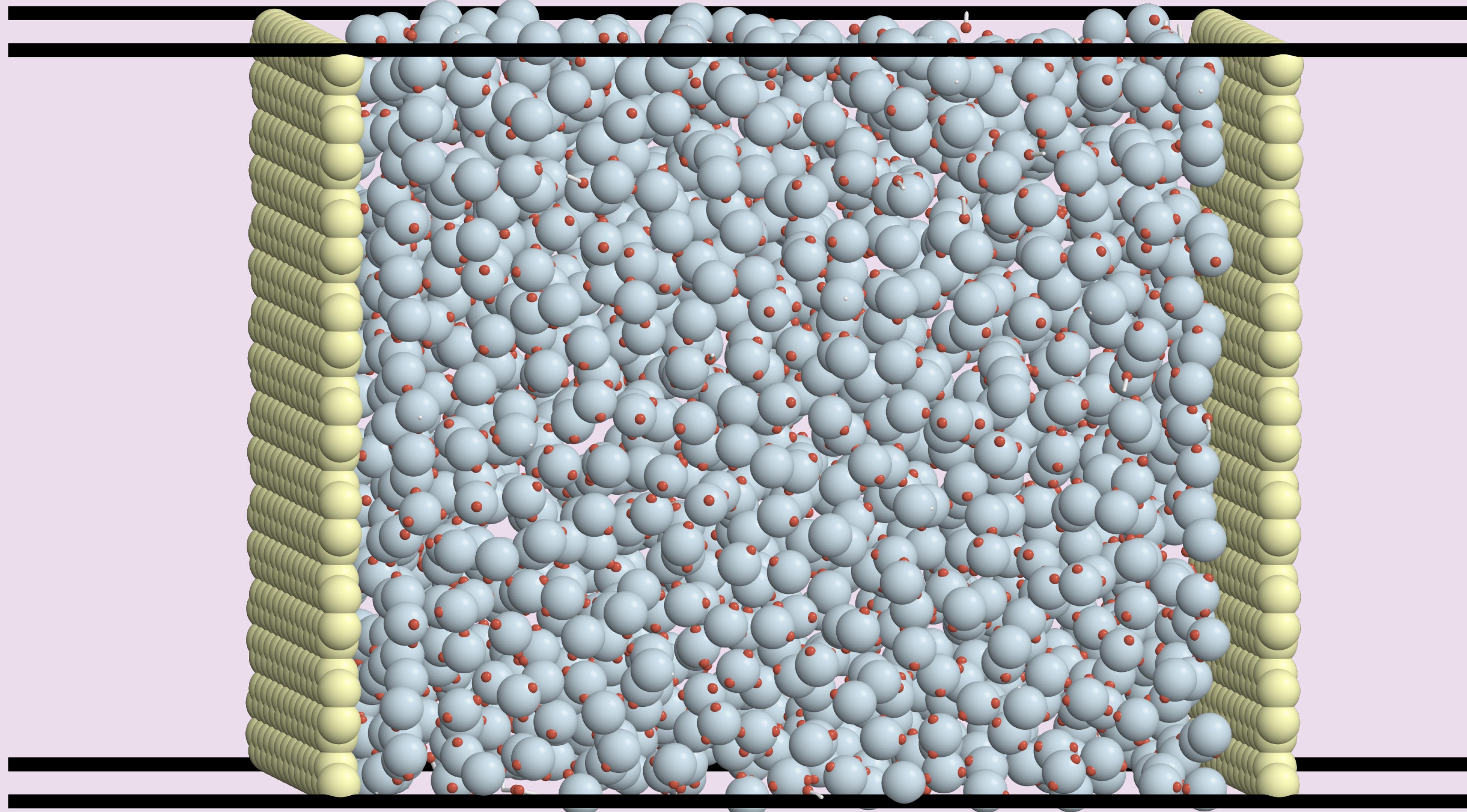
*All thermodynamic, structural & transport properties
are functions of position.*

Simulating Confined Systems

- **Implementation Details:**
 - Employing new ensembles/algorithms might be necessary.
 - Long-range interactions treated differently.
 - System initialization is more challenging, necessitating specialized tools.
- **Analysis:**
 - Characterizing position-dependence of properties of interest achieved using binning:
 - Not straightforward for certain properties (e.g., transport coefficients).

Example 1: Water within a Slit Pore

TIP4P/2005 Water within a Graphene Nanopore

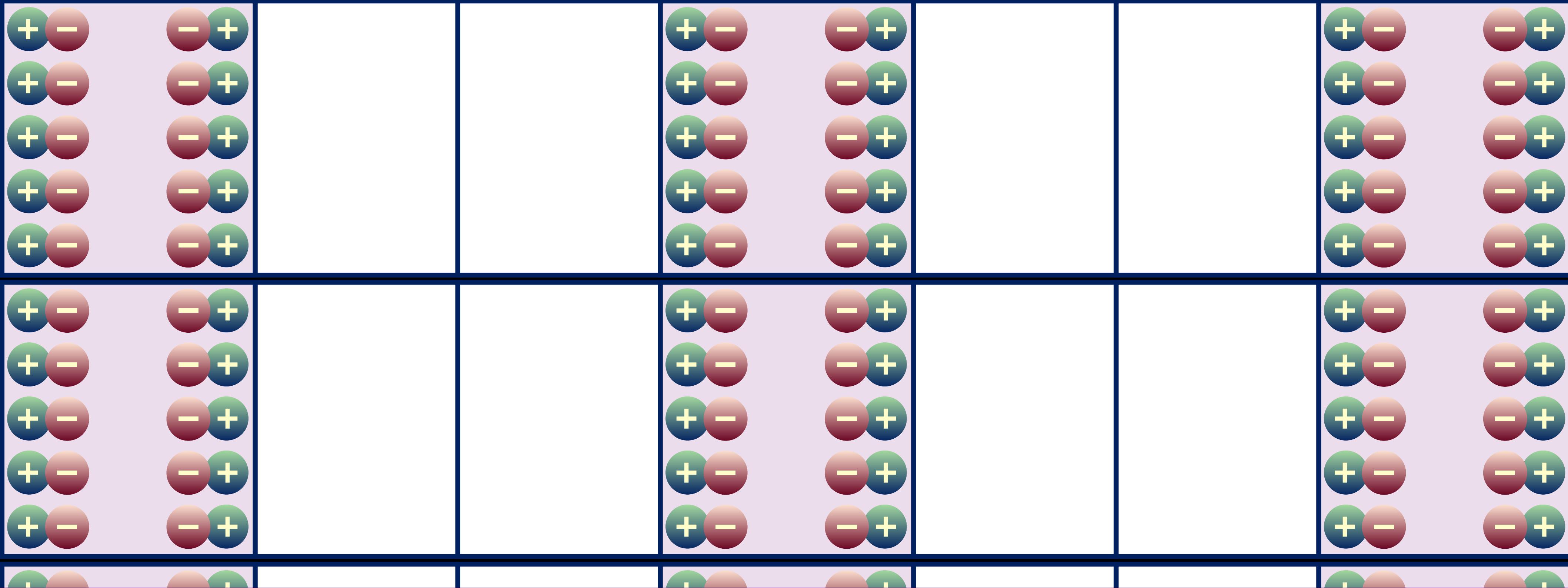


Example 1: Water within a Slit Pore

TIP4P/2005 Water within a Graphene Nanopore

```
units real
boundary p p f
atom_style full
neighbor 2.0 bin
neigh_modify delay 0 every 1 check yes
pair_style lj/cut/tip4p/long 1 2 1 1 0.1546 12.5
pair_modify mix arithmetic
processors * * 1
bond_style harmonic
angle_style harmonic
read_data ${inFileName}
kspace_style pppm/tip4p 0.0001000000000000
kspace_modify slab 3.000000000000000
dielectric 1.0
bond_coeff 1 5000 0.9572 # water TIP4P-2005, the K coeff is irrelevant as we are using a rigid model for water
angle_coeff 1 500 104.52 #water TIP4P-2005, The value for K is not used as we are using a rigid model of water
pair_coeff 1 1 0.1852 3.1589 # O-water #TIP4P-2005
pair_coeff 2 2 0.0 0.0 # H-water
pair_coeff 3 0.0859 3.3997 # C_piston # same as graphene systems
pair_coeff 4 4 0.0859 3.3997 # C_piston # same as graphene systems
group hydWater type 2
group oxWater type 1
group pist1 type 3
group pist2 type 4
group waterGrp union oxWater hydWater
group pistonGrp union pist1 pist2
fix myNVT waterGrp nvt temp 300.00000000000000 300.00000000000000 200.00000000000000 # Allow energy to fluctuate (remove high energies)
fix wallLowStr all wall/lj93 zlo EDGE 1.0000000000000000 1.0000000000000000 1.1000000000000000
fix wallHighStr all wall/lj93 zhi EDGE 1.0000000000000000 1.0000000000000000 1.1000000000000000
fix shakeFixwaterGrpStr waterGrp shake 0.0001 200 0 b 1 a 1
thermo 100
timestep 2.0
run 1000000
```

Spurious Interactions in Heterogeneous Systems



Slab Ewald/PPPM is a trick to avoid such spurious interactions

Periodic boundary conditions along x and y only.

