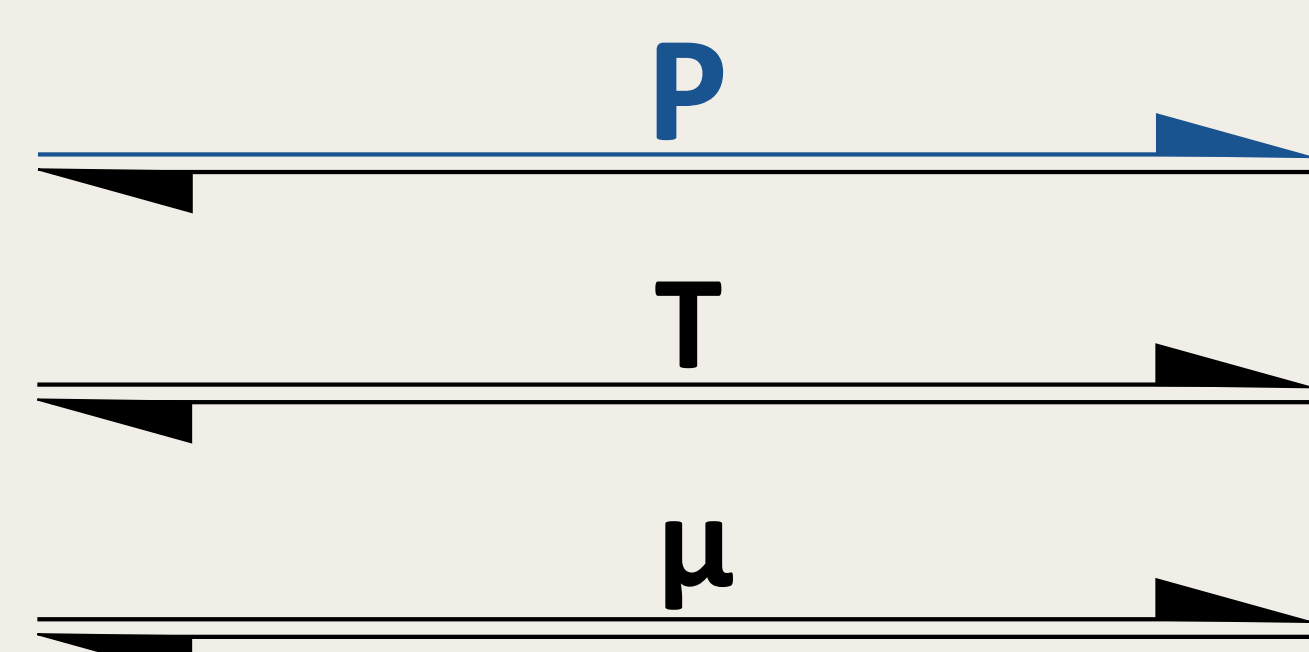
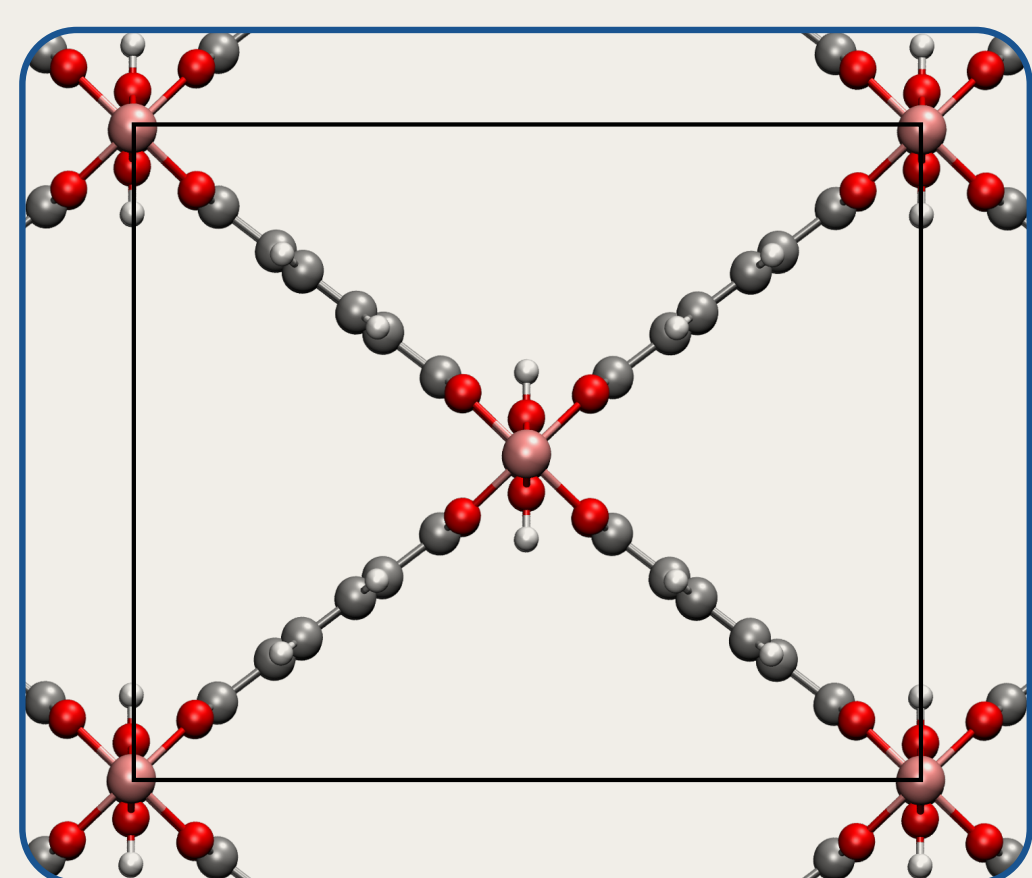
