Comparative Analysis of Cerium Nanoparticle Modelling: Montecarlo Algorithm vs. CHARMM-Based Methods

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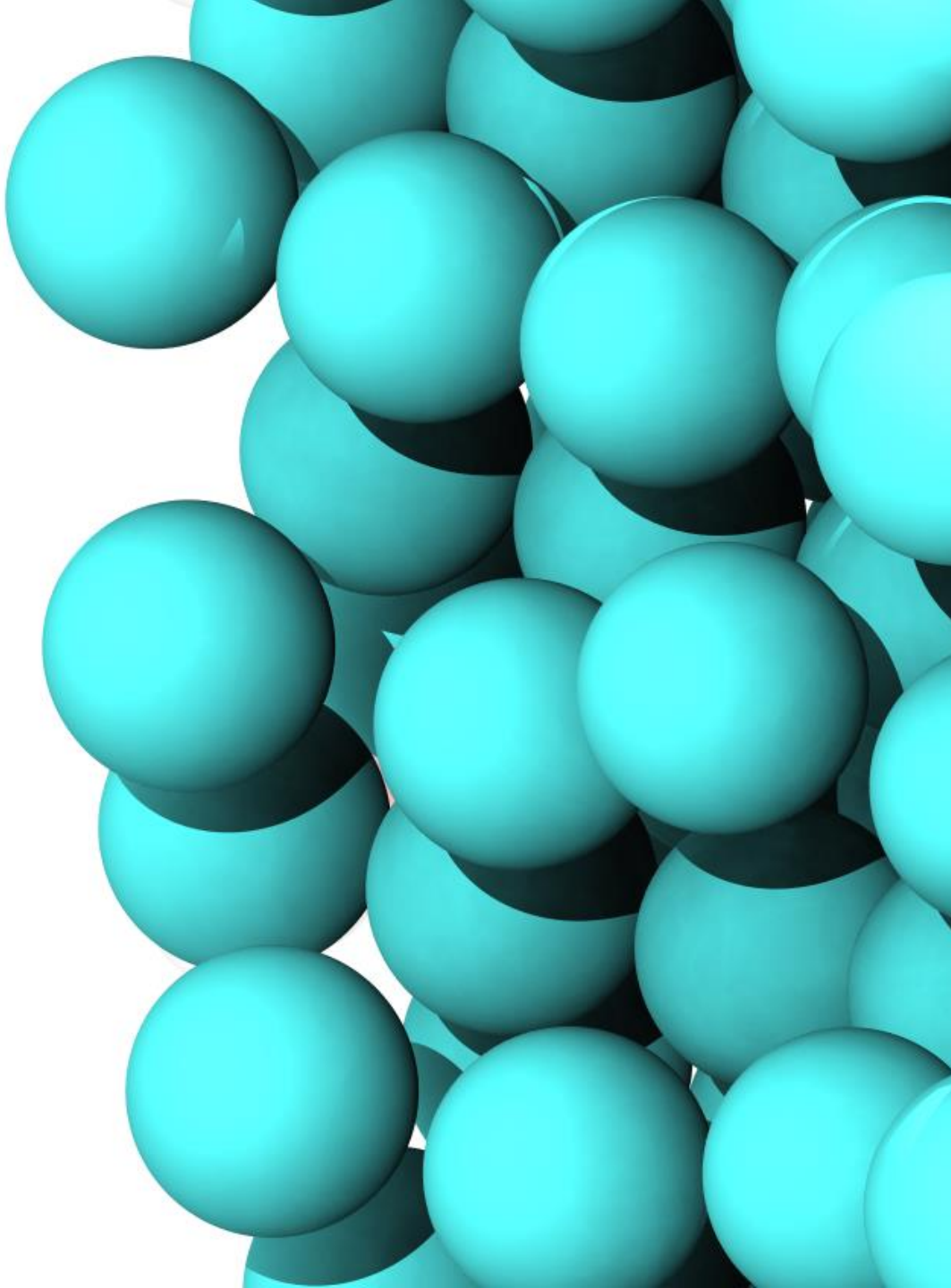

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Introduction

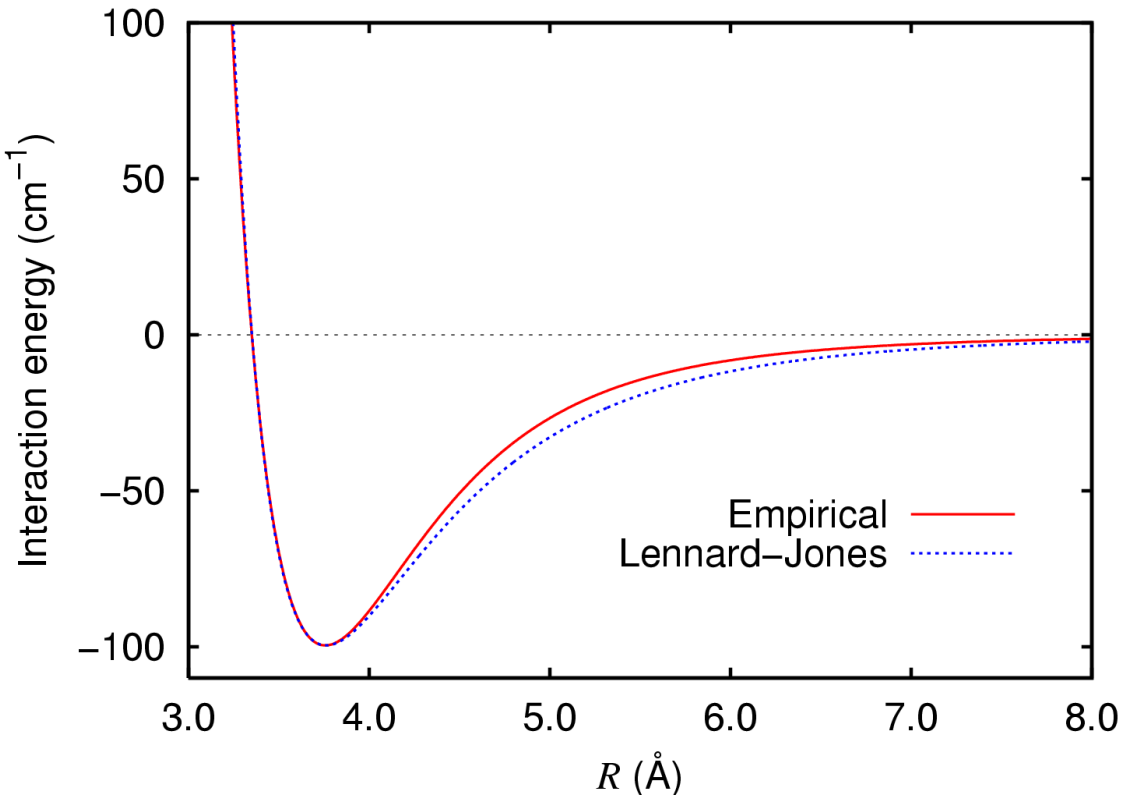
Atomistic methods, although reliable, are not desired for nanoparticle synthesis for latter simulation. Physically correct and *ab initio* techniques are much suitable for big arrays of atoms, due to less computational power involved.