Example 1: Water within a Slit Pore

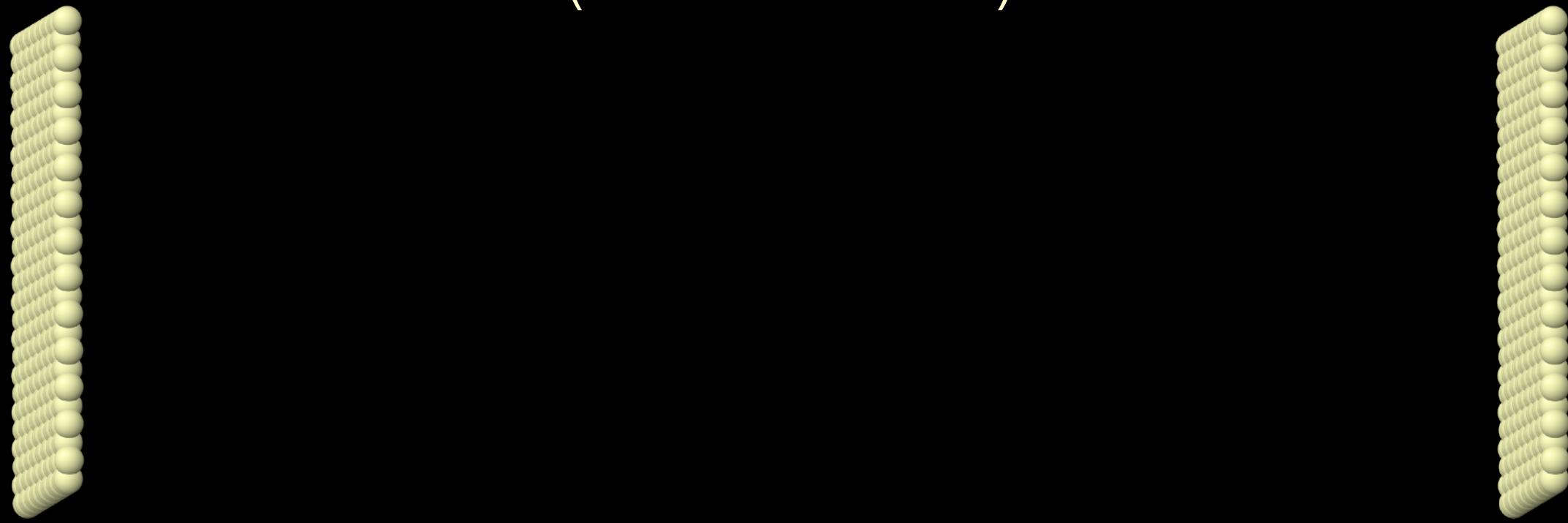
TIP4P/2005 Water within a Graphene Nanopore

