

From Boltzmann's dream to Binder's reality:

*Understanding condensed matter systems
with Monte Carlo simulations*

Christoph Dellago
University of Vienna, Austria

Vienna - Stephansplatz



1903

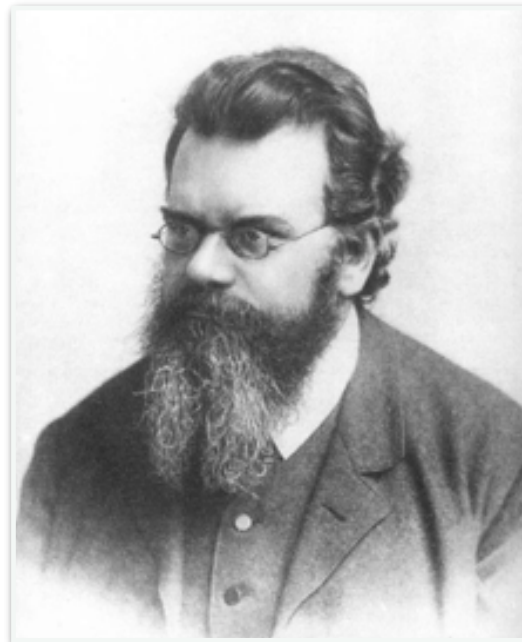
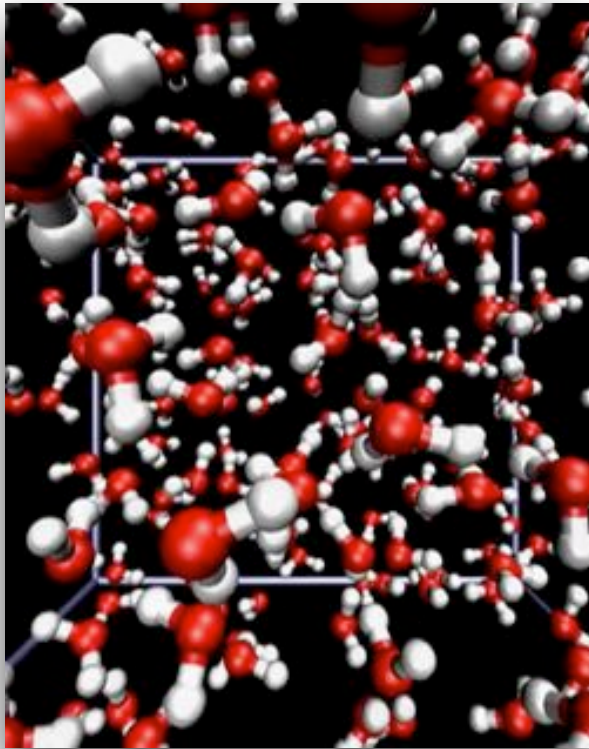


1963



2023 2

Ludwig Boltzmann's dream



Ludwig Boltzmann

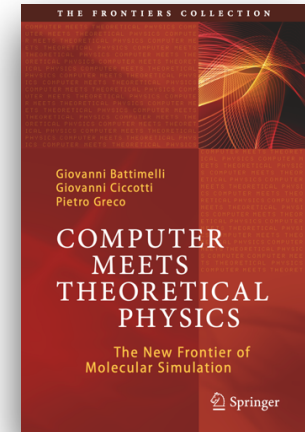


What would Boltzmann do?

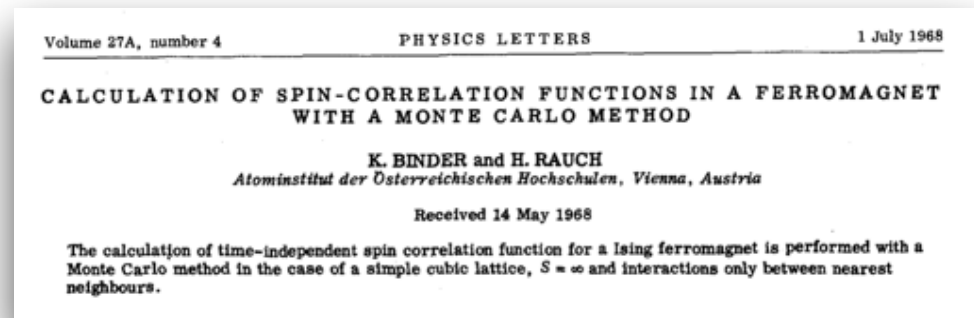


Kurt Binder - pioneer of computer simulation

- 1953: Metropolis Monte Carlo (Metropolis, Rosenbluth, Rosenbluth, Teller, Teller)
- 1957: MD simulation for hard Spheres/disks (Wainwright, Alder)
- 1957: MC for hard spheres (Wood, Jacobsen)
- 1964: MD of liquid argon (Rahman)
- 1971: MD of liquid water (Rahman, Stillinger)