Is it possible to create such methods? Let's find out!

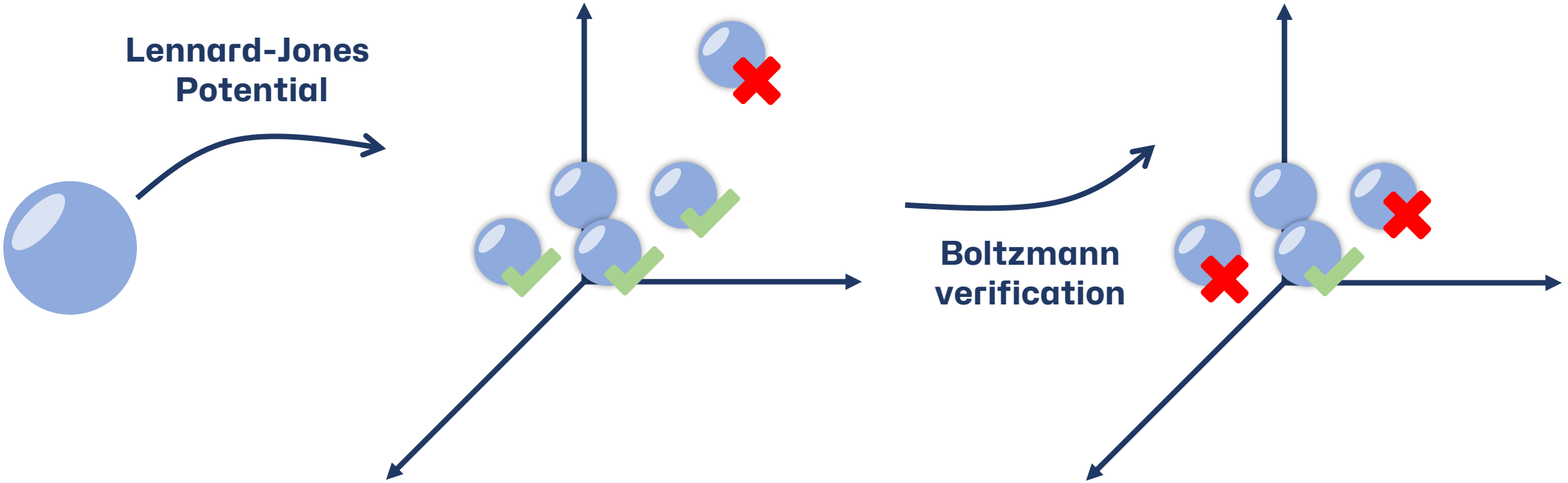
Methods: foundations

Lennard-Jones Potential

$$V(r) = 4 \cdot \varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$



Methods: the algorithm (I)



Methods: the algorithm (II)

```
def lennard_jones_potential(r):
    return 4 * epsilon * ((sigma / r)**12 - (sigma / r)**6)

# Return fictice temperature factor
def calculate_temperature_factor(x, y, z, center, max_radius):
    distance_to_center = np.linalg.norm(np.array([x, y, z]) - center)
    # Normalize the distance to the range [0, 1]
    normalized_distance = distance_to_center / max_radius
    # Calculate the temperature factor as a function of the normalized distance
    temperature_factor = normalized_distance
    return temperature_factor


def get_neighbors(x, y, z):
    # Returns a list of the coordinates of the neighbors of the point (x, y, z)
    neighbors = []
    for dx in [-1, 0, 1]:
        for dy in [-1, 0, 1]:
            for dz in [-1, 0, 1]:
                if dx != 0 or dy != 0 or dz != 0:  # Exclude the point itself
                    neighbors.append(((x + dx) % grid_size, (y + dy) % grid_size, (z + dz) % grid_size))
    return neighbors
```

Methods: the algorithm (III)

Reading the loop:

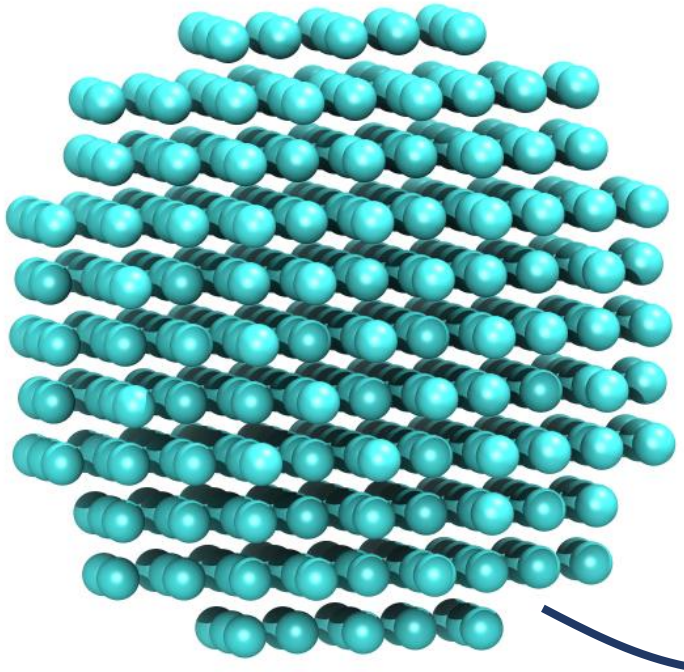
```
...

# Calculate the energy change due to the addition of another atom
    delta_E = 0
    for i, j, k in get_neighbors(x, y, z):
        if grid[i, j, k] == 1:
            r = np.sqrt((x - i)**2 + (y - j)**2 + (z - k)**2)
            delta_E += lennard_jones_potential(r)
    # delta_E -= calculate_crystallinity(x, y, z)  # Decrease the energy when the number of nearest neighbors increases

    # Metropolis-Hastings algorithm
    if delta_E < 0:
        # If the energy decreases, accept the change
        grid[x, y, z] = 1
    else:
        # If the energy increases, accept the change with a probability given by the Boltzmann factor
        if np.random.uniform(0, 1) < np.exp(-delta_E / (k_B * T)):
            grid[x, y, z] = 1

...
```

Methods: CHARMM-GUI based NPs



Cerium metallic nanoparticle

CHARMM-GUI uses Lennard-Jones optimization for solvent interaction, but the structure is immediately constructed through compositional data!

Methods: particle evaluation

1. Solvation and analysis of agglomeration

2. Isobaric expansion

Future applications

3. Usage of ReaxFF for oxidizing the surface

Methods: final touches

```
# Save protein data bank file
with open('structure1.pdb', 'w') as f:
    f.write('MODEL\n')
    x, y, z = np.where(grid == 1)
    num_atoms = np.sum(grid)
    for i in range(len(x)):
        x_coord = "{:8.3f}".format(x[i] * grid_spacing)
        y_coord = "{:8.3f}".format(y[i] * grid_spacing)
        z_coord = "{:8.3f}".format(z[i] * grid_spacing)
        e = "{:4d}".format(i+1)
        h = "{:5d}".format(i+1)
        temp_factor = 10*calculate_temperature_factor(x[i], y[i], z[i], center, radius)
        temp_factor_str = "{:6.2f}".format(temp_factor)
        f.write(f'ATOM  {h}  CE  ICEM {e}    {x_coord}{y_coord}{z_coord}  1.00{temp_factor_str}      CEM\n')

    f.write(f'TER  {num_atoms+1:4.0f}      ICEM  {num_atoms + 1:0f}\n')
    f.write('ENDMDL\n')
```

Methods: final touches

Creation of the pdb file

```
REMARK original generated coordinate pdb file
ATOM      1  CE   ICEMX   1     124.569 227.202 163.561  1.00  0.00      NP1
ATOM      2  CE   ICEMX   2     124.569 230.852 159.911  1.00  0.00      NP1
ATOM      3  CE   ICEMX   3     124.569 230.852 163.561  1.00  0.00      NP1
ATOM      4  CE   ICEMX   4     124.569 230.852 167.210  1.00  0.00      NP1
ATOM      5  CE   ICEMX   5     124.569 234.502 156.261  1.00  0.00      NP1
ATOM      6  CE   ICEMX   6     124.569 234.502 159.911  1.00  0.00      NP1
ATOM      7  CE   ICEMX   7     124.569 234.502 163.561  1.00  0.00      NP1
ATOM      8  CE   ICEMX   8     124.569 234.502 167.210  1.00  0.00      NP1
ATOM      9  CE   ICEMX   9     124.569 234.502 170.861  1.00  0.00      NP1
ATOM     10  CE   ICEMX  10     124.569 238.152 159.911  1.00  0.00      NP1
ATOM     11  CE   ICEMX  11     124.569 238.152 163.561  1.00  0.00      NP1
ATOM     12  CE   ICEMX  12     124.569 238.152 167.210  1.00  0.00      NP1
ATOM     13  CE   ICEMX  13     124.569 241.802 163.561  1.00  0.00      NP1
ATOM     14  CE   ICEMX  14     128.219 223.552 159.911  1.00  0.00      NP1
ATOM     15  CE   ICEMX  15     128.219 223.552 163.561  1.00  0.00      NP1
ATOM     16  CE   ICEMX  16     128.219 223.552 167.210  1.00  0.00      NP1
ATOM     17  CE   ICEMX  17     128.219 227.202 156.261  1.00  0.00      NP1
ATOM     18  CE   ICEMX  18     128.219 227.202 159.911  1.00  0.00      NP1
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ATOM     22  CE   ICEMX  22     128.219 230.852 152.611  1.00  0.00      NP1
ATOM     23  CE   ICEMX  23     128.219 230.852 156.261  1.00  0.00      NP1
ATOM     24  CE   ICEMX  24     128.219 230.852 159.911  1.00  0.00      NP1
ATOM     25  CE   ICEMX  25     128.219 230.852 163.561  1.00  0.00      NP1
ATOM     26  CE   ICEMX  26     128.219 230.852 167.210  1.00  0.00      NP1
ATOM     27  CE   ICEMX  27     128.219 230.852 170.861  1.00  0.00      NP1
ATOM     28  CE   ICEMX  28     128.219 230.852 174.511  1.00  0.00      NP1
ATOM     29  CE   ICEMX  29     128.219 234.502 152.611  1.00  0.00      NP1
ATOM     30  CE   ICEMX  30     128.219 234.502 156.261  1.00  0.00      NP1
ATOM     31  CE   ICEMX  31     128.219 234.502 159.911  1.00  0.00      NP1
```