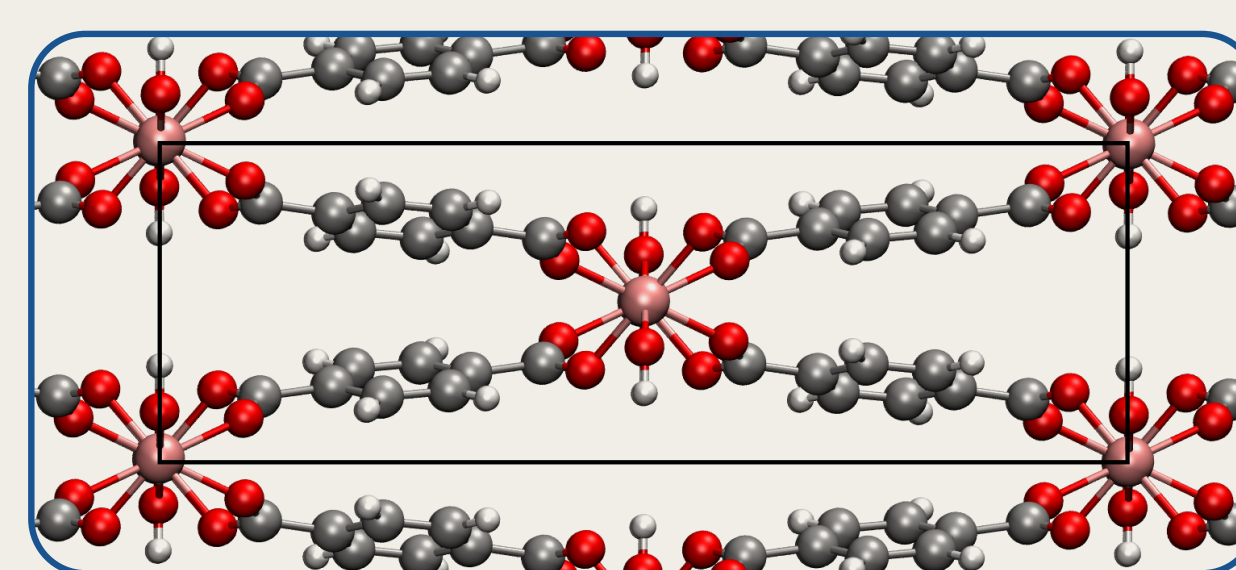