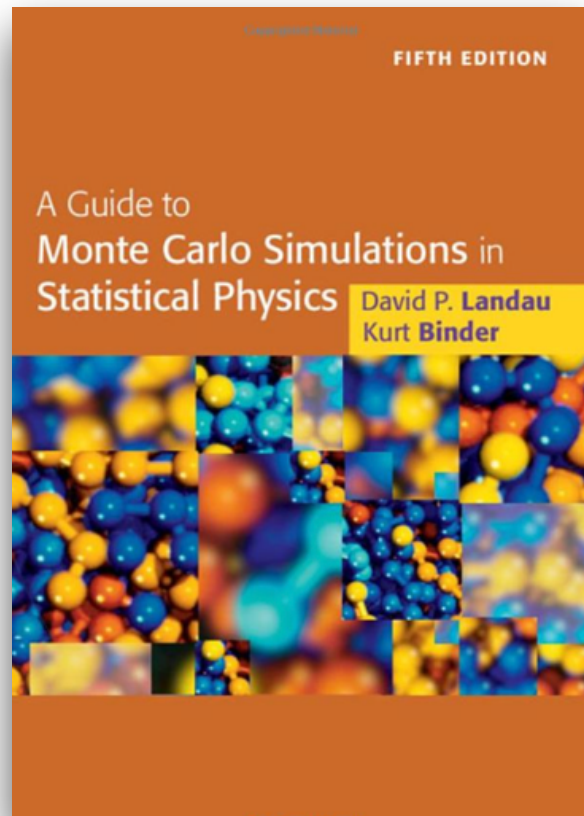


Kurt Binder 1968

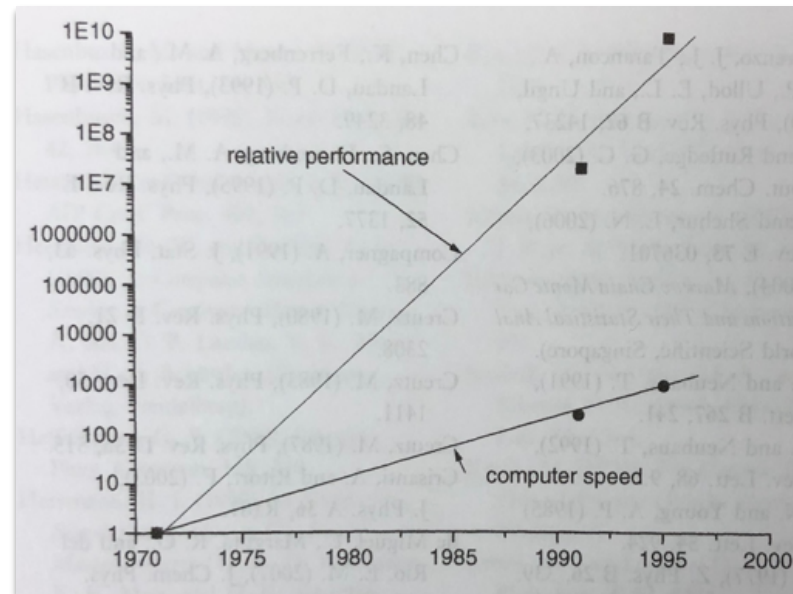


M. Mareshal, "From Varenna (1970) to Como (1995): Kurt Binder's long walk in the land of criticality", Eur. Phys. J. H 44, 161 (2019)

The importance of algorithms

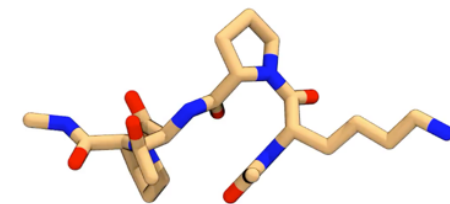
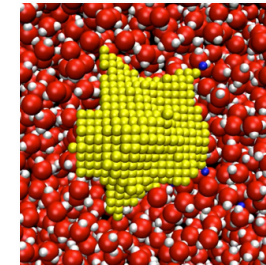
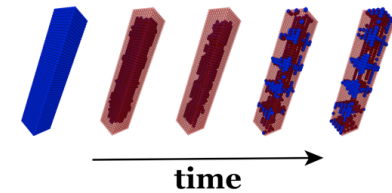


Simulation of the Ising model



Monte Carlo of configurations, trajectories and both

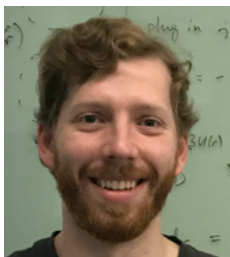
- Monte Carlo in *configuration space*:
cation exchange in nanocrystals
- Monte Carlo in *trajectory space*:
cavitation in water under tension
- Monte Carlo in *configuration and trajectory space*:
isomerization of proline in the KPTP tetrapeptide



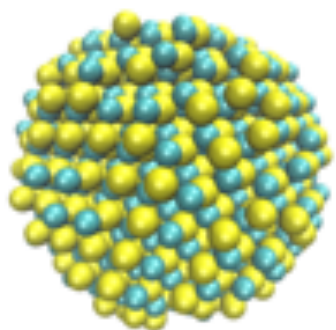
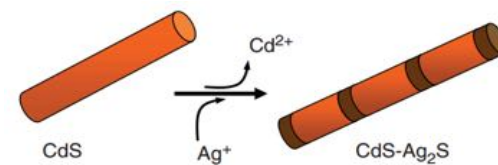
Nano-heterostructures by cation exchange



Phill Geissler
(1974-2022)

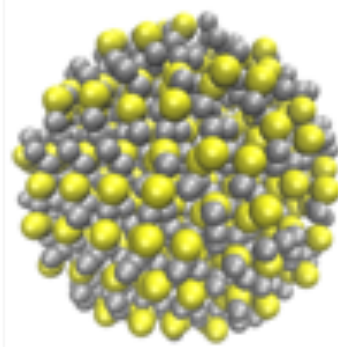


Layne Frechette

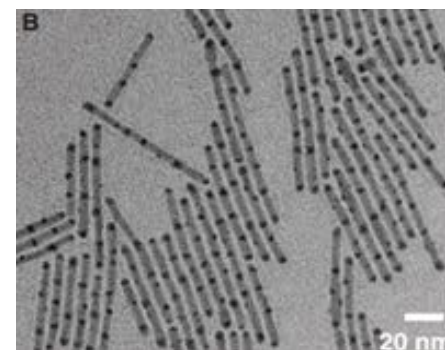


CdS

Ag-rich solution

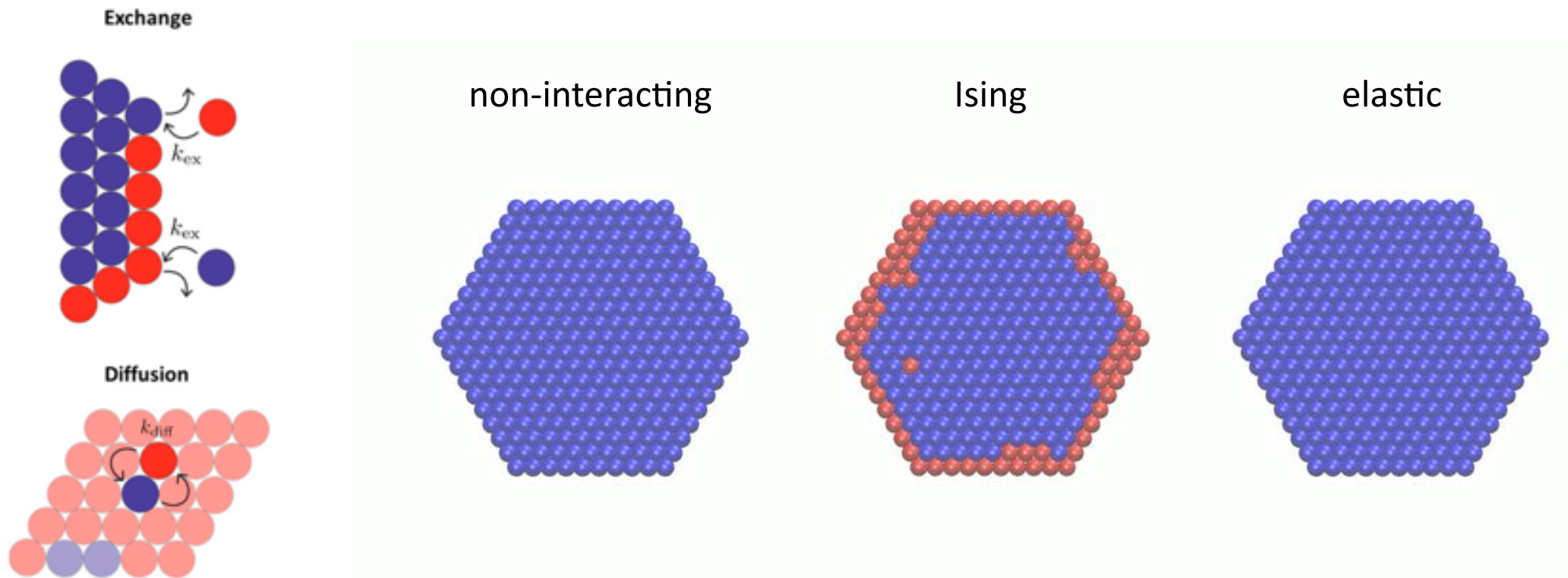


Ag₂S



R.D. Robinson et al. *Science* **2007**, 317, 355-358.