Creation of the psf file -- PSFgen

```
PSF

      12 !NTITLE
 REMARKS original generated structure x-plor psf file
 REMARKS topology /usr/local/lib/vmd/plugins/noarch/tcl/readcharmmtop1.2/top_all27_prot_lipid_na.inp
 REMARKS topology structure1_autopsf-temp.top
 REMARKS topology /usr/local/lib/vmd/plugins/noarch/tcl/solvate1.7/wat.top
 REMARKS segment NP1 { first ; last ; auto none  }
 REMARKS segment X01 { first ; last ; auto none  }
 REMARKS segment NP2 { first ; last ; auto none  }
 REMARKS segment X02 { first ; last ; auto none  }
 REMARKS segment WT1 { first NONE; last NONE; auto none  }
 REMARKS segment WT2 { first NONE; last NONE; auto none  }
 REMARKS segment WT5 { first NONE; last NONE; auto none  }
 REMARKS segment WT6 { first NONE; last NONE; auto none  }

   45780 !NATOM
       1 NP1  1    ICEM CE   ICE    0.000000      140.1160           0
       2 NP1  2    ICEM CE   ICE    0.000000      140.1160           0
       3 NP1  3    ICEM CE   ICE    0.000000      140.1160           0
       4 NP1  4    ICEM CE   ICE    0.000000      140.1160           0
       5 NP1  5    ICEM CE   ICE    0.000000      140.1160           0
       6 NP1  6    ICEM CE   ICE    0.000000      140.1160           0
       7 NP1  7    ICEM CE   ICE    0.000000      140.1160           0
       8 NP1  8    ICEM CE   ICE    0.000000      140.1160           0
       9 NP1  9    ICEM CE   ICE    0.000000      140.1160           0
      10 NP1  10   ICEM CE   ICE    0.000000      140.1160           0
      11 NP1  11   ICEM CE   ICE    0.000000      140.1160           0
      12 NP1  12   ICEM CE   ICE    0.000000      140.1160           0
      13 NP1  13   ICEM CE   ICE    0.000000      140.1160           0
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      23 NP1  23   ICEM CE   ICE    0.000000      140.1160           0
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      26 NP1  26   ICEM CE   ICE    0.000000      140.1160           0
      27 NP1  27   ICEM CE   ICE    0.000000      140.1160           0
      28 NP1  28   ICEM CE   ICE    0.000000      140.1160           0
      29 NP1  29   ICEM CE   ICE    0.000000      140.1160           0
      30 NP1  30   ICEM CE   ICE    0.000000      140.1160           0
      31 NP1  31   ICEM CE   ICE    0.000000      140.1160           0
      32 NP1  32   ICEM CE   ICE    0.000000      140.1160           0
```
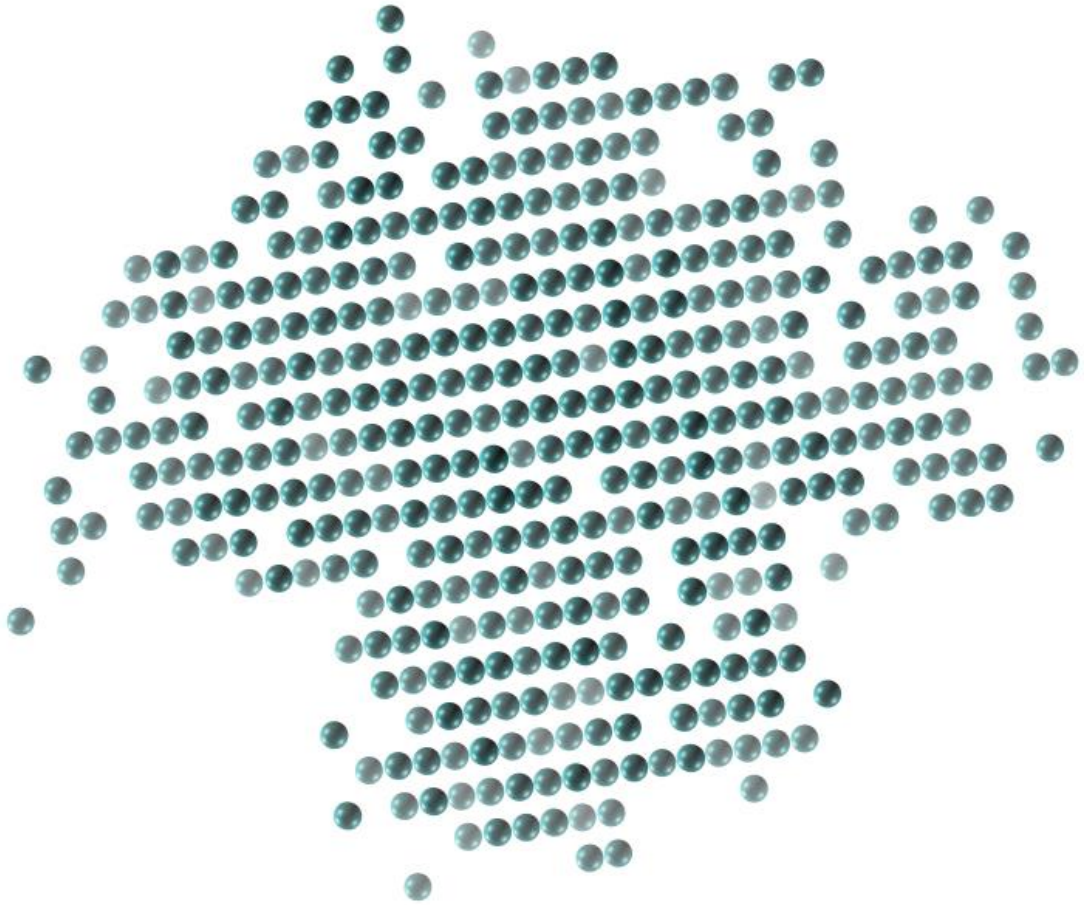
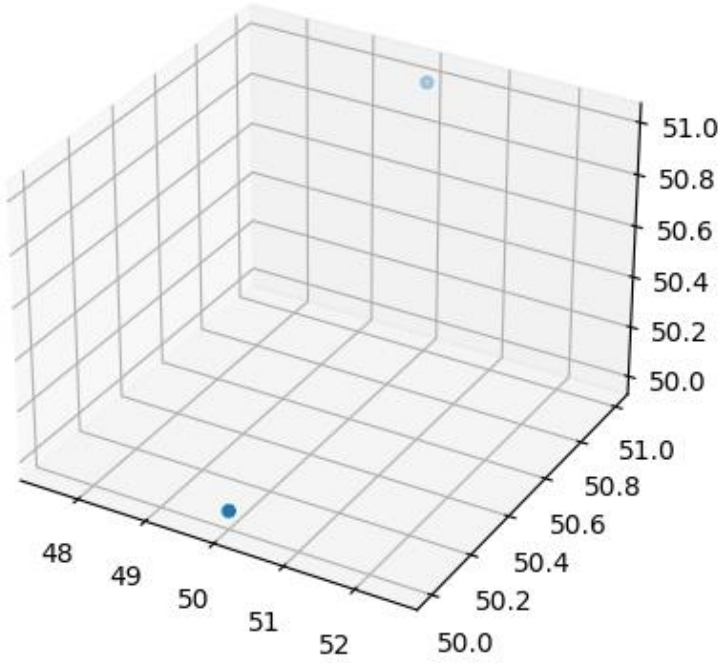
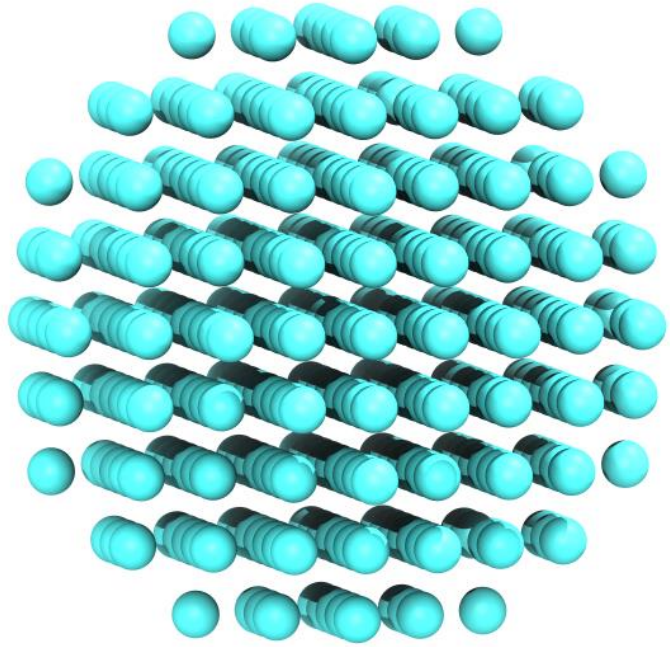

