1 Simulation of the Breathing Phase Transition of MOF Nanocrystallites: Volume Change over Time

For the DMOF-1 NCs, the decrease in volume normalized to one pore is plotted against the simulation time in Figure 1. All systems show a sigmoidal curve with a sharp transition from a pore volume of $1170 \text{ Å}^3$ to $610 \text{ Å}^3$. The volume curve of the 9x9x9 system differs due to the interface in which the pore size is larger than in the remaining closed pores, but it ends up at the same closed pore volume. Therefore, the pore closing time correlates with the NC size. This holds up to the 6x6x6 size. For the 6x6x6 NC up to the 9x9x9 NC, the pore closing starts at nearly the same time. Since a pressure ramp simulation was performed, in which an external pressure is increased linearly, the simulation time is directly connected to the applied external pressure, i.e., the external pressure is increasing as time progresses.

![Figure 1](image_url)

Figure 1: The volume is decreasing during the pressure ramp simulation of the DMOF-1 NCs with the sizes 3x3x3 up to 9x9x9 normalized to the volume of one pore.
For the DUT-8 NCs, the volume change during the simulation is plotted for investigated sizes from the 3x3x3 NC up to the 9x9x9 NC with the respective conformation in Figure 2. The volume decrease during the simulation shows slightly different trends than the model system. For conformation 1 (see Figure 2a), the impact of the system size is the smallest, i.e., the differently sized NCs start the pore closing at nearly the same time, which differs from the model system. For conformation 2 (see Figure 2b) and conformation 3 (see Figure 2c), the phase transitions of the NCs with the sizes 5x5x5 up to 9x9x9 occurs nearly simultaneously, i.e., in DUT-8 NCs, the system size is less critical for the initialization point than in the model system. For conformation 4 (see Figure 2d), the phase transition of the 5x5x5 and the 6x6x6 NC occurs nearly simultaneously, whereas, for the 7x7x7 NC up to the 9x9x9, the phase transitions require higher pressure to be initialized. However, independent of the conformation, most DUT-8 NCs start their phase transition between 0.5 ns and 1.0 ns, depending on the system size. An exception is the 3x3x3 NC with the conformation 3 (see Figure 2c), which starts before 0.5 ns.

In Figure 2, the total volume of the NCs of the DUT-128 NCs is plotted against the simulation for each system and normalized to the size of one pore. All phase transitions, in which the pore volume decreases from 2250 Å³ to 700 Å³, occur between 0.5 ns and 1 ns except for those of the 3x3x3 NC, which is similar to the 3x3x3 DUT-8 NC with conformation 3. The curves overlap for the 6x6x6 NC up to the 9x9x9 NC, i.e., they close nearly simultaneously. For the 4x4x4 NC (orange), the 5x5x5 NC (green), and the 7x7x7 NC (purple), the curves show small plateaus, which means that the pores do not close as coherently as in the model system. This could be caused by the pore closing along different spatial diagonals. Higher pressures are needed to close the interfacial pores completely, which are provided later by the linear pressure increasing during the simulation.

Figure 2: The volume is decreasing during the pressure ramp simulation of the four investigated conformations of DUT-8 NCs with the sizes 3x3x3 up to 9x9x9 normalized to the volume of one pore. Independent of the conformation, most phase transitions start between 0.5 ns and 1.0 ns.

In Figure 3, the total volume of the NCs of the DUT-128 NCs is plotted against the simulation for each system and normalized to the size of one pore. All phase transitions, in which the pore volume decreases from 2250 Å³ to 700 Å³, occur between 0.5 ns and 1 ns except for those of the 3x3x3 NC, which is similar to the 3x3x3 DUT-8 NC with conformation 3. The curves overlap for the 6x6x6 NC up to the 9x9x9 NC, i.e., they close nearly simultaneously. For the 4x4x4 NC (orange), the 5x5x5 NC (green), and the 7x7x7 NC (purple), the curves show small plateaus, which means that the pores do not close as coherently as in the model system. This could be caused by the pore closing along different spatial diagonals. Higher pressures are needed to close the interfacial pores completely, which are provided later by the linear pressure increasing during the simulation.

Figure 2: The volume is decreasing during the pressure ramp simulation of the four investigated conformations of DUT-8 NCs with the sizes 3x3x3 up to 9x9x9 normalized to the volume of one pore. Independent of the conformation, most phase transitions start between 0.5 ns and 1.0 ns.
Figure 3: The volume is decreasing during the pressure ramp simulation of the DUT-128 NCs with the sizes 3x3x3 up to 9x9x9 normalized to the volume of one pore. Up to the 6x6x6 NC, the phase transition starts later if the system size is increased. For the 6x6x6 NC up to the 9x9x9 NC, the pore closing is initialized nearly simultaneously.

2 Additional Pore Size Analyses for DUT-8 and DUT-128

The DUT-8 and the DUT-128 NC show additional pore closing mechanisms compared to the model system DMOF-1. To sketch them in detail, pore size analyses were performed equivalent to the procedure performed for the model system. Due to the ndc linker in DUT-8 and the bpdc linker in DUT-128, the individual pore size is larger than for DMOF-1 constructed with the bdc linker.