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neigh_modify delay 0 every 1 check yes
pair_style lj/cut/tip4p/long 1 2 1 1 0.1546 12.5
pair_modify mix arithmetic
processors * * 1
bond_style harmonic
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read_data ${inFileName}
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group hydWater type 2
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group pist2 type 4
group waterGrp union oxWater hydWater
group pistonGrp union pist1 pist2
fix myNVT waterGrp nvt temp 300.000000000000000 300.000000000000000 200.000000000000000 # Allow energy to fluctuate (remove high energies)
fix wallLowStr all wall/lj93 zlo EDGE 1.000000000000000 1.000000000000000 1.100000000000000
fix wallHighStr all wall/lj93 zhi EDGE 1.000000000000000 1.000000000000000 1.100000000000000
fix shakeFixwaterGrpStr waterGrp shake 0.0001 200 0 b 1 a 1
thermo 100
timestep 2.0
run 1000000
```

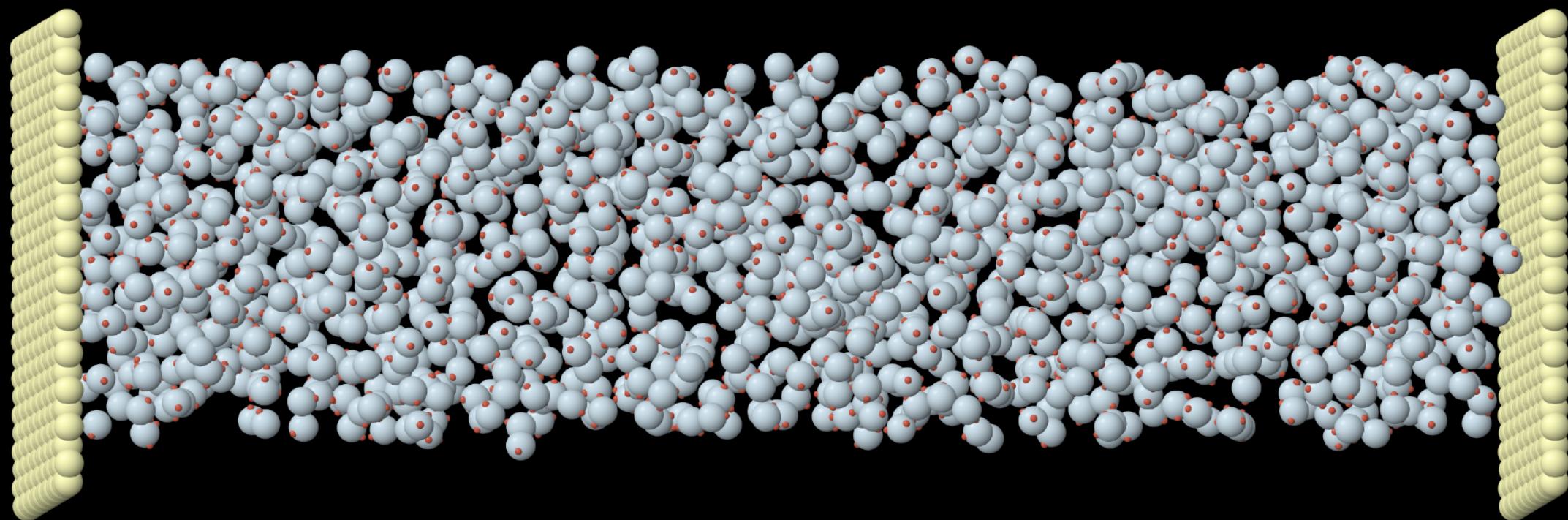
Ensemble fix applied to a subset of the system.

System Preparation

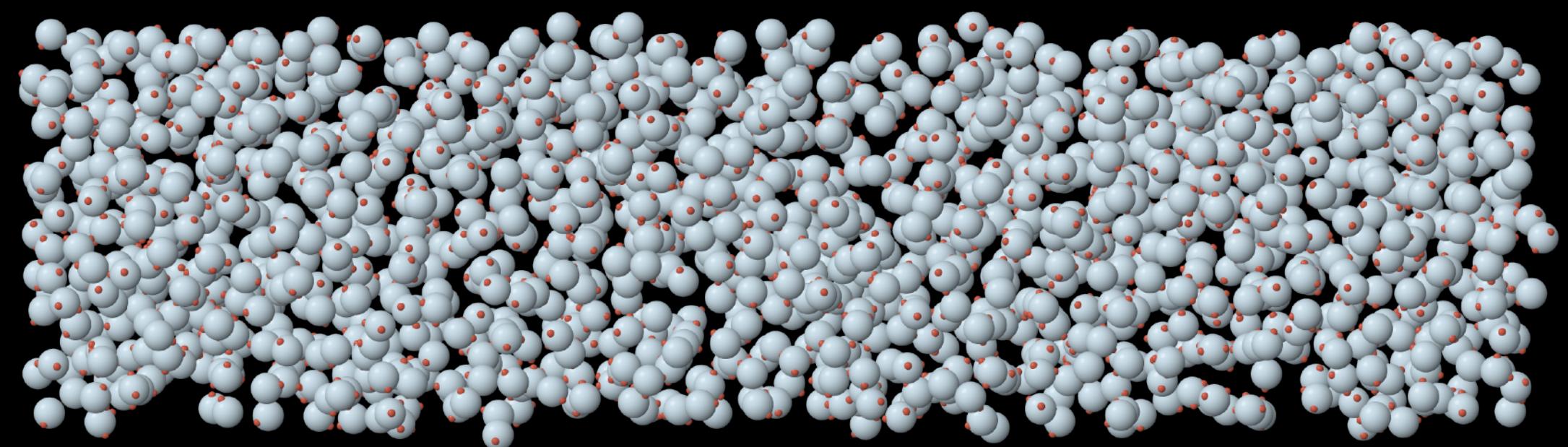
Step 1: Create graphene sheets using VMD
(Nanobuilder)



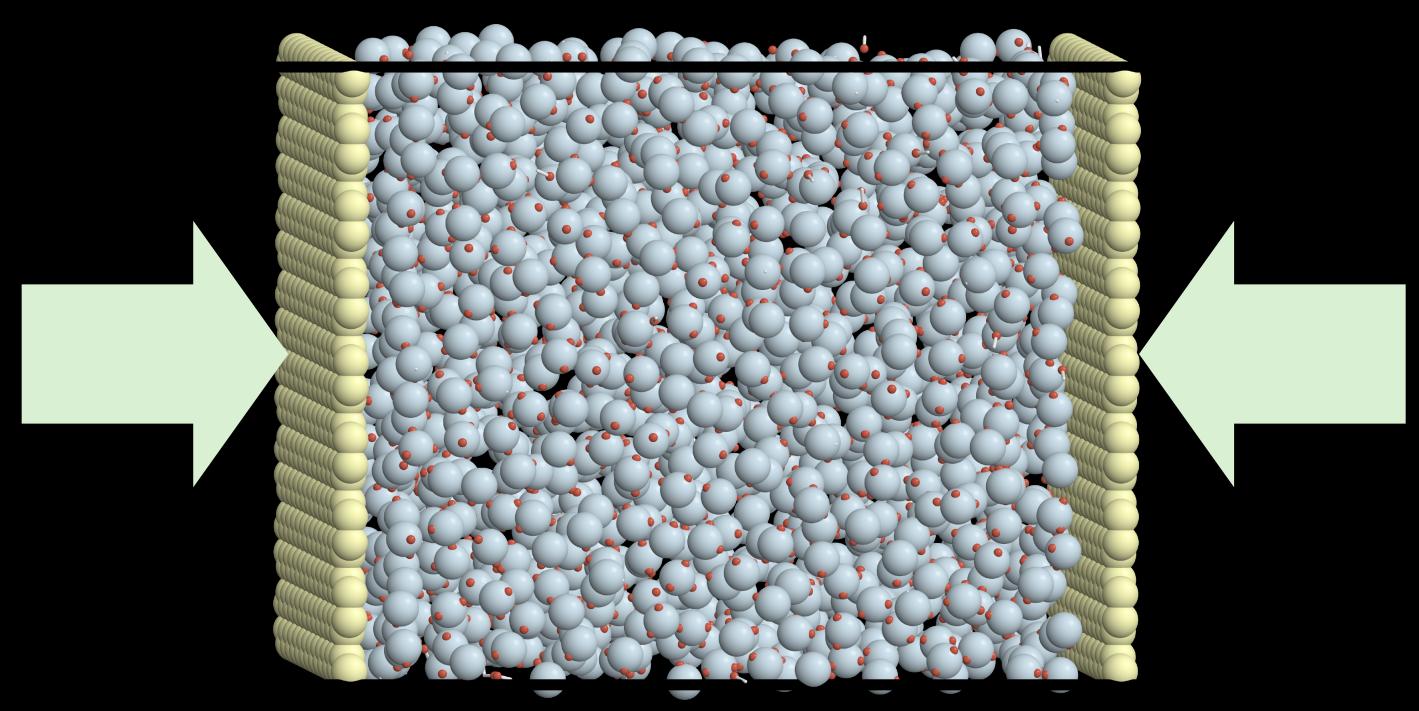
Step 3: Create the simulation box by combining the two structures using Python.

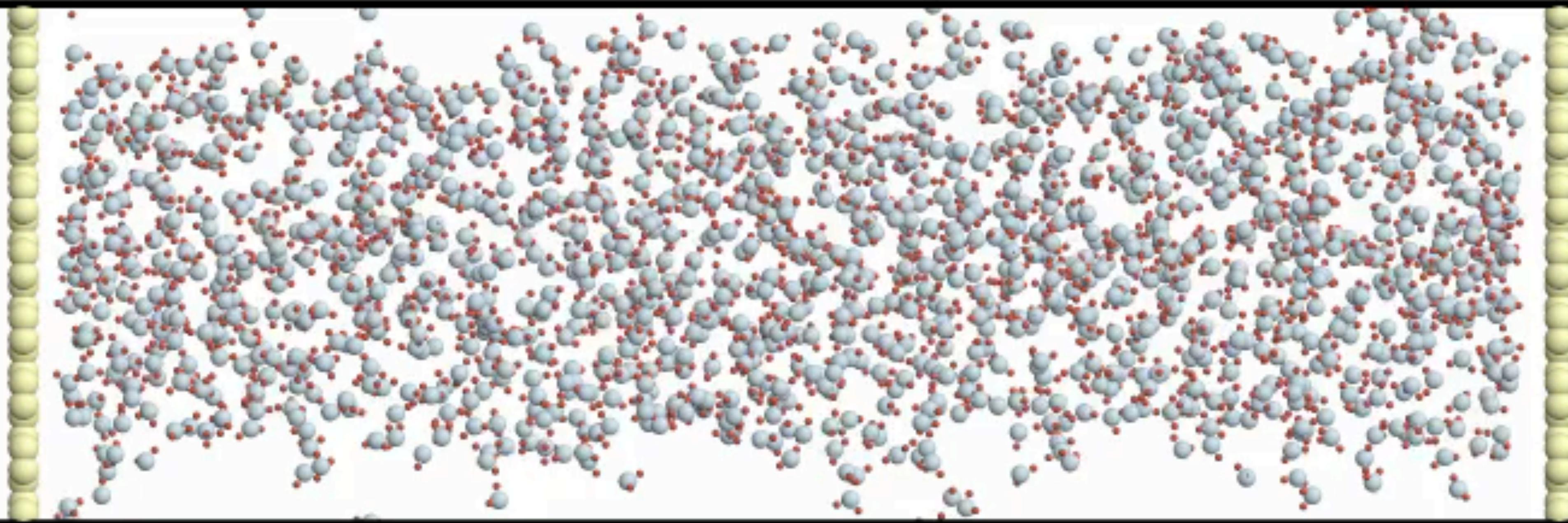


Step 2: Create a box of water molecules using PACKMOL.



Step 4: Apply forces to both pistons to compress and equilibrate water.





Analysis of Confined System

fix ave/chunk

Step 1: Partition the simulation box into 0.01-nm bins along the z axis.

```
compute binId waterGrp chunk/atom bin/1d z lower 0.1 units box
```

Step 2: Compute per-atom potential energy and charge.

```
compute qVal waterGrp property/atom q
compute peVal waterGrp pe/atom
```

Step 3: Compute the dipole moment in each bin.

```
compute dipoleCmp waterGrp dipole/tip4p/chunk binId
```

Step 4: Average density, charge, potential energy, and dipole moment per bin.

```
fix avDen all ave/chunk 100 1 100 binId density/mass c_qVal c_peVal ave running file ${tag}-num-Den.txt overwrite
fix avDpl all ave/time 100 1 100 c_dipoleCmp[*] file ${tag}.dpl.out mode vector ave running
```

Have Your Adventures with Confined Water

Step 1: Copy the input and slurm scripts as well as your group's designated input file to an appropriate folder.