Results: Montecarlo simulation



Results: Montecarlo simulation

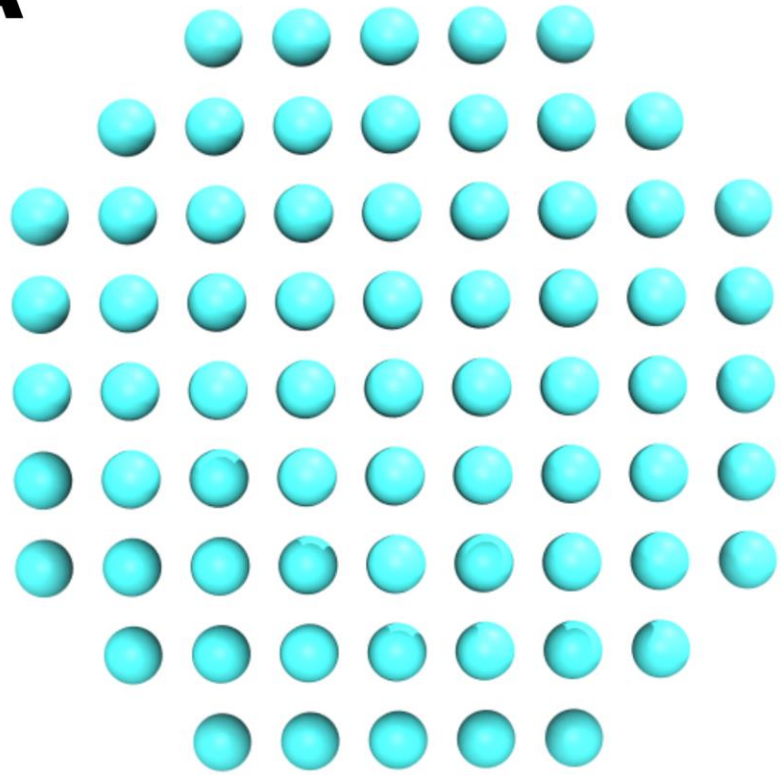


2000 steps, 10 min

