On the comparison of different barostat implementations for the prediction of the breathing behavior in MIL-53 frameworks

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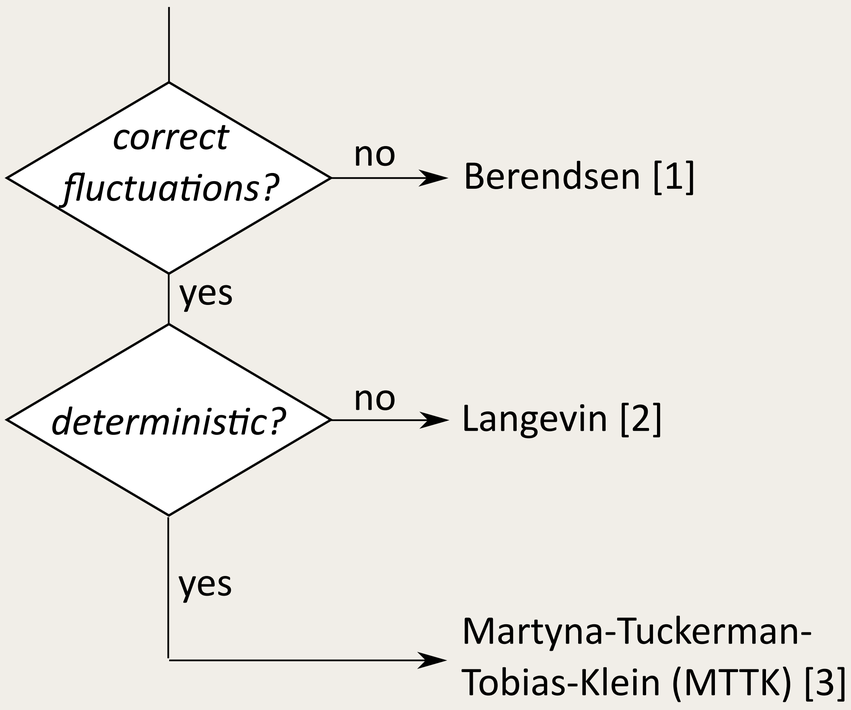
Methodology: Barostats to control the pressure in MD simulations

Choice of barostat



Case study: MIL-53(Al)

Force field based MD [4]

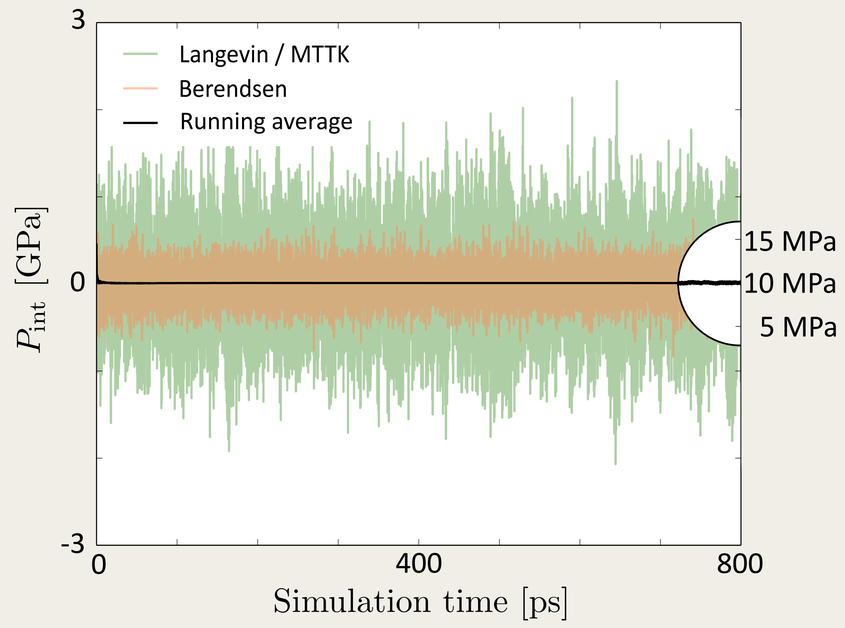
Breathing behavior: reversible deformation between two structures

Observation

$\sigma_{P_{\text{int}}} \gg \langle P_{\text{int}} \rangle = P_0$

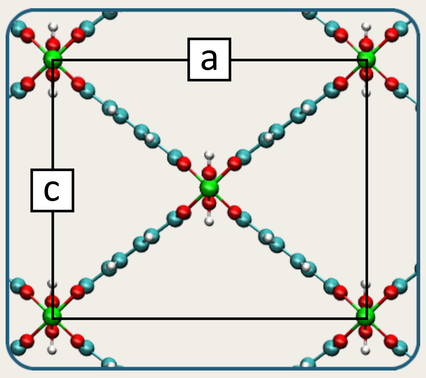
How does this affect the dynamics?