```
cp /ocean/projects/see220002p/shared/LAMMPS/Water-Slit-Pore/in.water-conf-prod-nvt .
cp /ocean/projects/see220002p/shared/LAMMPS/Water-Slit-Pore/analysis.cmd .
cp /ocean/projects/see220002p/shared/LAMMPS/Water-Slit-Pore/relaxed-${N}H2O-10.dat.out .
```

Step 2: Submit the Slurm script as follows.

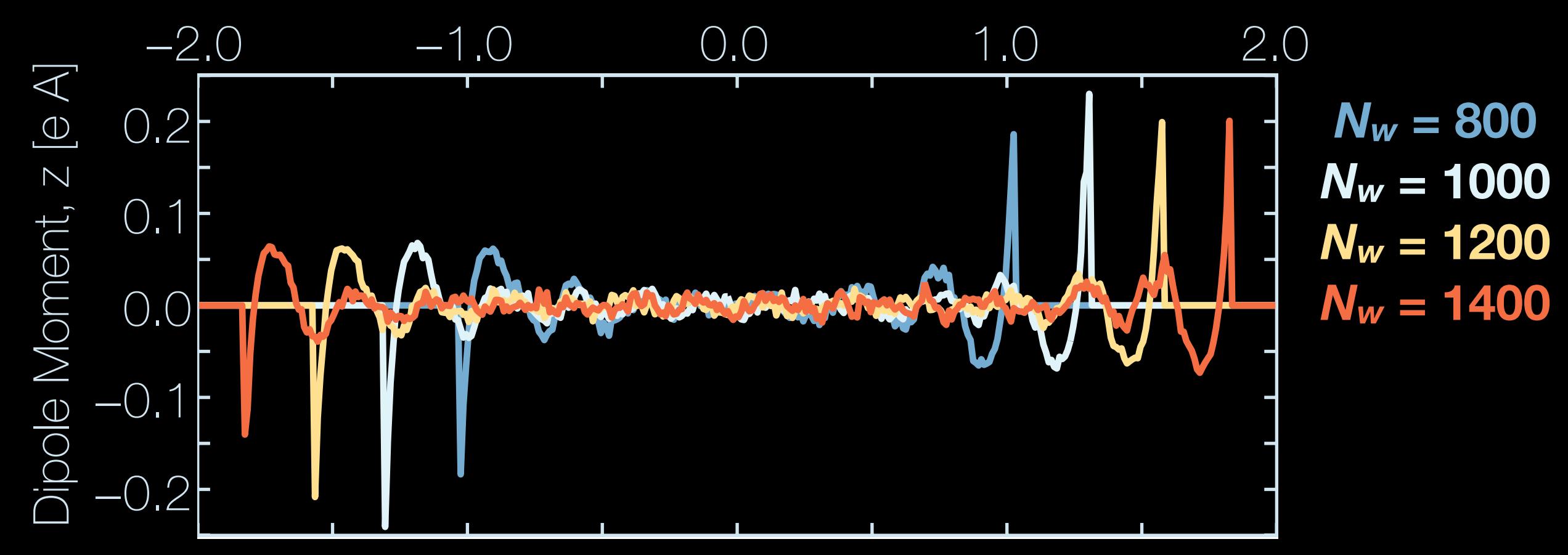
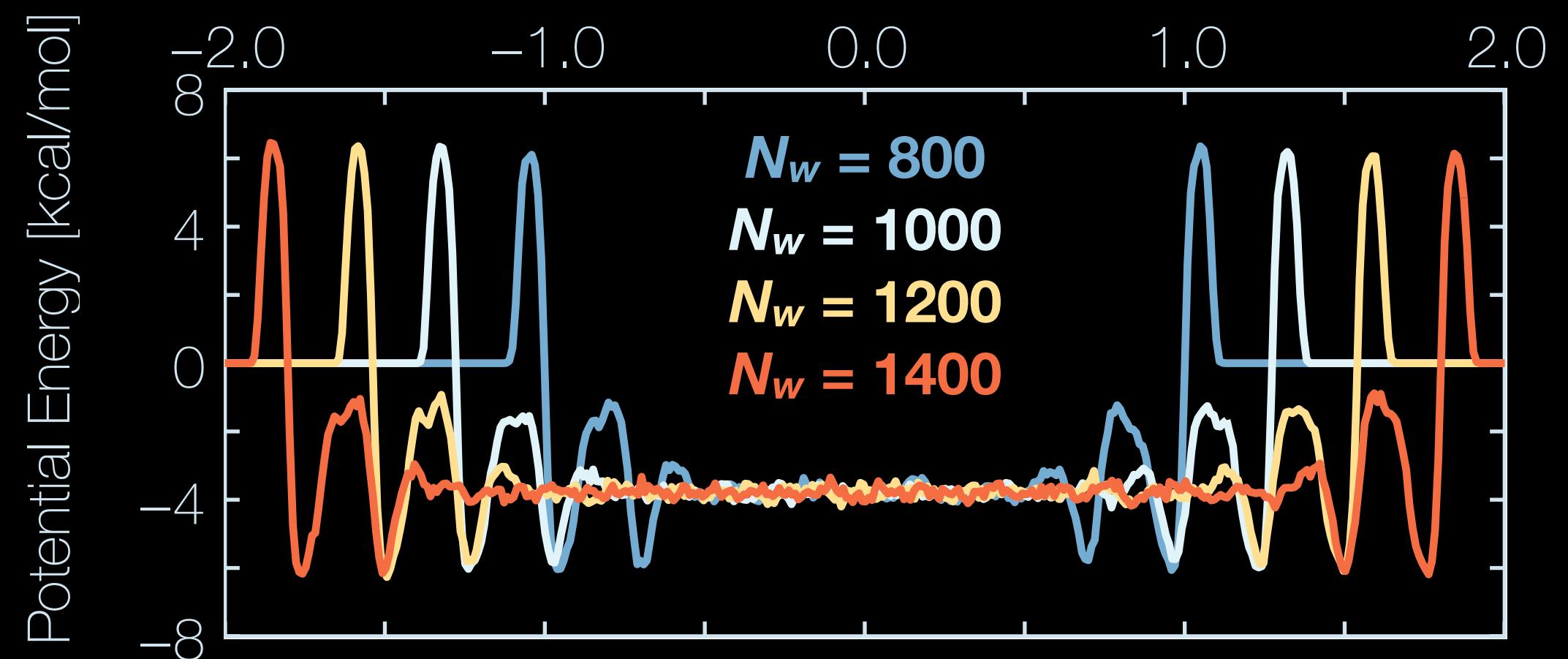
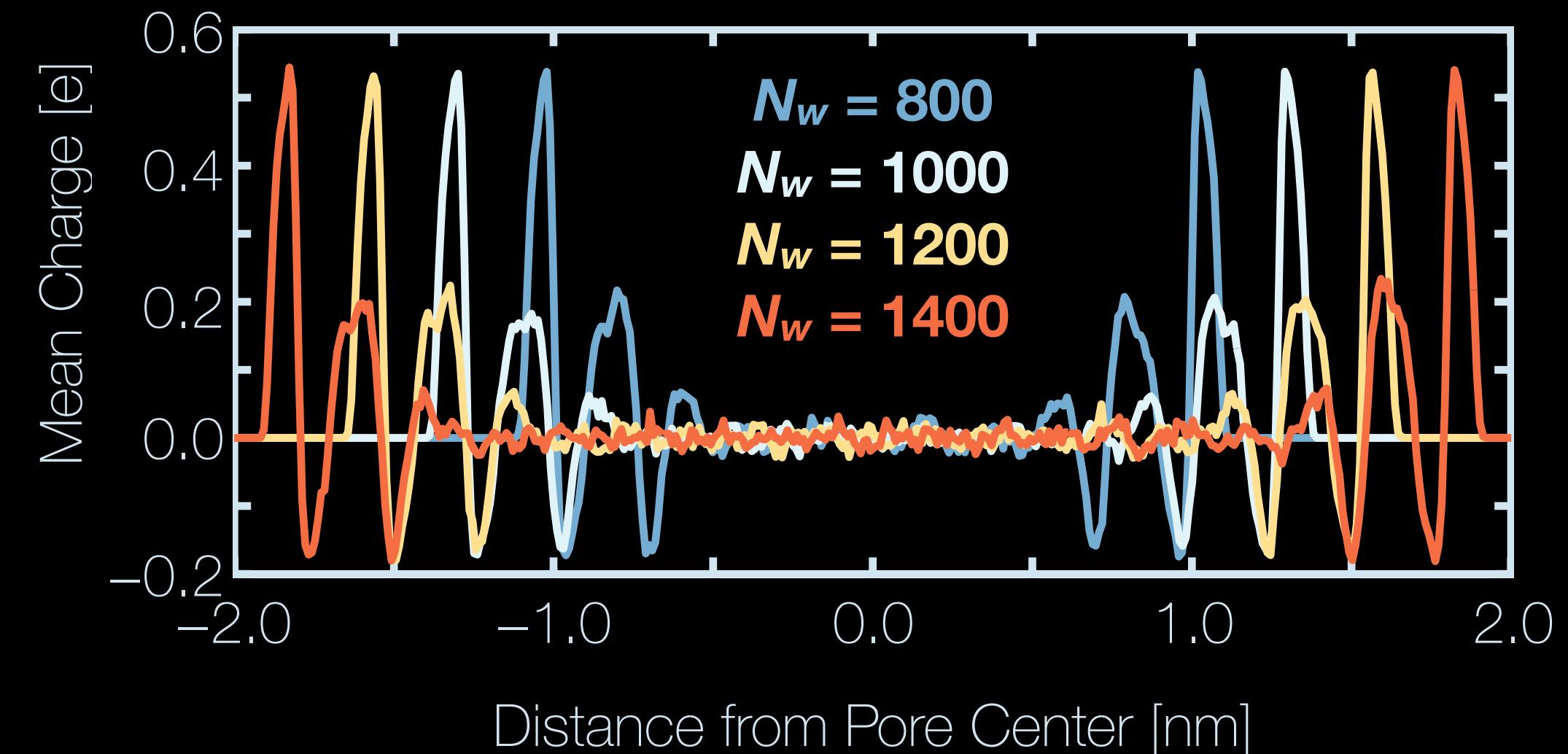
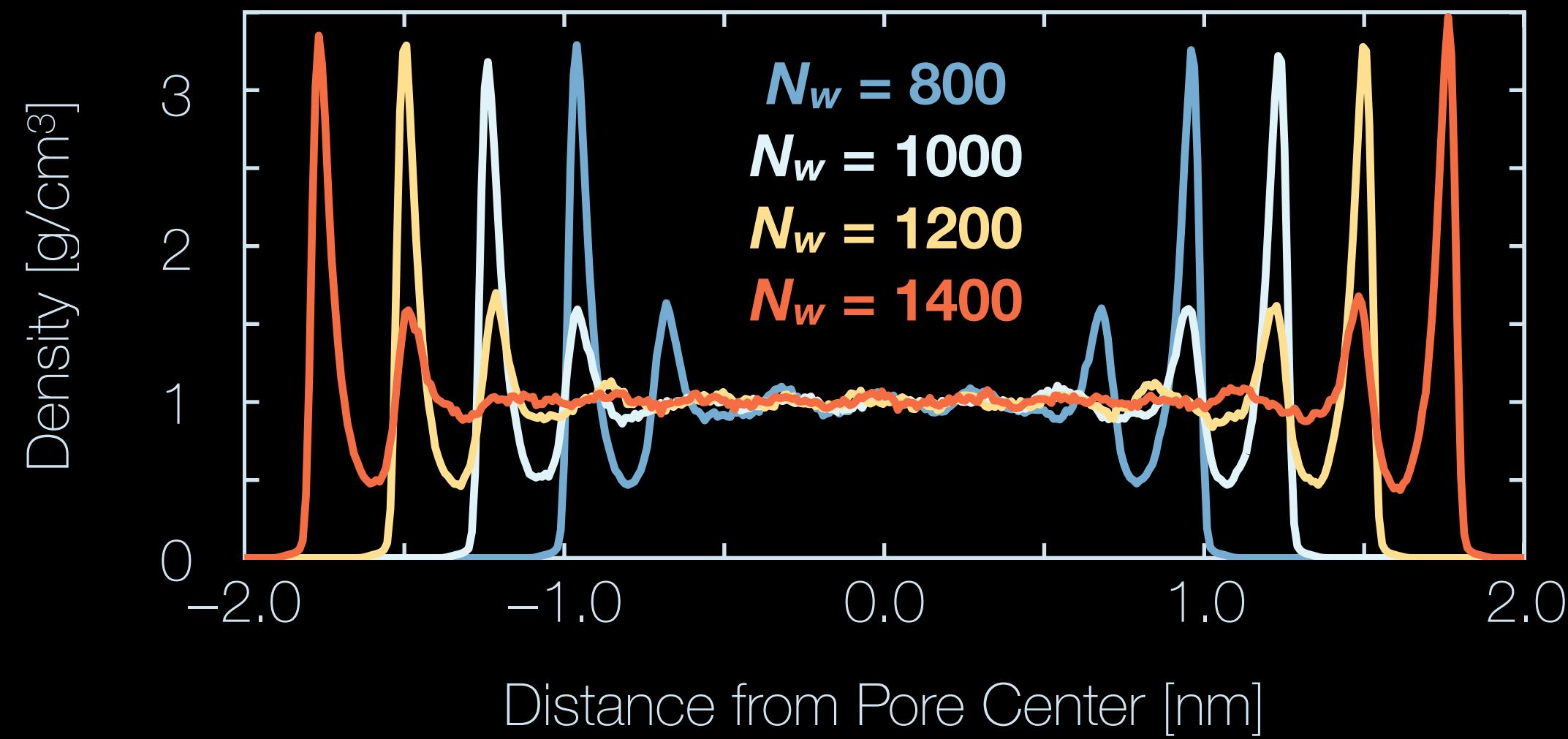
```
sbatch analysis.cmd ${N} 10
```