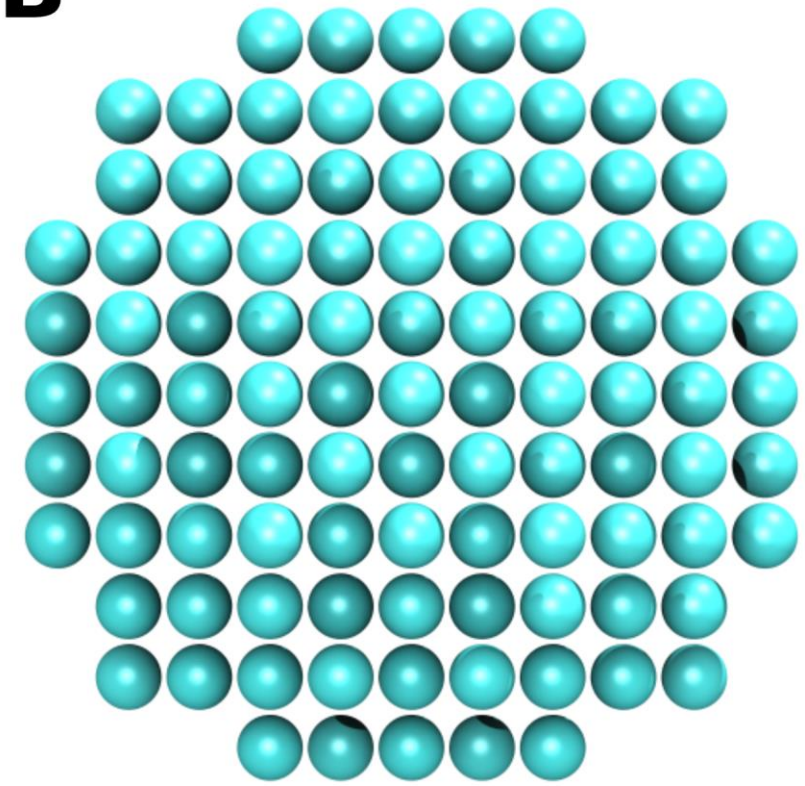


Results: comparison

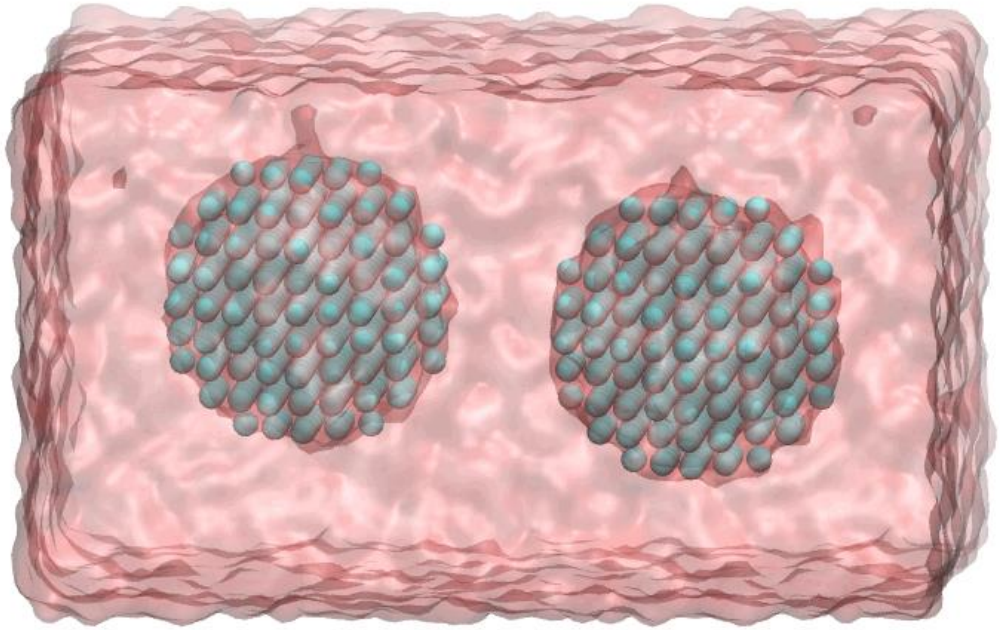
A



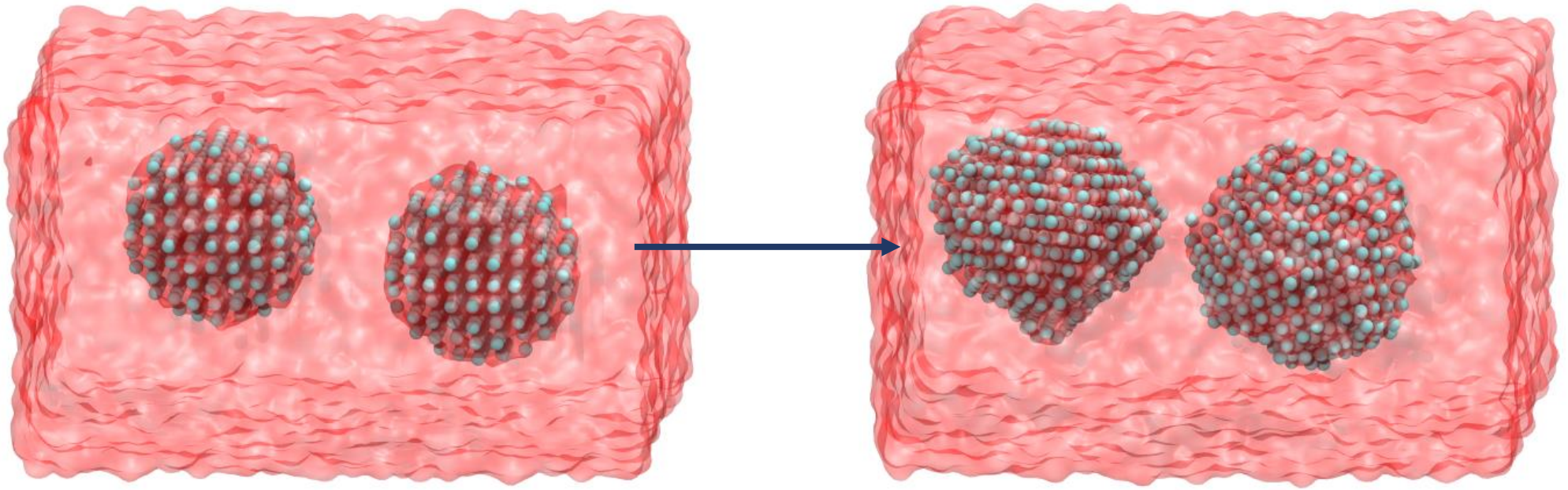
B