## MIL-53(Al) as a prototype example of a flexible MOF

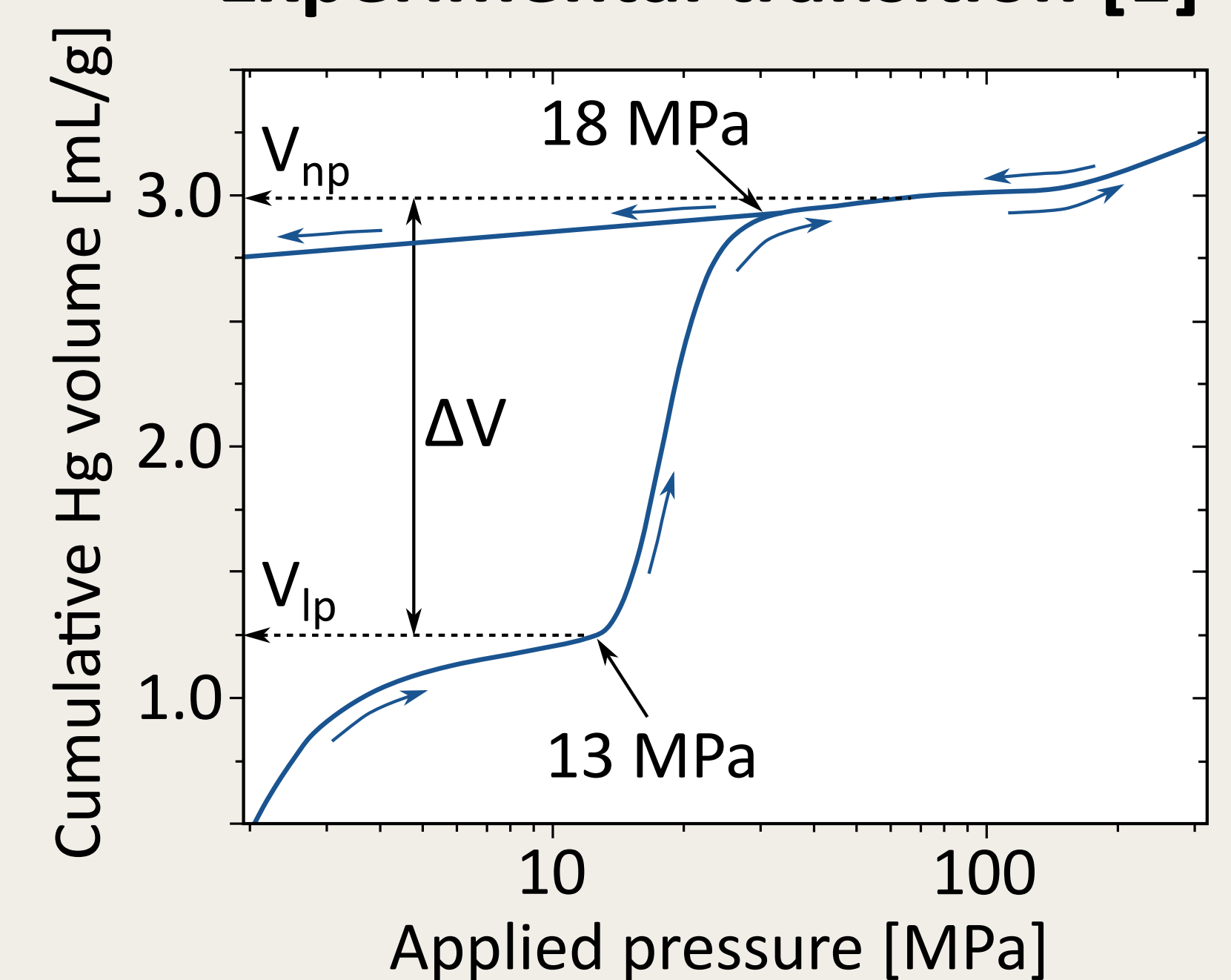