Step 3: Use the -num-Den.txt to plot mass and charge density as well as mean potential energy vs. the distance from the pore center.

Step 4: Use the dpl.all.txt file and the code provide to compute the components of the dipole vector vs. distance from pore center.

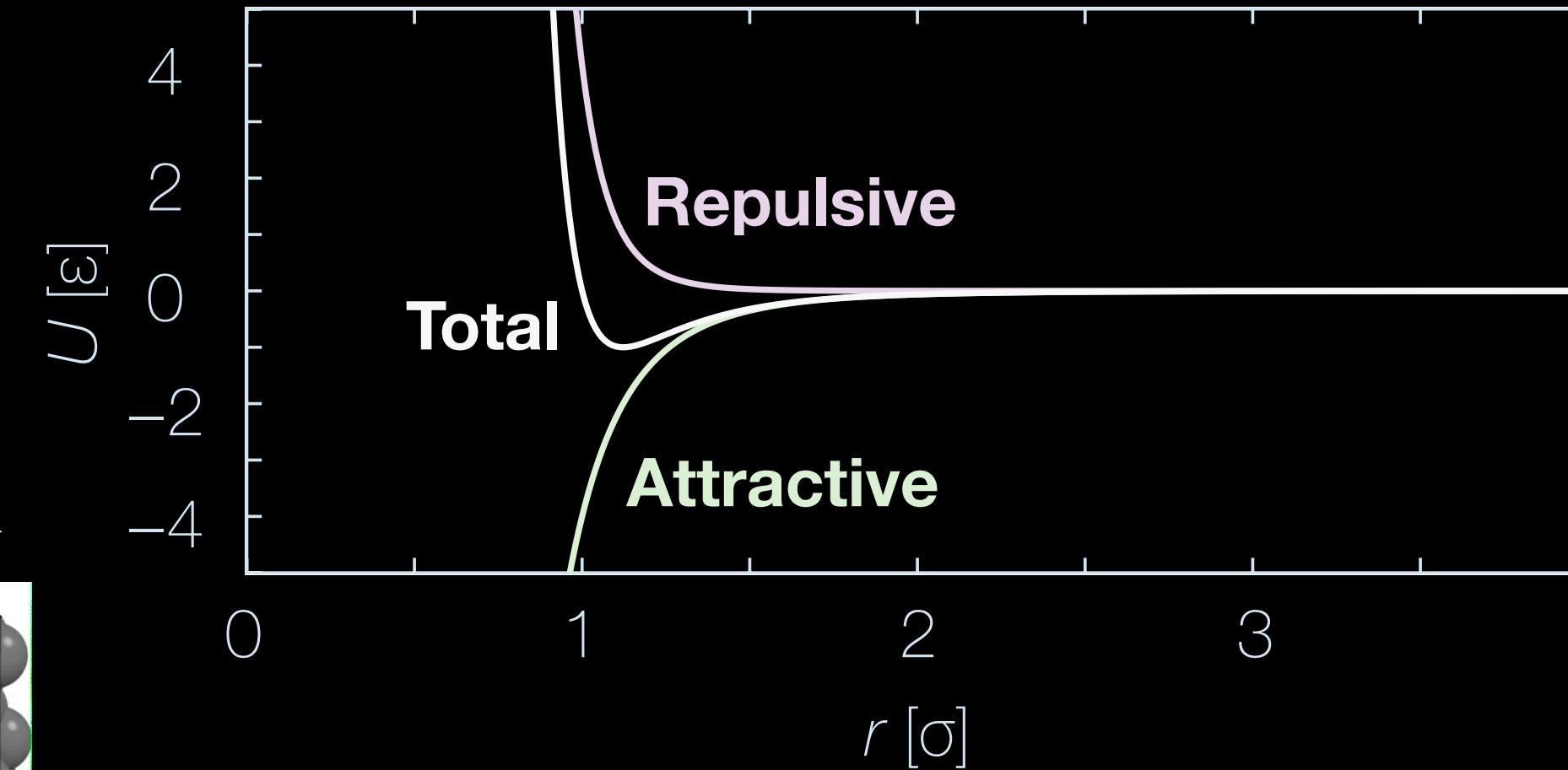
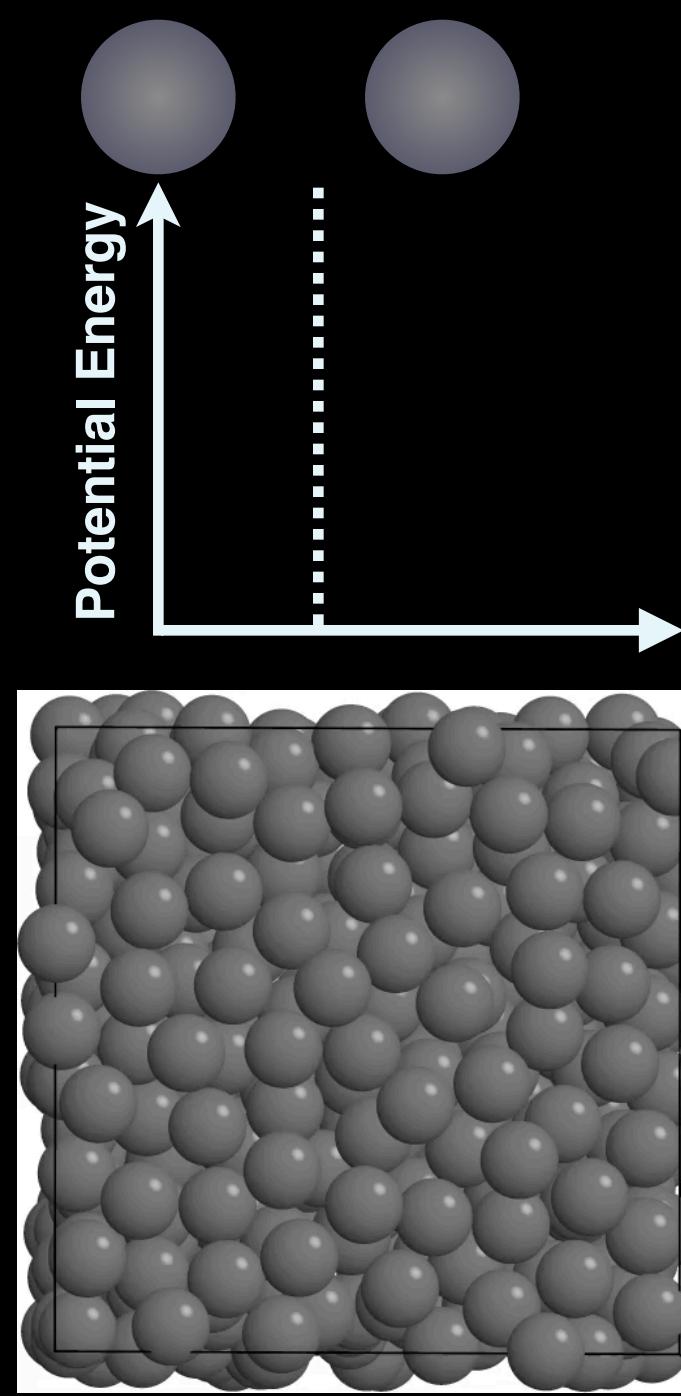
Group ID	Number of Water Molecules
1	800
2	1000
3	1200
4	1400

Results

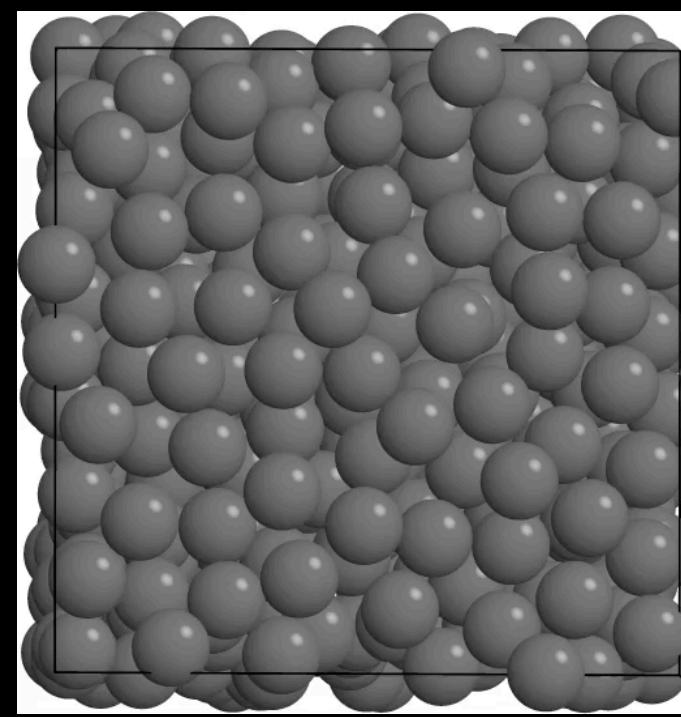


Example 2: Hard Particles in a Slit Pore

How to Simulate Hard Spheres in MD Simulations?



$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$