Simple lattice model for cation exchange



MC moves

$$E_0 = -h \sum_{\mathbf{R}} \sigma_{\mathbf{R}}$$

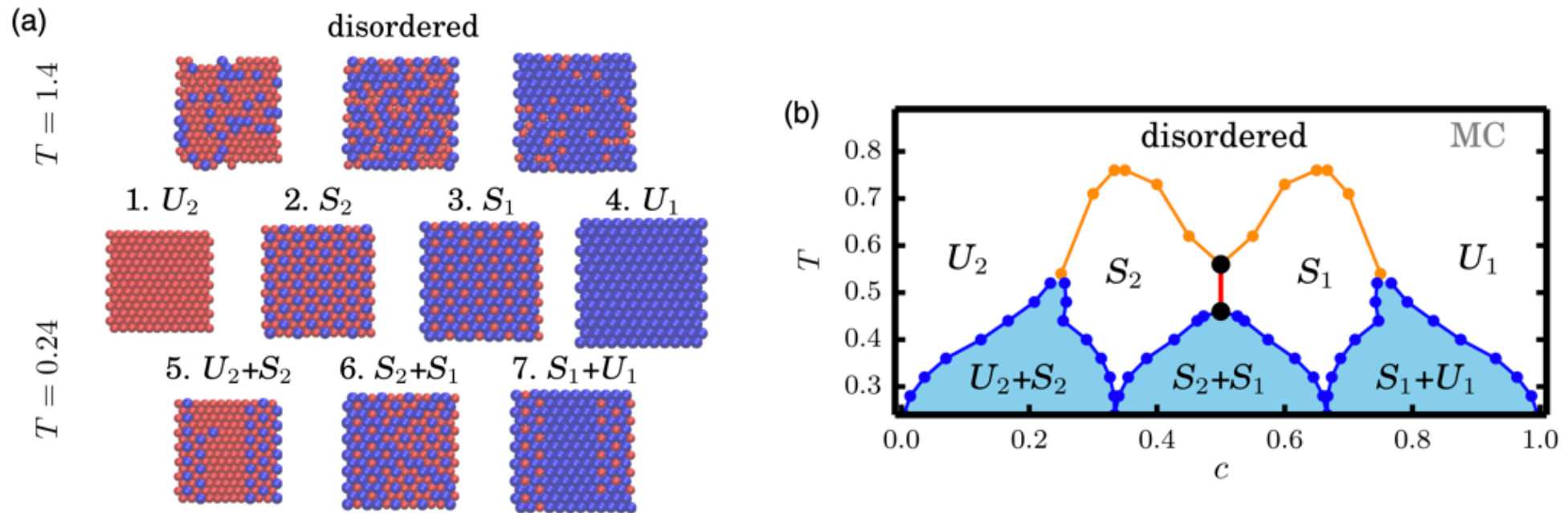
$$E_{\text{Ising}} = -J \sum_{\langle \mathbf{R}, \mathbf{R}' \rangle} \sigma_{\mathbf{R}} \sigma_{\mathbf{R}'}$$

$$E_{\text{elastic}} = \frac{\epsilon}{2} \sum_{\mathbf{R}, \mathbf{R}'} \sigma_{\mathbf{R}} V_{\text{elastic}}(\mathbf{R}, \mathbf{R}') \sigma_{\mathbf{R}'}$$

Frechette, Dellago, Geissler, PNAS 118, e2114551118 (2021)

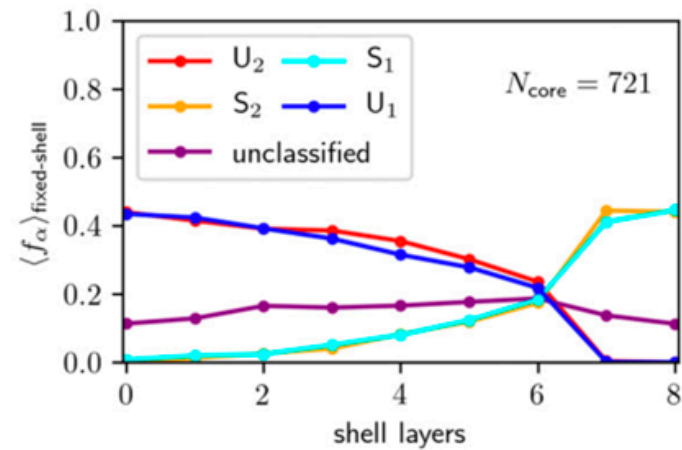
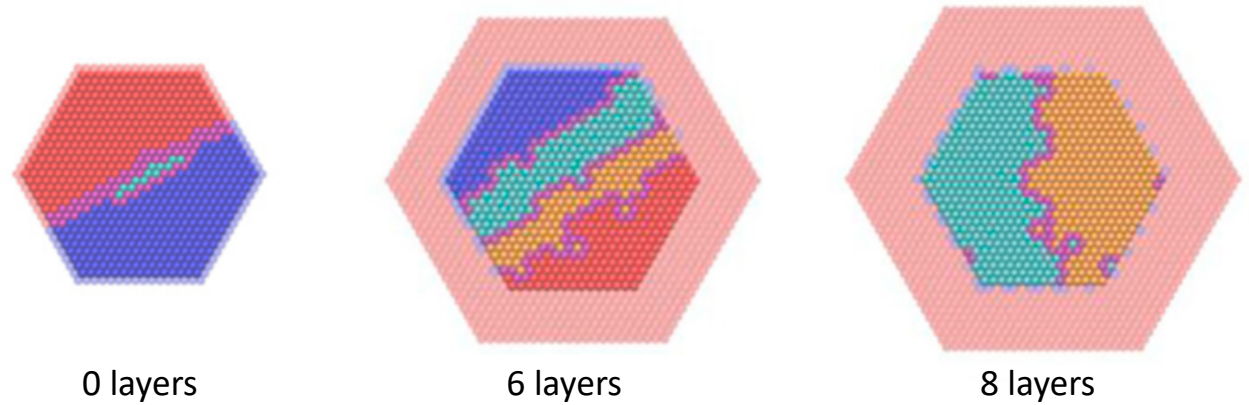
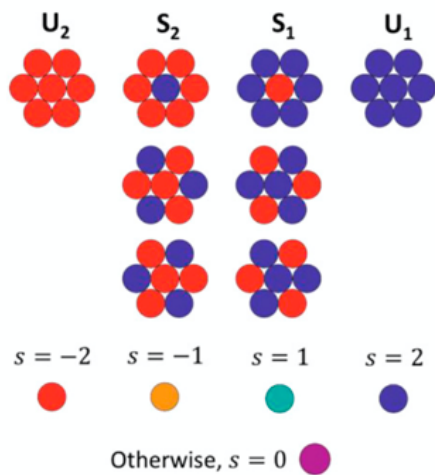
Schulz, Dünweg, Binder, Müller, PRL 95, 096101 (2005)