Large pore



Narrow pore

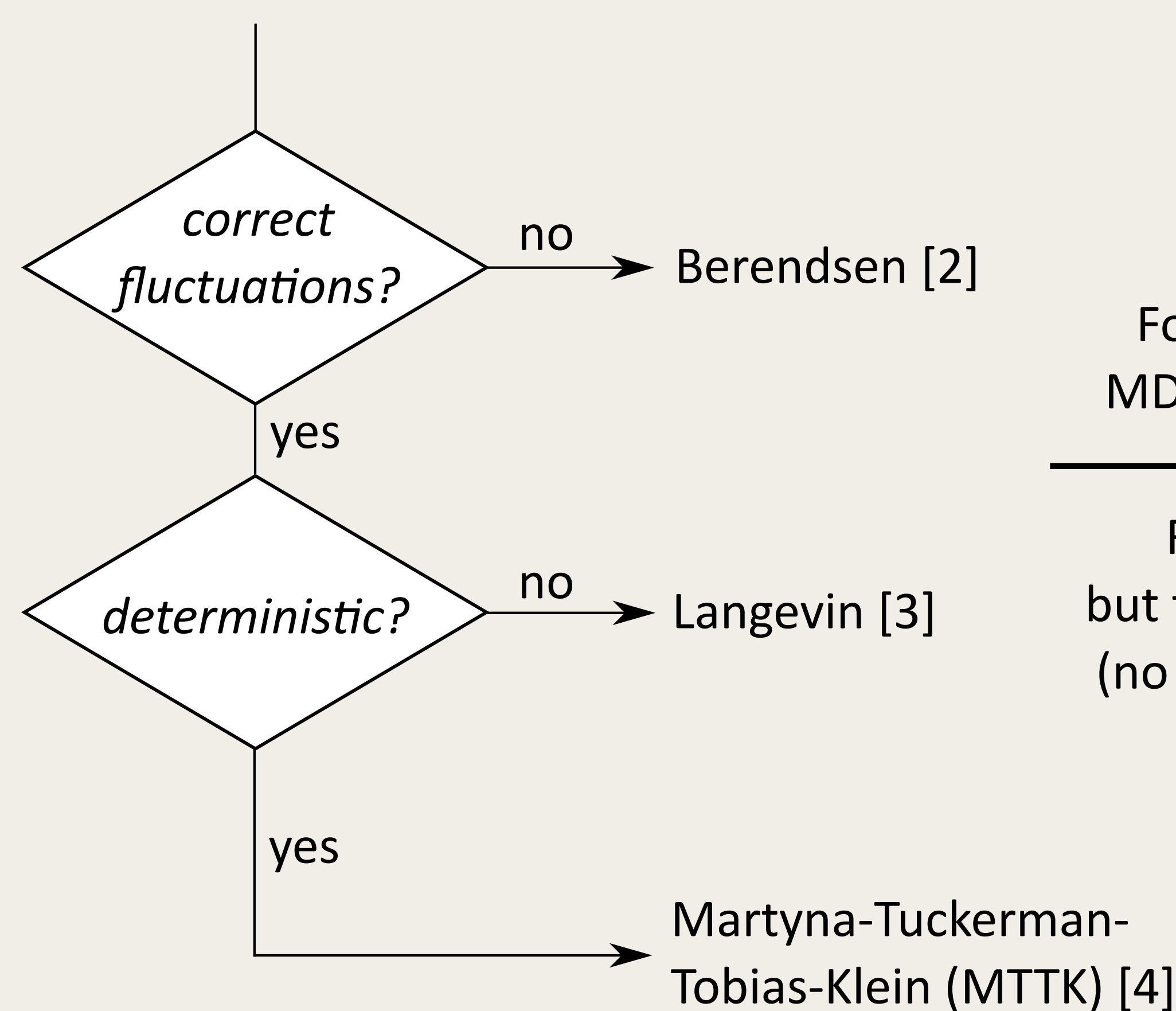


Experimental transition [1]