*Hard particles
generally
studied using
Monte Carlo*

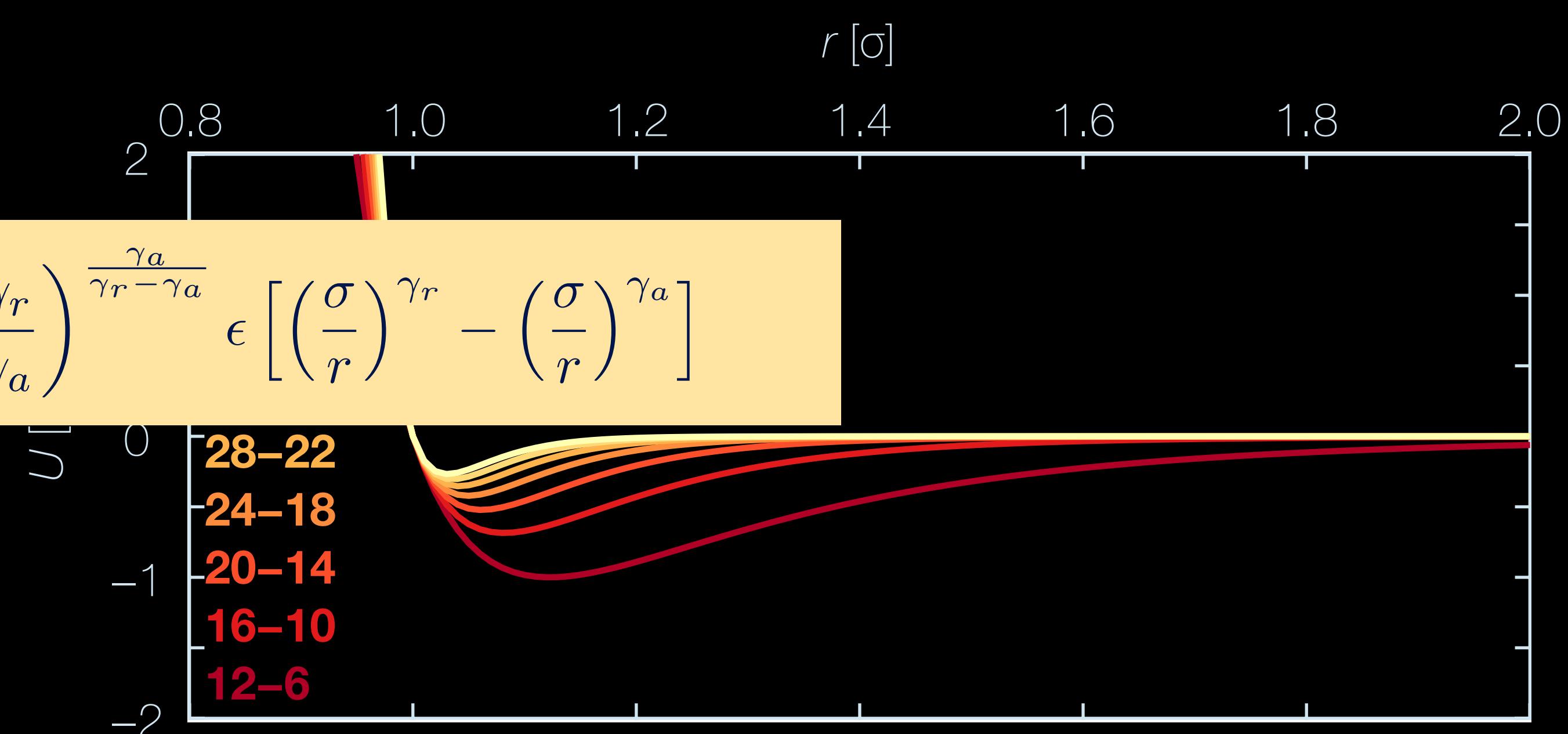
Mie Potential

$$U_{\text{Mie}}(r) = \left(\frac{\gamma_r}{\gamma_r - \gamma_a} \right) \left(\frac{\gamma_r}{\gamma_a} \right)^{\frac{\gamma_a}{\gamma_r - \gamma_a}} \epsilon \left[\left(\frac{\sigma}{r}\right)^{\gamma_r} - \left(\frac{\sigma}{r}\right)^{\gamma_a} \right]$$

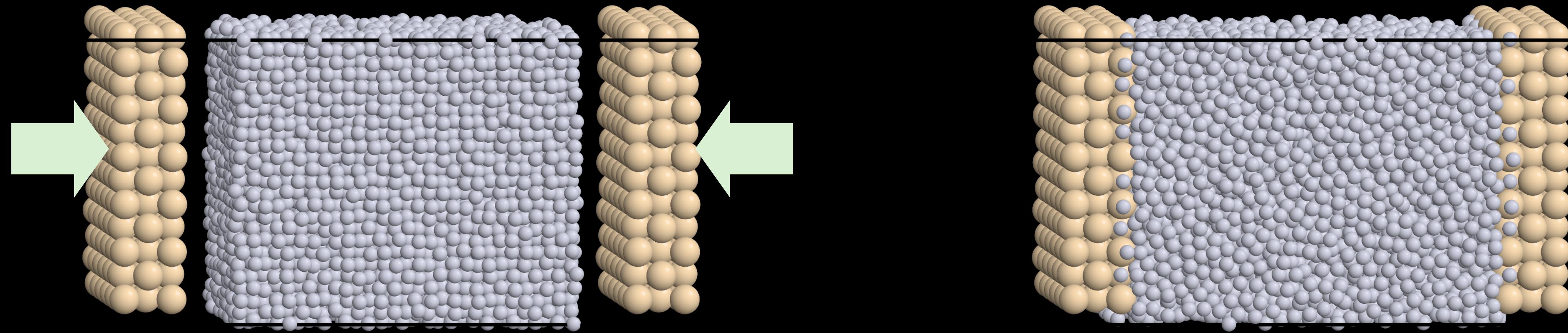
Pseudo-Hard Spheres

$$\gamma^r = 50$$

$$\gamma^a = 49$$

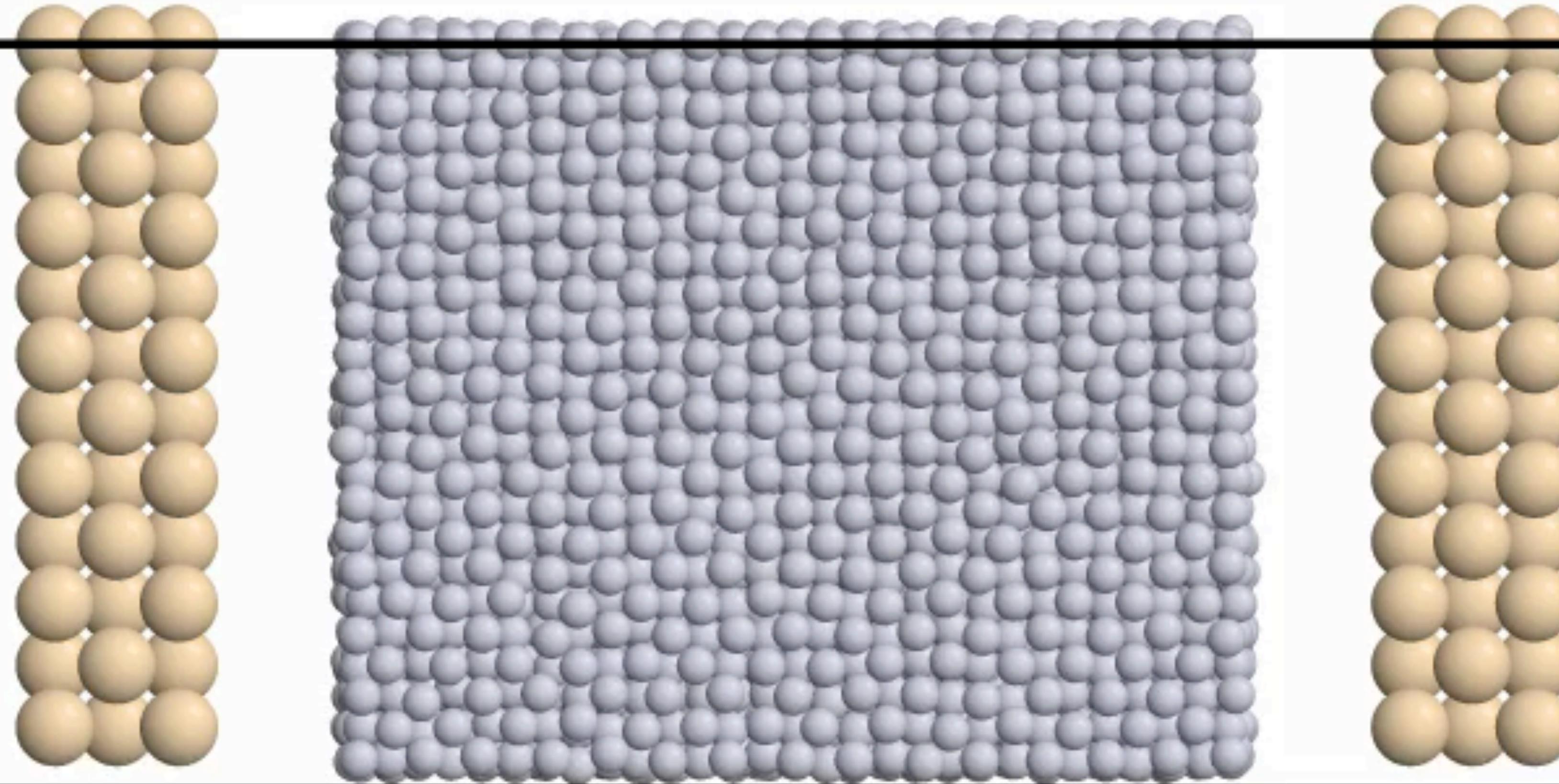


Example 2: Hard Particles in a Slit Pore