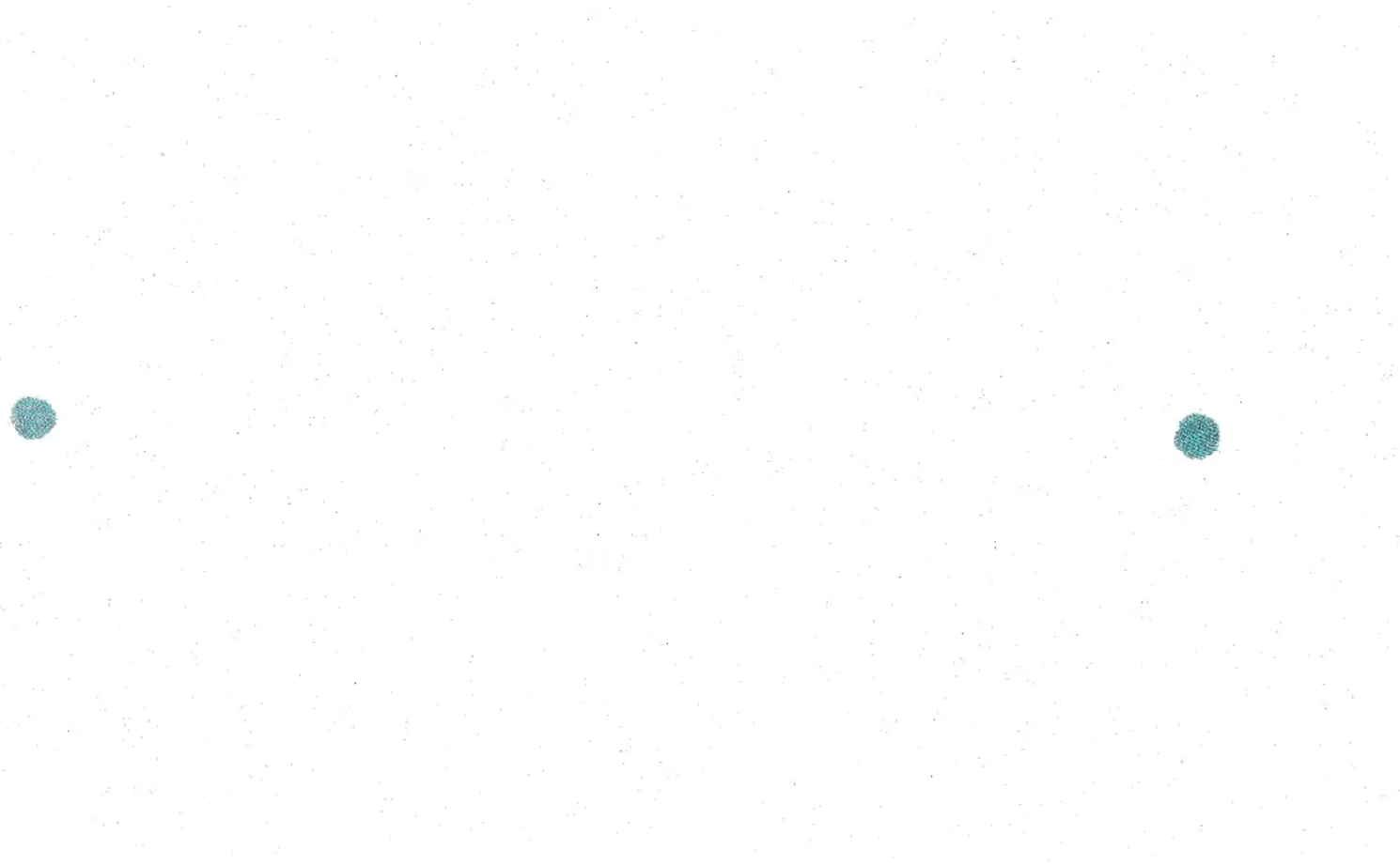
Results: solvation & evolution (I)



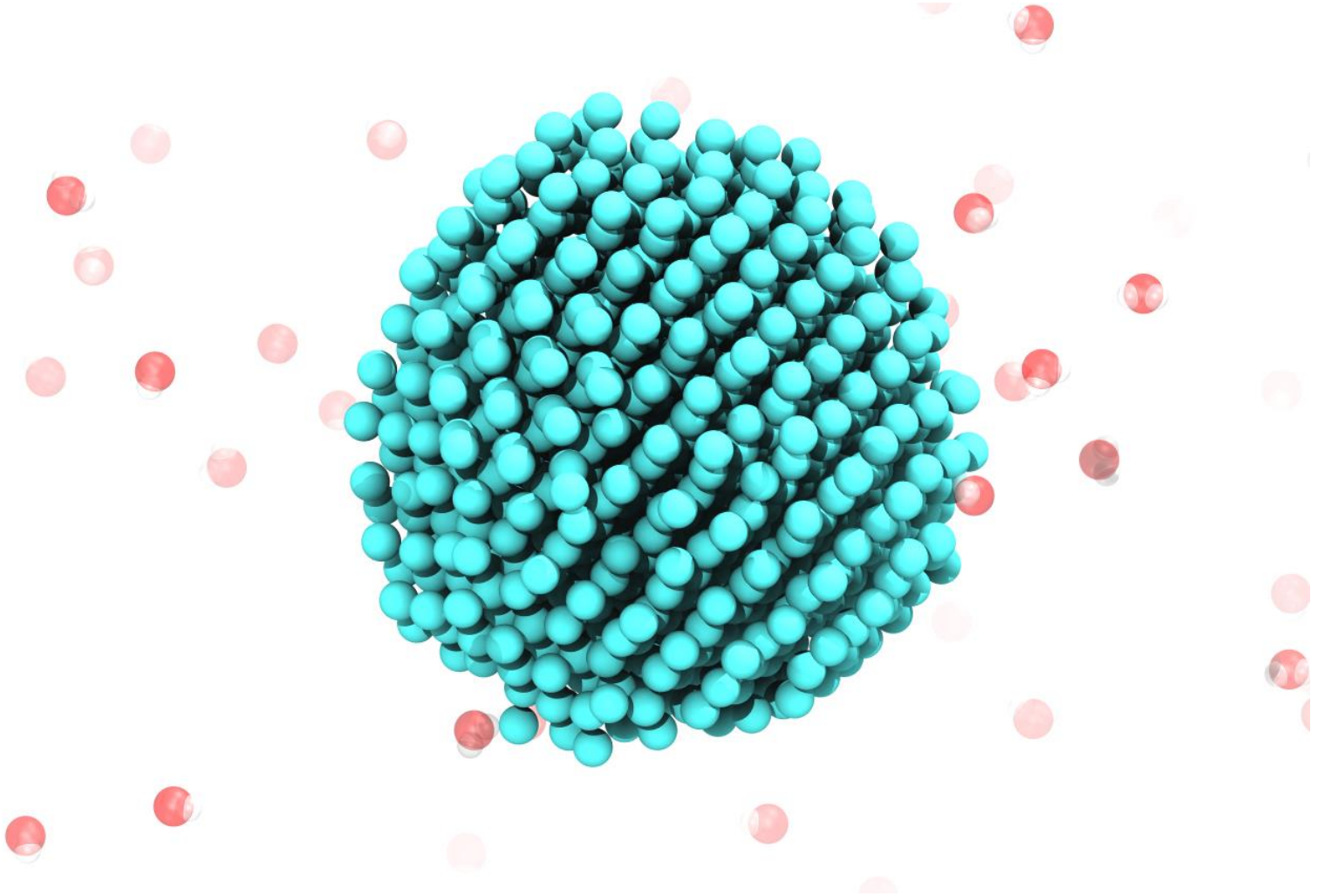
Results: solvation & evolution (II)