Equilibrium bulk phase diagram

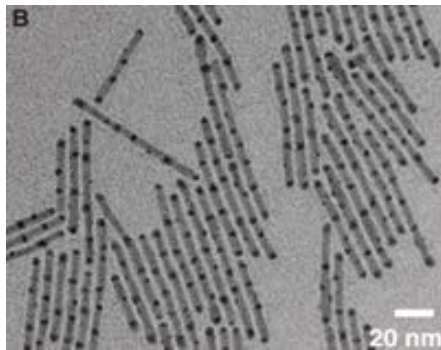
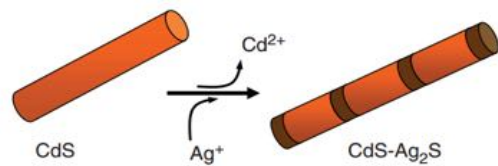


Core-shell phase diagram: effect of stiff shells

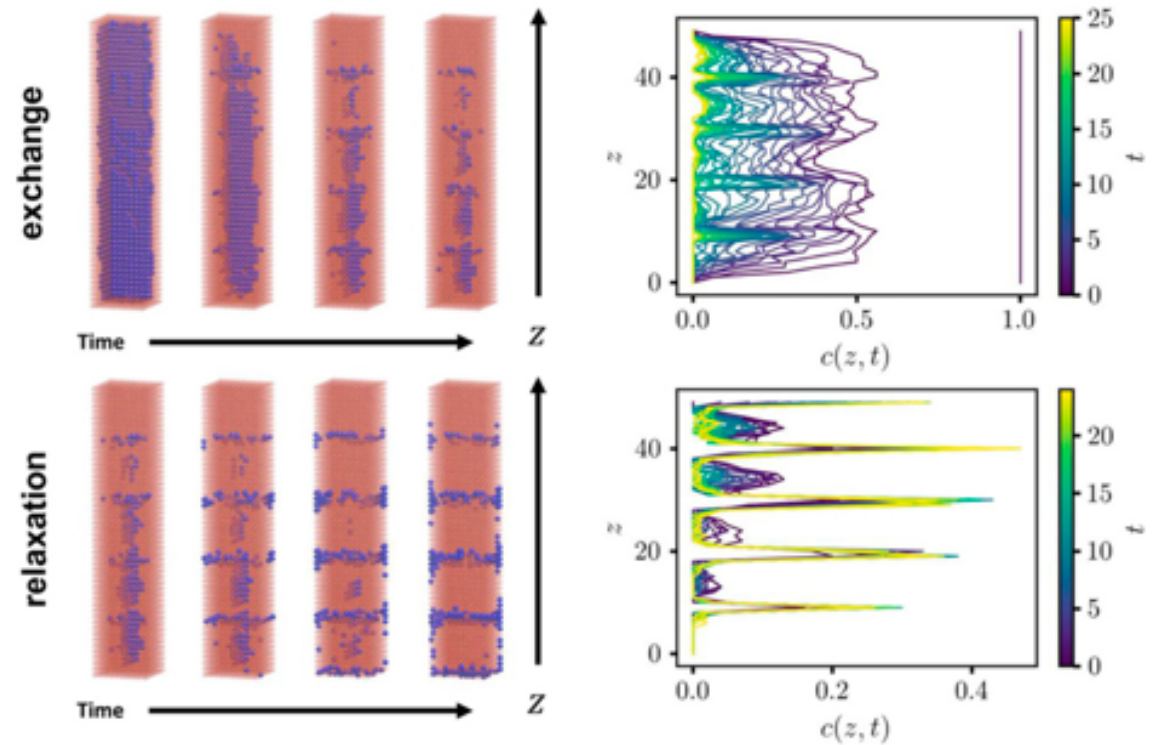
identification of phases



Elastic forces drive non-equilibrium pattern formation

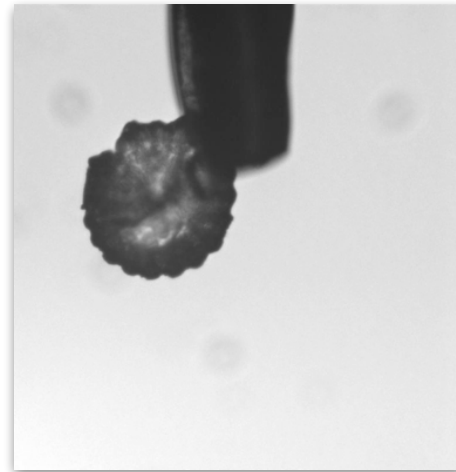
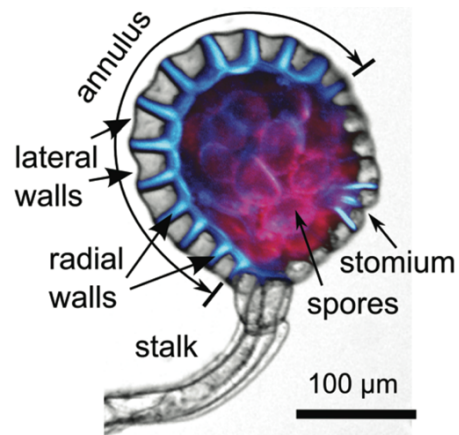


R.D. Robinson et al. *Science* **2007**, 317, 355-358.