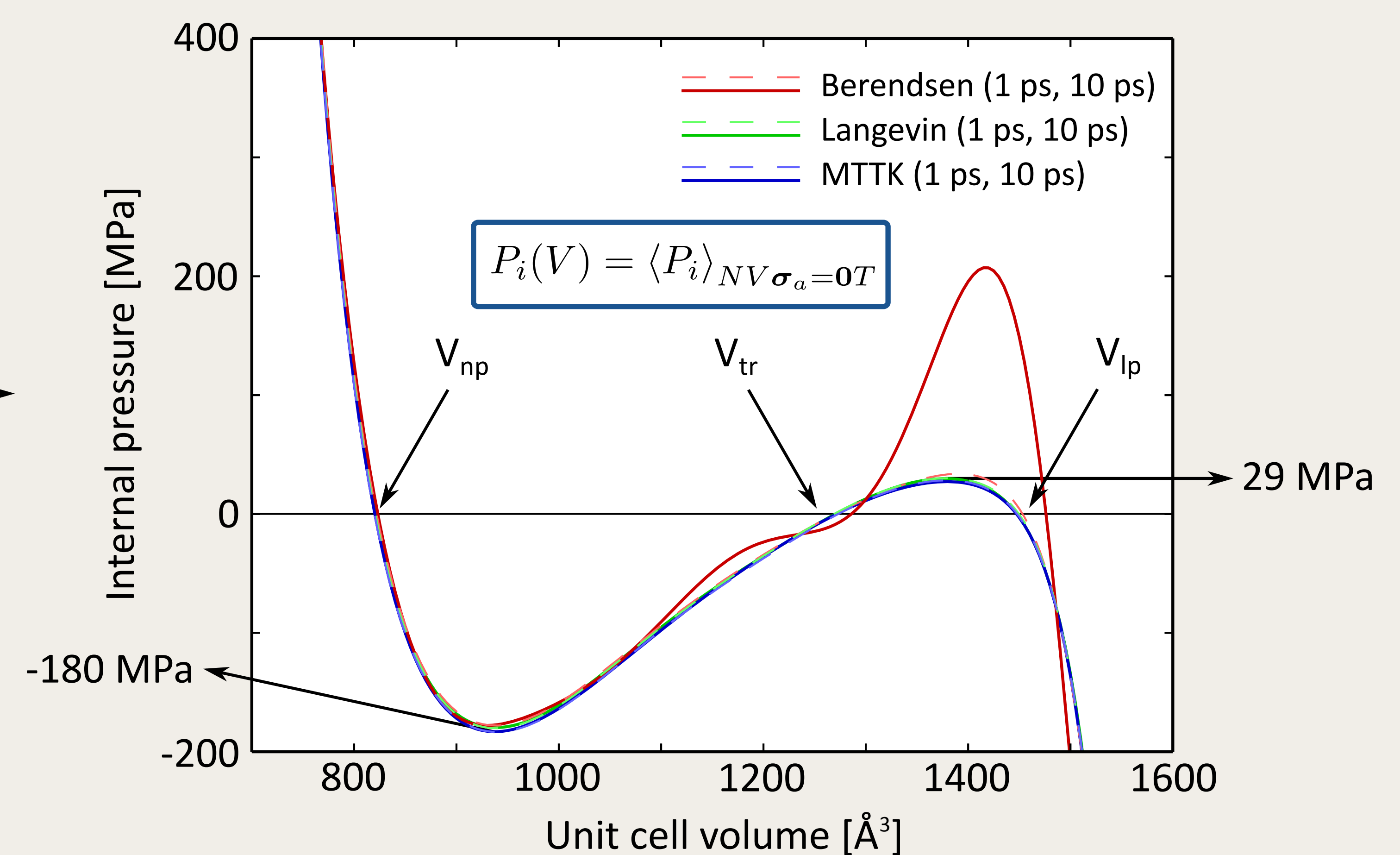


## Simulated pressure profile to confirm and extend experimental results

Choice of thermostat/barostat

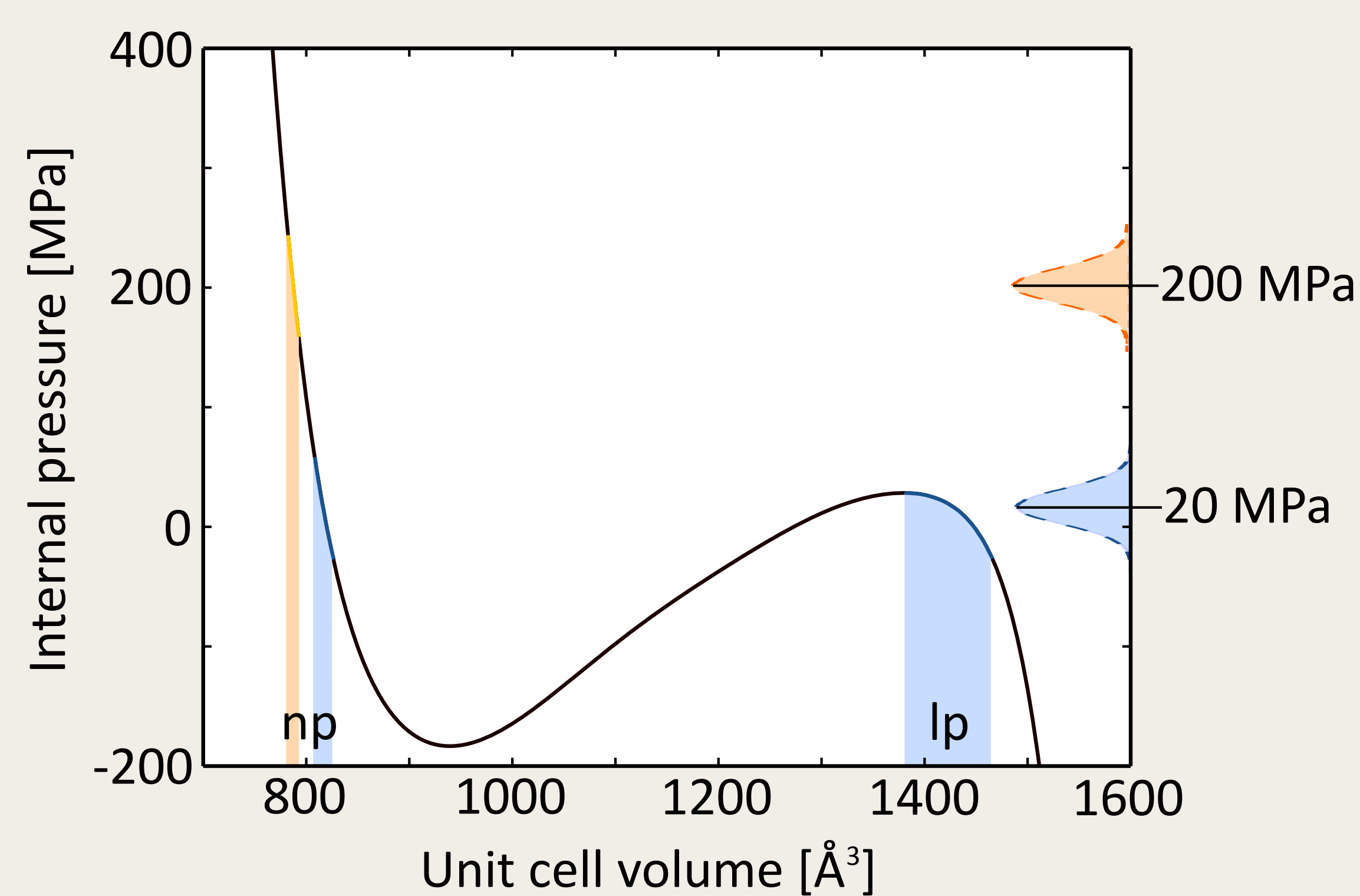


Average internal pressure as function of unit cell volume



## What do regular NPT MD simulations predict?

Transition to np at any isotropic pressure



Even at low pressures, transition to np takes place  
Direct consequence of the width of the pressure distribution

## Conclusions

Alternative technique to derive transition pressures, allowing for cell fluctuations, proves to be in good agreement with experiment

Langevin and MTTK results almost exactly coincide, but Berendsen results deviate, especially for large relaxation times

Regular NPT MD simulations with Langevin / MTTK always predict a lp-to-np transition, even below experimental transition pressure

$$P \ll P_{tr}$$

$$P \gg P_{tr}$$

Stochastic transitions

Deterministic transitions

Driven by pressure fluctuations

Driven by mean pressure

'High' time to transition

'Low' time to transition

Poissonlike transitions

Gaussianlike transitions

## References

- [1] Yot, P.G., Boudene, Z., Macia, J., Granier, D., Vanduyfhuys, L., Verstraelen, T., Van Speybroeck, V., Devic, T., Serre, C., Férey, G., Stock, N., Maurin, G., *Chem. Commun.*, 50:9462 (2014)
- [2] Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., DiNola, A., Haak, J.R., *J. Chem. Phys.*, 81:3684 (1984)
- [3] Feller, S.E., Zhang, Y., Pastor, R.W., Brooks, B.R., *J. Chem. Phys.*, 103:4613 (1995)
- [4] Martyna, G.J., Tobias, D.J., Klein, M.L., *J. Chem. Phys.*, 101:4177 (1994)
- [5] Vanduyfhuys, L., Verstraelen, T., Vandichel, M., Waroquier, M., Van Speybroeck, V., *J. Chem. Theory Comput.*, 8:3217 (2012)
- [6] Rogge, S.M.J., Vanduyfhuys, L., Verstraelen, T., Waroquier, M., Maurin, G., Van Speybroeck, V., *In preparation*