```
units lj
atom_style atomic
variable wallSize equal 2
variable wallRat equal 1/v_wallSize
variable wallDen equal v_wallRat*v_wallRat*v_wallRat
variable sigMix equal (1.0+v_wallSize)/2.0
variable cutoffB equal 1.0204*v_wallSize
variable cutoffM equal 1.0204*v_sigMix
processors * * 1
print ${wallDen}
lattice fcc ${wallDen}
region myBox block 0 6 0 6 -18 18
create_box 2 myBox
region hardWall1 block 0 5.99 0 5.99 -6 -5
region hardWall2 block 0 5.99 0 5.99 5 6
region hardWall union 2 hardWall1 hardWall2
create_atoms 2 region hardWall
```

```
lattice fcc 1.0
region liqReg block 0 11.99 0 11.99 -7 7
create_atoms 1 region liqReg
group hw1Grp region hardWall1
group hw2Grp region hardWall2
pair_style mie/cut 2.5
pair_modify shift yes
pair_coeff 1 1 1.0 1.0 50.0 49.0 1.0204
pair_coeff 1 2 1.0 ${sigMix} 50.0 49.0 ${cutoffM}
pair_coeff 2 2 1.0 ${wallSize} 50.0 49.0 ${cutoffB}
mass 1 1.0
mass 2 1.0
neighbor 2.5 bin
neigh_modify every 1 delay 0 check yes page 100000
group mobileGrp type 1
fix momentumFix mobileGrp momentum 1 linear 1 1 1
fix ensFix mobileGrp nvt temp 1.5 1.5 0.1
```



Example 2: Hard Particles in a Slit Pore

Step 1: Copy the input scripts and starting configurations to an appropriate folder.