Spore release in ferns

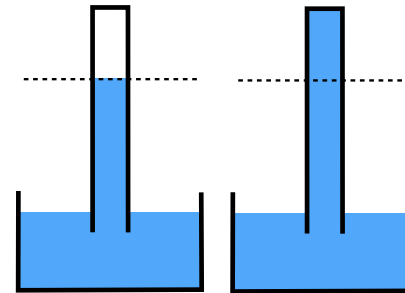


Xavier Noblin, LMPC Nice

Negative pressure in experiments



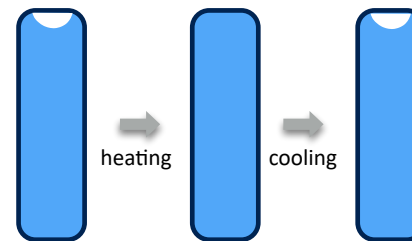
C. Huyghens (1672)



-0.1 MPa



M. Berthelot (1850)

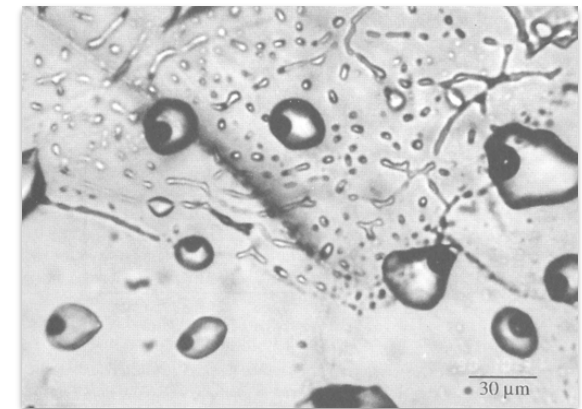
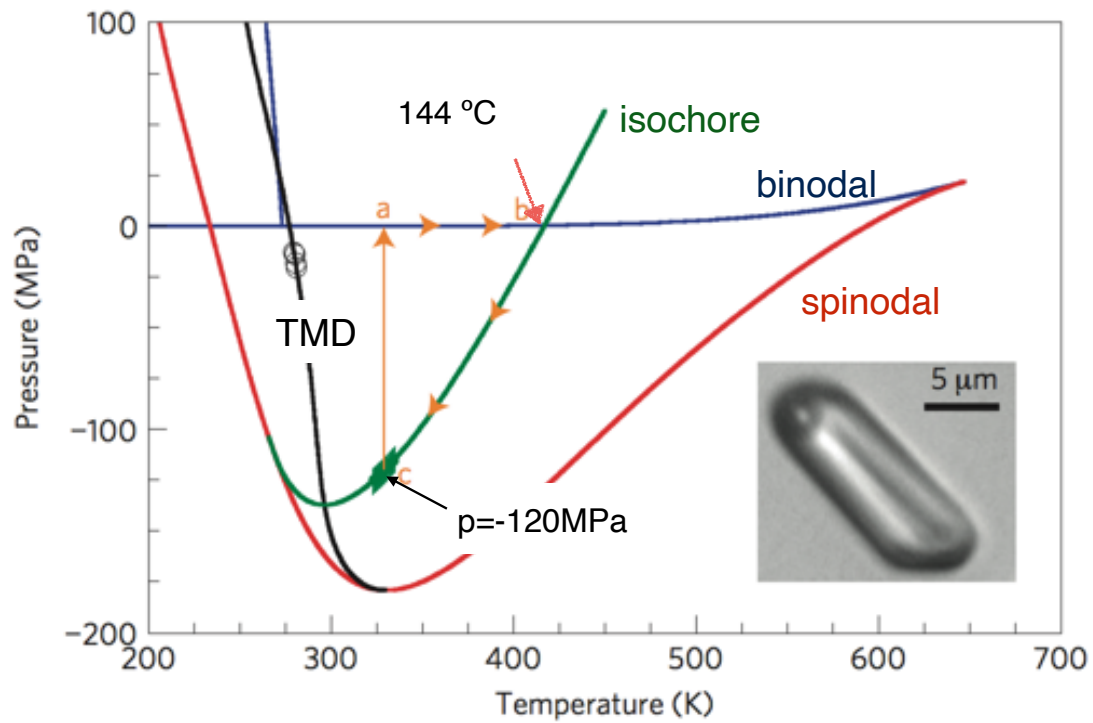