For DUT-8, blue-colored pores represent closed pores with a volume of approximately 1800 Å³, whereas red-colored pores represent the open pores with a volume of approximately 610 Å³. The first additional pathway shown in Figure 4a for the 7x7x7 NC with the conformation 1 starts at one corner and propagates first in one direction and then in the other direction. At t = 0.790 ns, the top layer is entirely closed, which induces that at t = 0.798 ns, a middle layer adjacent to open pore layers, close its pores. Since all pores are closed along the same spatial diagonal, the two remaining layers close along those spatial diagonal to end up in the diamond-shaped structure. The second additional pathway is shown in Figure 4b for the 7x7x7 NC with the conformation 4. From t = 0.770 ns up to t = 0.850 ns, the pore closing occurs from two opposite corners along different spatial diagonals. This leads to a partial diamond-shaped transition structure. The remaining pores close either along with the one or the other spatial diagonal, which is why the structure is bent on the top and the right side up to t = 0.860 ns. If the pressure is further increased, all pores are completely closed, but the structure keeps the disturbed diamond-shaped structure.

For DUT-128, blue-colored pores represent closed pores with a volume of approximately 2250 Å³, whereas red-colored pores represent the open pores with a volume of approximately 700 Å³. The first pathway resulting in the disturbed diamond-shaped structure is shown in Figure 5a for the 5x5x5 NC. The pore closing does not start at the corner of the NC as it is always observed for the model system but at one site. At t = 0.525 ns, one pore on the left side of the NC is completely closed. Up to t = 0.575 ns, the NC closes layer-by-layer induced by the adjacent closed pores. From t = 0.600 ns up to t = 0.700 ns, there are two competing effects affecting the pore closing of the still open outer layer. In addition to the adjacent
closed pores, the pressure bath medium mediates pressure to the outer layer. As a result, the outer layer on the right closes along another spatial diagonal ending in the disturbed diamond-shaped structure. The second mechanism has a spontaneous character, as it is shown in Figure 4 for the 6x6x6 NC. After the pore closing of one side, it continues in one of the middle layers as it can be seen for $t = 0.675$ ns up to $t = 0.712$ ns. This middle layer closes along a different spatial diagonal. Therefore, the direction of the pore closing changes spontaneously. In addition, the outer layer opposite to the first closed layer starts its pore closing simultaneously, i.e., the pressure bath medium induces the pore closing of this outer layer. Thus, the Z-shaped closed pore form results from two interfaces between layers closed along different spatial diagonals. The outer layers are closed along the same spatial diagonal, but some of the middle layers are closed along a different one. The third mechanism, shown in Figure 5 for the 8x8x8 NC, starts at one side similar to the formerly described ones. This induces the pore closing along another spatial diagonal of a nearly orthogonal middle layer from $t = 0.685$ ns up to $t = 0.700$ ns. At $t = 0.725$ ns, the pores of the opposite corner start to close along a third spatial diagonal. The pore closing continues from three directions to the centered pores resulting in the T-shaped closed pore form. At $t = 0.800$ ns, the centered pores have a larger pore volume than the remaining closed pores, which does not become smaller if the pressure is further increased. This can be explained by the geometry of the closed pore form. There is no possibility of folding these pores further to get the completely closed form due to the adjacent pores closed along different spatial diagonals. The fourth observed pathway, shown in Figure 5B, ends up in the perfectly diamond-shaped structure. Starting in one corner, the pore closing continues simultaneously in the x- and y-direction up to $t = 0.725$ ns. Then, the pore closing is fast in one direction. Despite this, all pores close along the same spatial diagonal. No pore closing is observed on other sides of the NC, which can be interpreted as a smaller impact of the pressure bath for this pore closing mechanism.

Figure 4: Pore size analysis of the 7x7x7 DUT-8 NC with the conformation 1 and 4. (a) The pore closing starts in the upper left corner and propagates in an asymmetrical layer-by-layer closing through the NC. Remarkably, the top layer closes fast, which induces a pore closing of a middle layer adjacent to open pore layers. Since all pores are closed along the same spatial diagonal, the closed pore form is the diamond-shaped structure. (b) The pore closing co-occurs from two corners along different spatial diagonals. This leads to a disturbed diamond-shaped structure.
Figure 5: Pore size analysis of the differently sized DUT-128 NC for different snapshots of the phase transition from open to closed pore structure averaged along the z-axis and viewed on the xy-plane. (a) For the 5x5x5 NC, the center of the pores is colored according to the respective size. The phase transition starts at one layer and induces a layer-by-layer closing. The last layer closes along a different spatial diagonal so that the closed pore form is a disturbed diamond-shaped structure. (b) For the 6x6x6 NC, the center of the pores is colored according to the respective size. In this pore closing mechanism, the layers inside the NC are closed, although their adjacent layers are still open. The Z-shaped closed pore structure results from adjacent layers closed along different spatial diagonals if the pressure increases. (c) For the 8x8x8 NC, the center of the pores is colored according to the respective size. The pore closing travels from three sides to the centered pores. Since the pores closing along different spatial diagonals, the centered pores cannot be completely closed. (d) For the 9x9x9 NC, the center of the pores is colored according to the respective size. A symmetrical pore closing mechanism is observed, i.e., it starts at one corner and travels along the diagonal of the NC to the opposite corner to end up in the diamond-structure.