```
cp /ocean/projects/see220002p/shared/LAMMPS/Hard-Sphere-Slit-Pore/in.hard-sphere-$W$X-rst .
cp /ocean/projects/see220002p/shared/LAMMPS/Hard-Sphere-Slit-Pore/hard-sphere-conf-melted-X$W$.dat.out .
```

Step 2: Launch a single-core interactive job, and run LAMMPS using the following command.

```
/ocean/projects/see220002p/shared/LAMMPS/bin/lmp_mpi -in in.hard-sphere-rst -v wallSize ${W} -v rstFileName hard-sphere-conf-melted-X$W$.dat.out -v outFileName hard-sphere-conf-equil-X$W$.dat.out -v prodSteps 100000
```

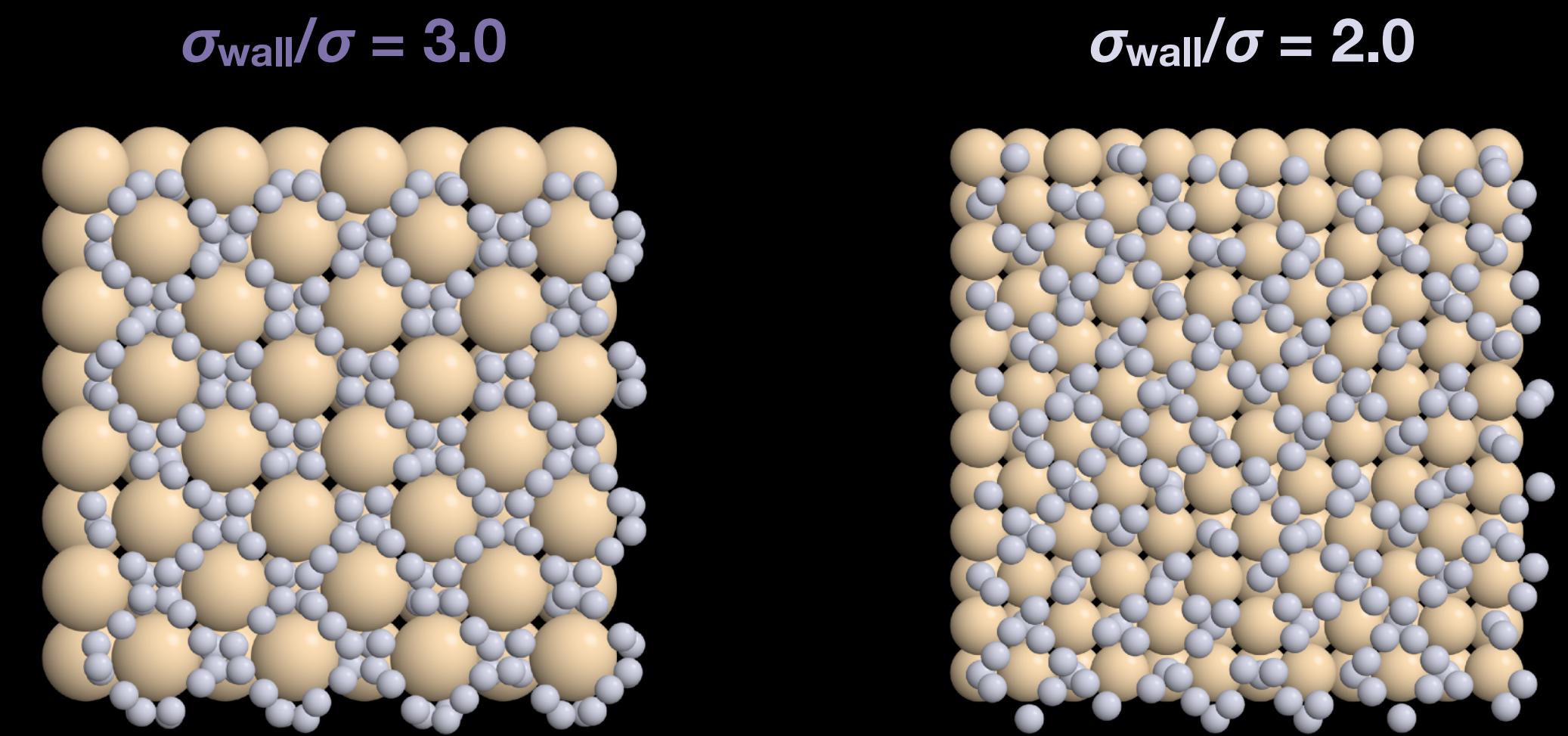
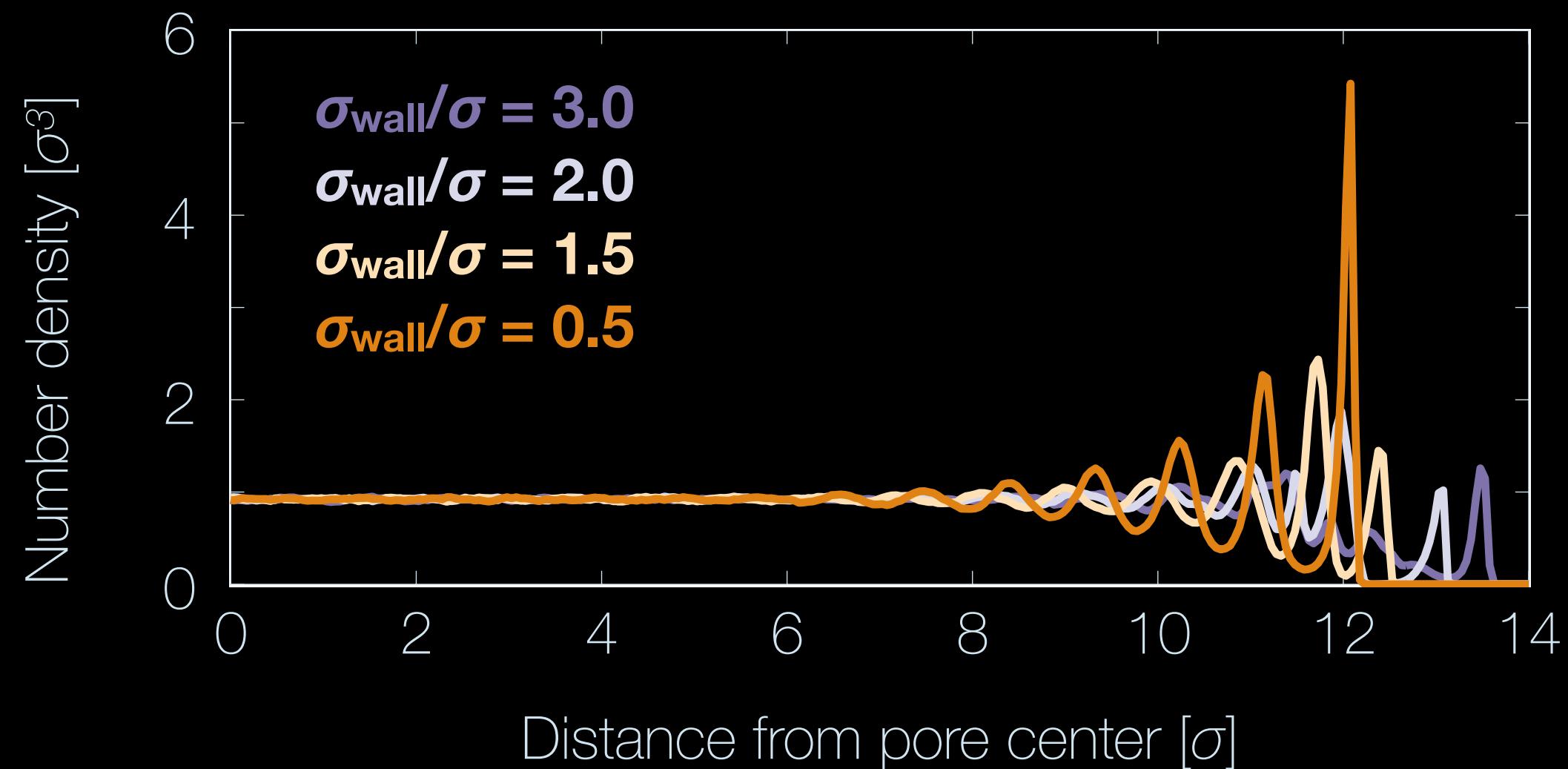
Step 3: End your interactive job.

Step 4: Use the .numDen.txt file to extract number density vs. distance from the pore center.

Group ID	Wall Particle Size
1	0.5
2	1.5
3	2.0
4	3.0

Example 2: Hard Particles in a Slit Pore

Number Density Profiles



Small extreme peaks arise due to particles occupying openings among large wall particles.