-5 MPa

Q. Zhen, D. J. Durben, G. H Wolf, and C. A. Angell Science 254, 829 (1991)

M. E.-M. Azouzi, C. Ramboz, J.-F. Lenain and F. Caupin, Nature Physics 9, 38 (2013)

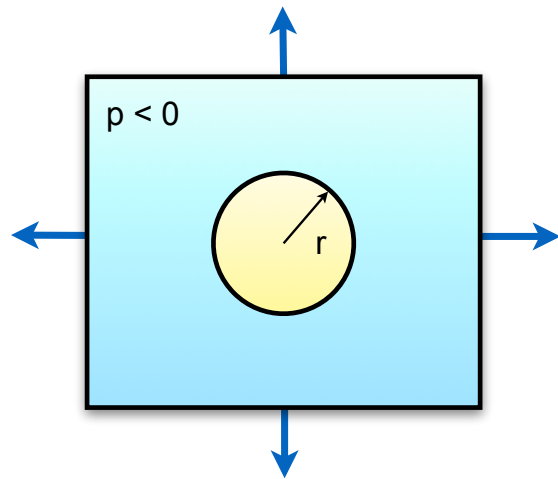
Stretching water in mineral inclusions



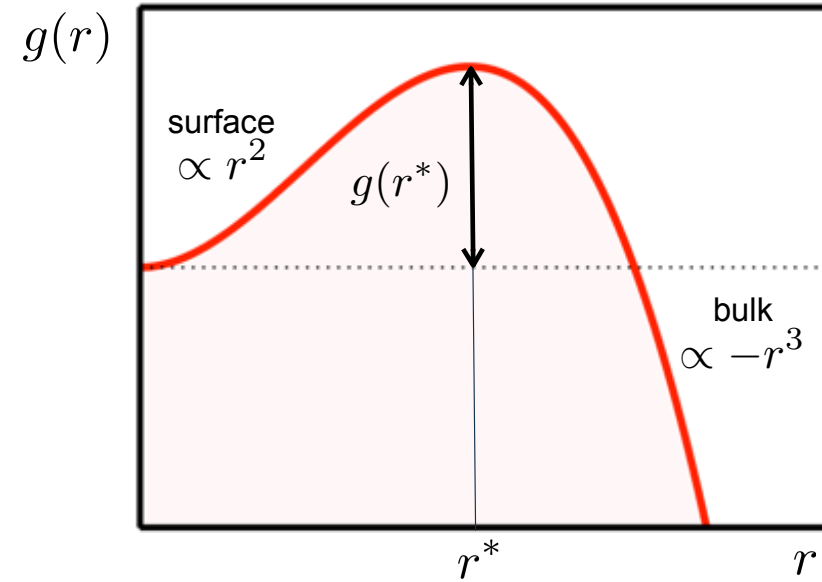
Mineral inclusions

-140 MPa

Bubble nucleation and growth

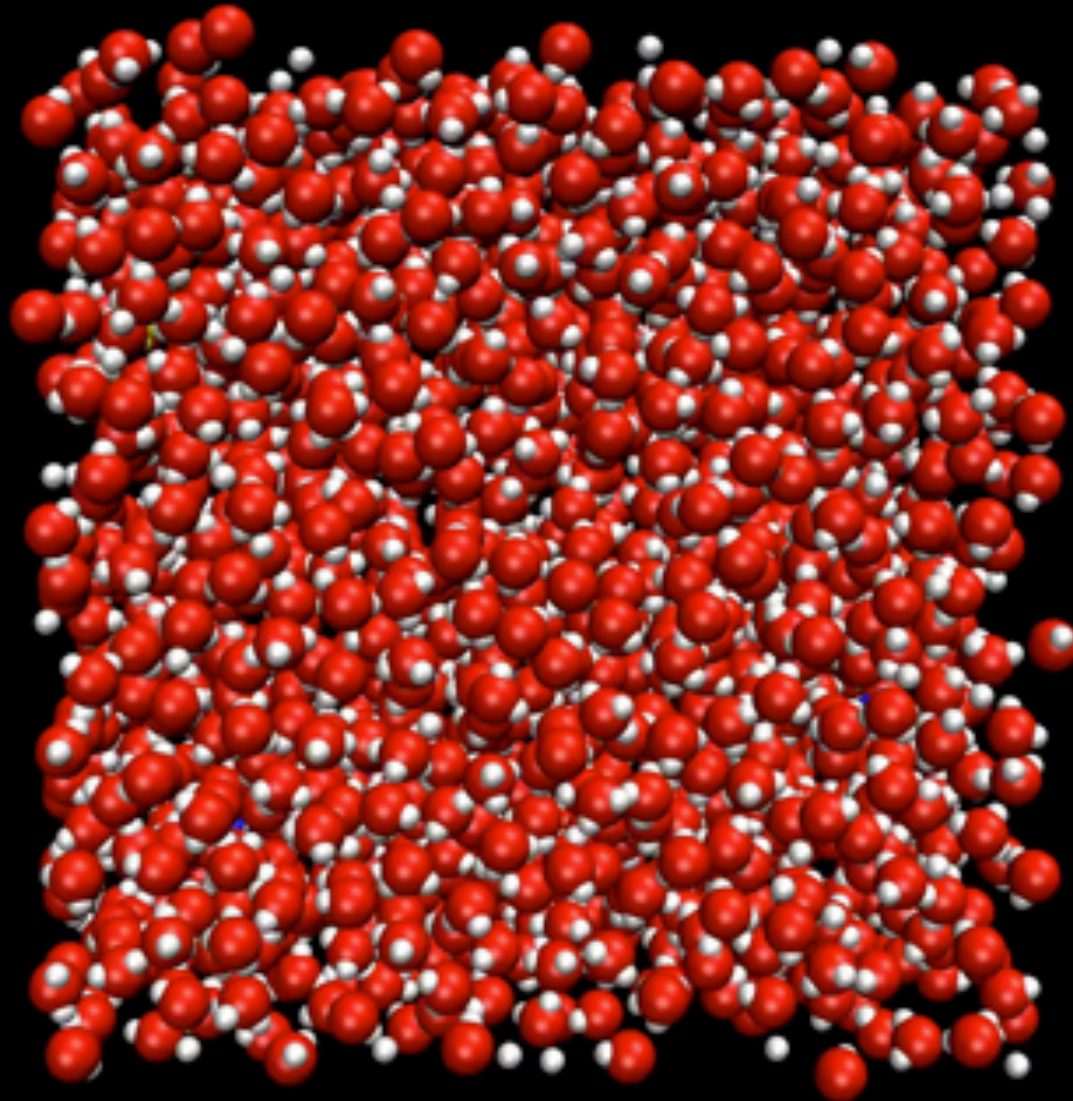


classical nucleation theory



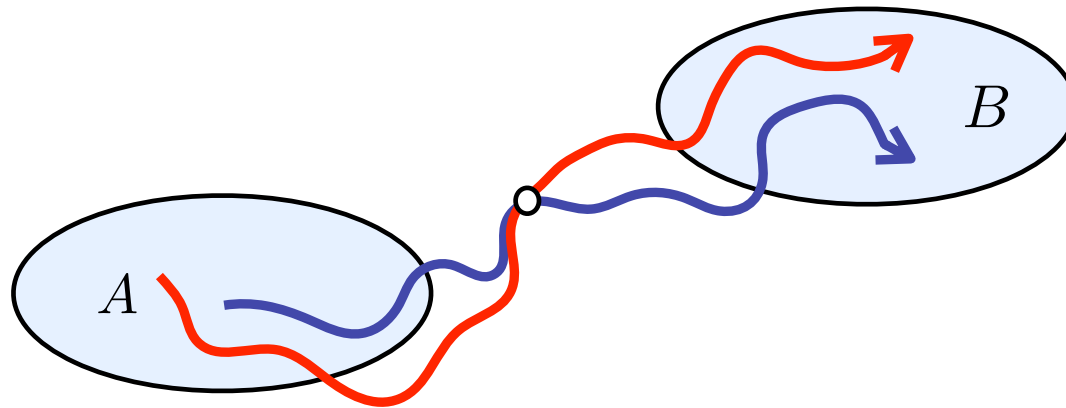
$$g(r) = 4\pi r^2 \gamma + \frac{4\pi r^3}{3} (p - p_{\text{bubble}})$$

P=-120 MPa
T=296 K
N=2000
TIP4P/2005



Monte Carlo in trajectory space: Transition path sampling

transition path ensemble $\mathcal{P}_{AB}[x(\mathcal{T})] \propto h_A(x_0)\rho(x_0) \prod_{i=0}^{\mathcal{T}/\Delta t-1} p(x_{i\Delta t} \rightarrow x_{(i+1)\Delta t})h_B(x_{\mathcal{T}})$



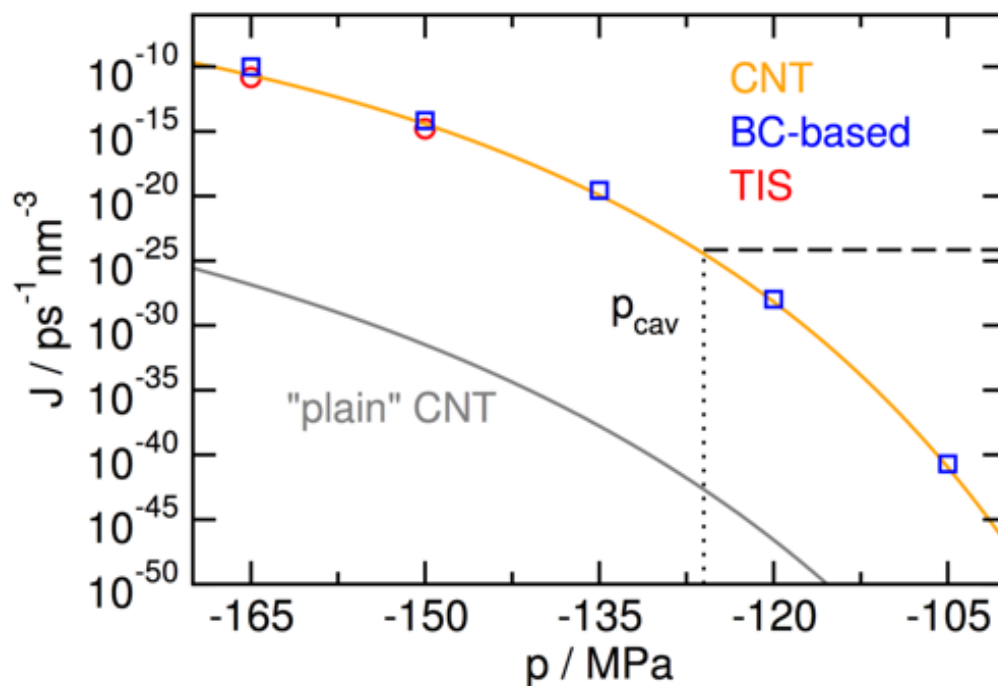
C. Dellago, P. G. Bolhuis, F. S. Csajka, D. Chandler, JCP 108, 1964 (1998)