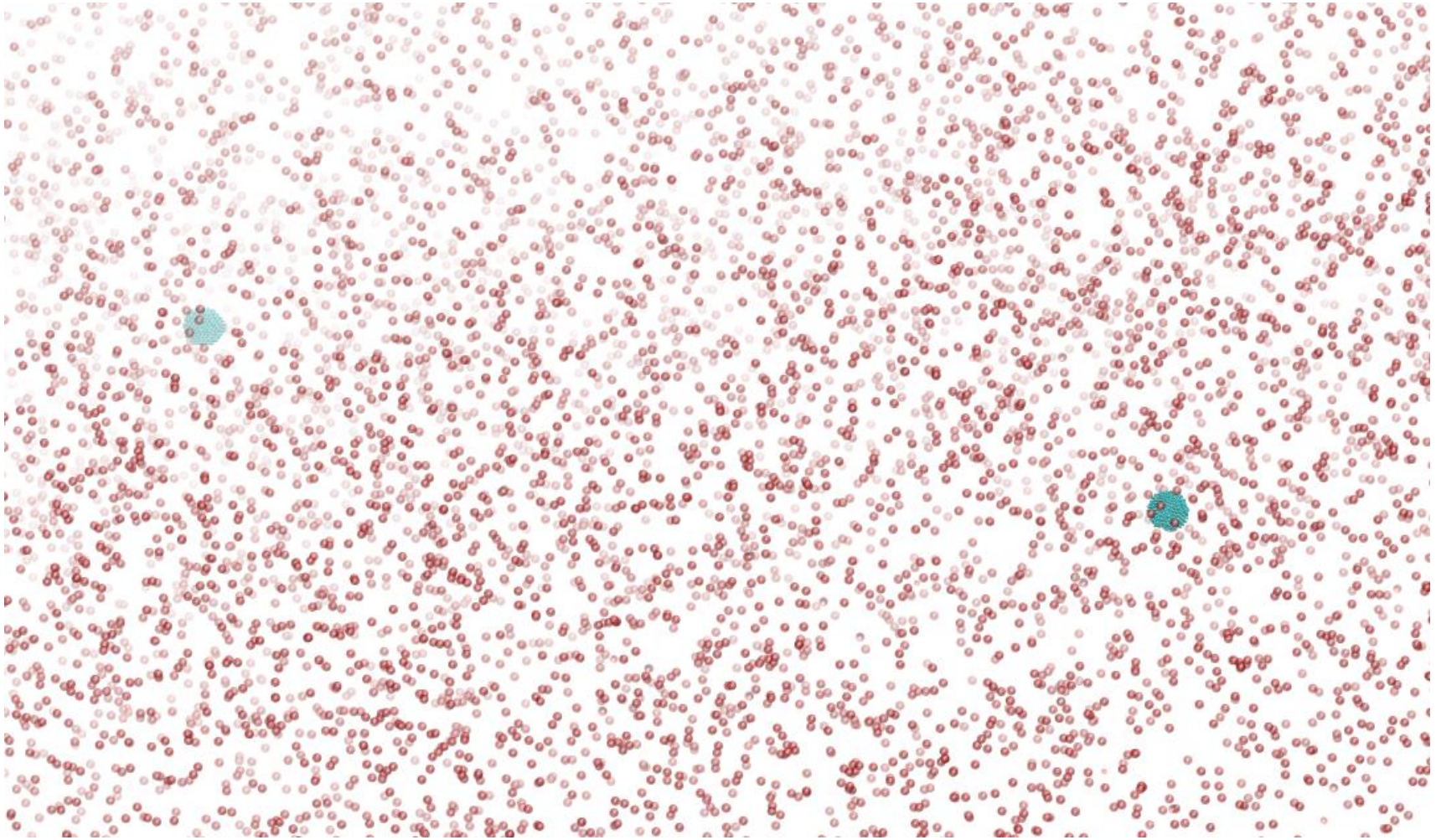
Results: isobaric expansion (I)



Results: isobaric expansion (II)



Results: isobaric expansion (III)



Conclusions

Were the objectives accomplished?
What else could be studied along the experimental design?