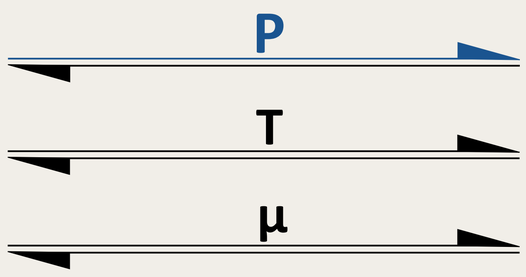
Instantaneous internal pressure fluctuates during an NPT MD simulation of MIL-53(Al) at 300 K and 10 MPa, with time constants of 0.1 ps (thermostat) and 1 ps (barostat).



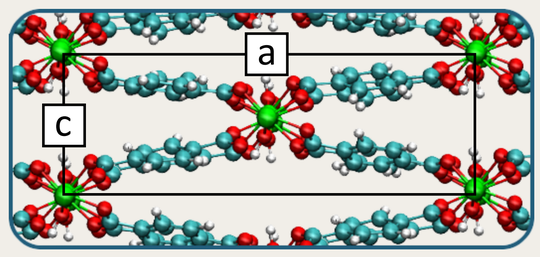
Validation: Cell parameters of the large- and narrow-pore structures of MIL-53(Al)

Large pore





Narrow pore



	Berendsen	Langevin†	MTTK†	Static [4]	Exp [5]
a [Å]	16.97	16.99	16.97	17.05	16.84
b [Å]	6.59	6.60	6.60	6.59	6.64
c [Å]	12.86	12.80	12.78	12.91	12.80
α [°]	90.00	89.93	90.00	90.00	90
β [°]	90.00	89.99	90.00	90.00	90
γ [°]	90.22	90.47	90.22	90.63	90
V [Å^3]	1437	1431	1428	1450	1430

†Only the initial 5 ps of the simulation are considered, since Langevin and MTTK always collapse to np.

Table: Unit cell dimensions of the large-pore structure of MIL-53(Al).

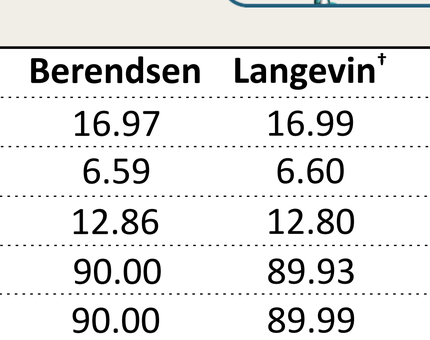
	Berendsen	Langevin	MTTK	Static [4]	Exp [5]
a [Å]	19.42	19.49	19.49	19.57	20.76
b [Å]	6.52	6.52	6.52	6.53	6.61
c [Å]	6.52	6.39	6.38	6.25	7.06
α [°]	90.20	90.01	90.00	87.89	90
β [°]	89.79	89.99	90.00	89.43	90
γ [°]	96.40	96.39	96.41	97.15	113.58
V [Å^3]	814.7	805.0	804.3	790.7	886.9

Table: Unit cell dimensions of the narrow-pore structure of MIL-53(Al).

Application: Pressure-induced breathing in MIL-53(Al)

Mean time for the lp to np transition in MIL-53(Al) as a function of the applied pressure.

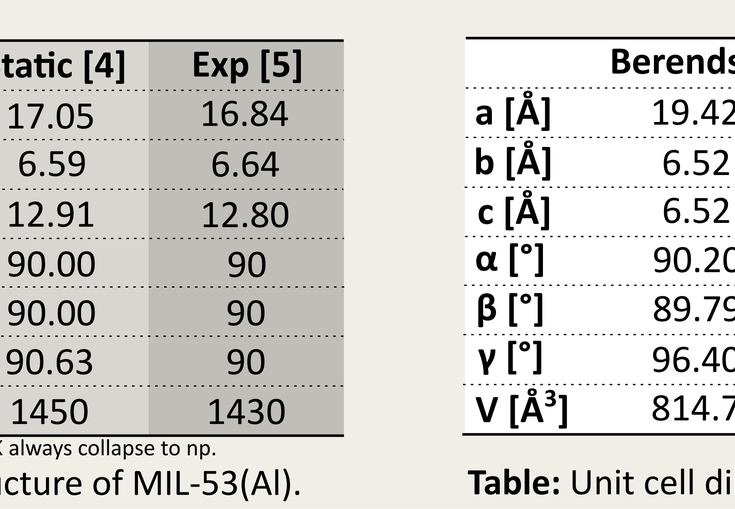
Low-pressure regime



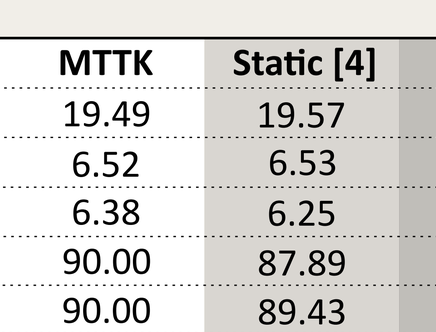
Lp to np transitions are driven by pressure fluctuations

These transitions are rare events, and hence Poisson distributed

'High' mean transition time



High-pressure regime



Lp to np transitions are driven by the average pressure

These transitions are frequent events, and hence Gaussian distributed

'Low' mean transition time

References

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