C. Dellago, P. L. Geissler, P. G. Bolhuis, Adv. Chem. Phys. 123, 1 (2002)

Cavitation rate vs. pressure

Rayleigh-Plesset equation +
thermal fluctuations + CNT

$$J = \frac{\sqrt{k_B T \gamma^3}}{\eta |p|} \rho_0 e^{-\beta g(v^*)}$$



Georg Menzl



Chantal Valeriani

cavitation pressure

experiment: $p_{\text{cav}} = -120 \text{ MPa}$

Shooting point exchange: MC in configuration & path space



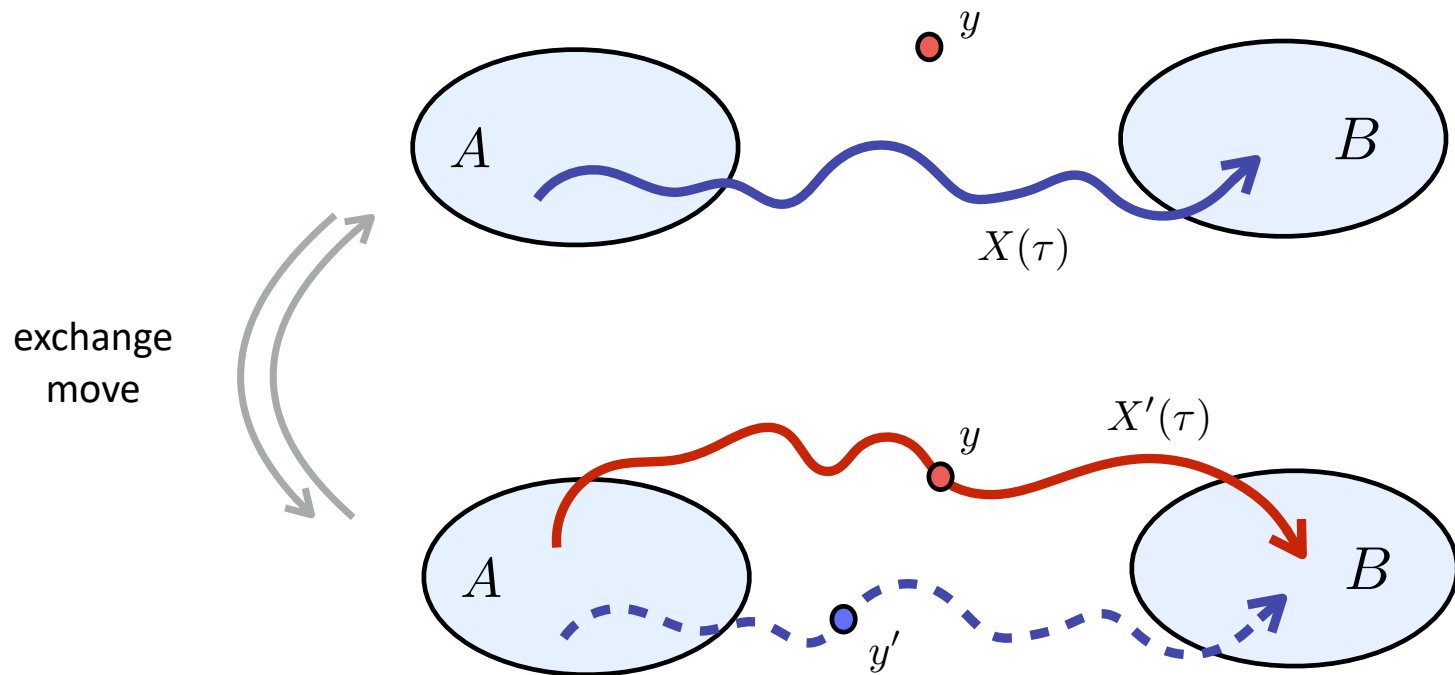
Sebastian Falkner



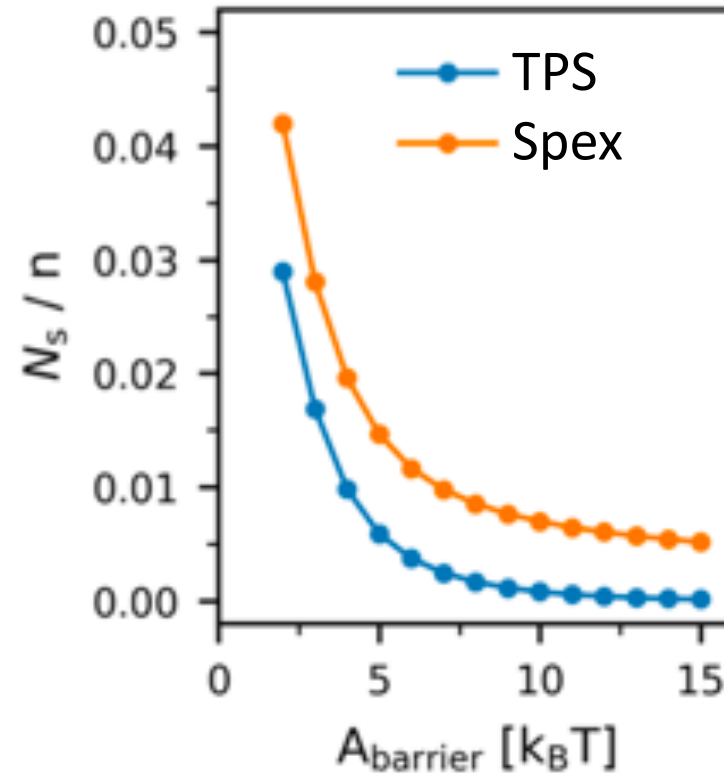
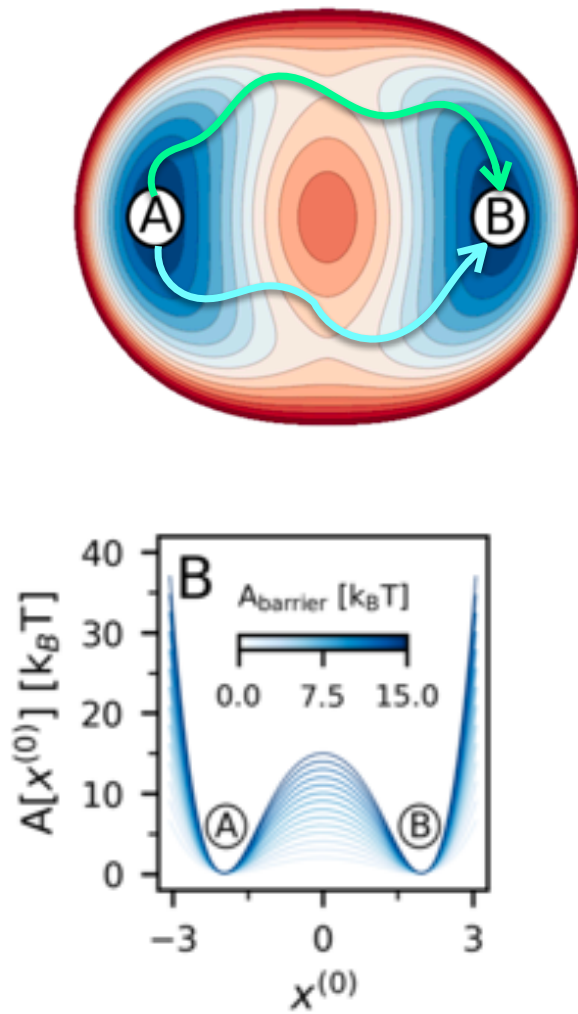
Alessandro Coretti

Generalized path ensemble $P_z(z) = p_y(y) P_X^{AB} [X(\tau)]$

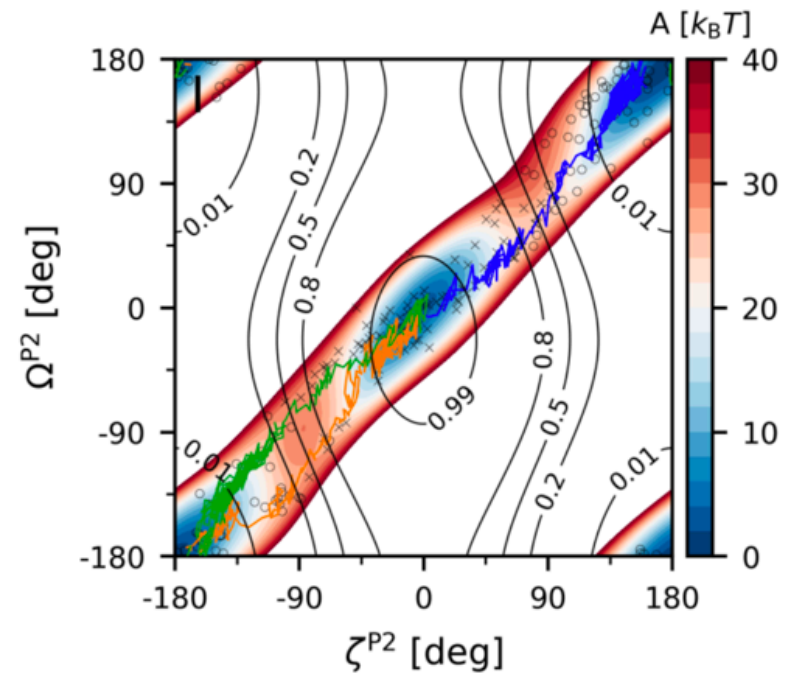
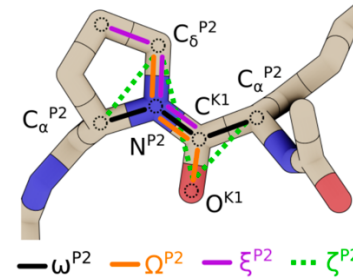
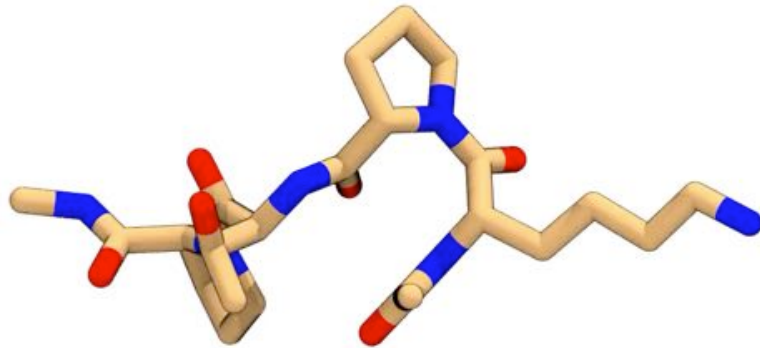
\uparrow configuration \uparrow trajectory



Enhanced sampling of multiple channels

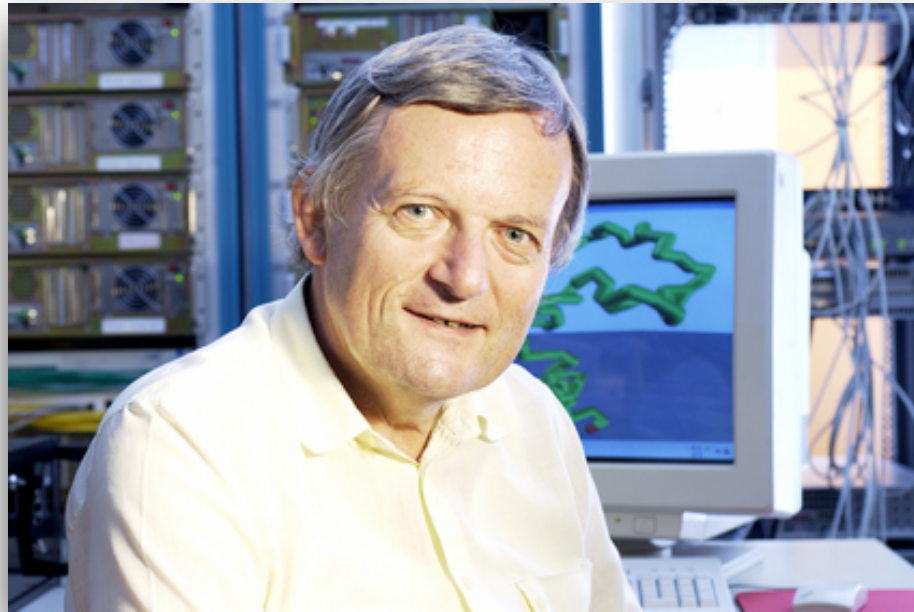


Isomerization of proline in the KPTP tetrapeptide



Falkner, Coretti, Dellago, PRL, to be rejected (2023)
Jung, Covino, Arjun, Bolhuis, Hummer, arXiv:2105.06673 (2021)

On the shoulders of giants



Kurt Binder (1944-2022)