Discrete relaxation path sampling of Morse clusters

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Summary

A two-dimensional cluster of six Morse discs ($Morse_6^{2D}$) is a useful model system for studying self-assembly. A previous theoretical study [M2D] using discrete path sampling [DPS] qualitatively agrees with experiments [E2D].

In the present work, discrete relaxation path sampling [DRPS], a recently developed method for efficient simulation of rare events, is explained and applied to this system. The systematic approach of DRPS produces an accurate master equation at a relatively low computational cost. The results are in satisfactory quantitative agreement with experiments.

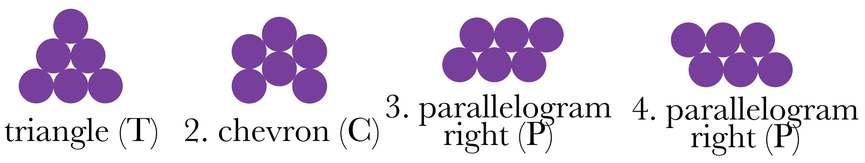
Characteristics of the system

- 6 solid polymer (polystyrene, density ~ of water) spheres with diameter of about 1.3 μm are strongly bound to a coverslip of a sample cell at T = 300K
- sodium dodecyl sulfate (SDS) micelles in salty water cause individual polymer cells to attract each other via depletion interactions of around bk_BT, where $b \in (1,10)$
- the system is simulated via Morse potential

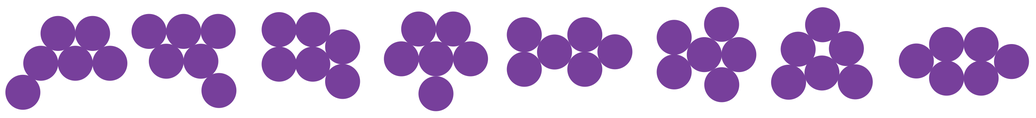
$$V(r) = e^{\rho(1-r)}(e^{\rho(1-r)} - 2) \ ,$$

where all distances are measured in σ_0 = 1.3 μm and the energy in $\varepsilon_0 = bk_BT$ with the range parameter ρ=30, mass $\mu_0 \sim 10^{-15}$ kg, time $\tau_0 \sim 10^{-4}$ s
- evaporation of the cluster is prevented by constraining the simulation to a circular box with diameter $r_{box} = 3\ \sigma_0$
- the system has 4 minima (considering optical isomers)

structures of the minima



- numbers of transitions between minima are experimentally observed
- 11 states can be obtained from the minima by breaking 1 contact



- 20 additional (7-contact) structures were also considered as states for DRPS; all 6- and less-contact structures were lumped into a single state
- friction constant (simulating water resistance) $\gamma \sim 3000\ \mu_0 / \tau_0$

Thermodynamics

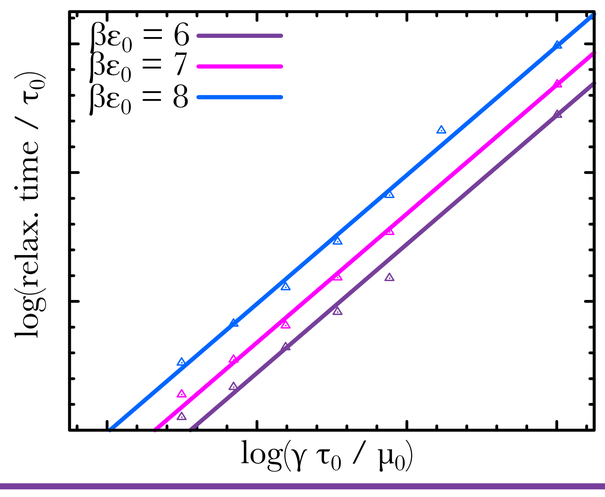
- parallel tempering simulations for 13 reciprocal temperatures between $\beta\varepsilon_0$=3 to $\beta\varepsilon_0$=9.

β	1	2	3	8 B	7 B	< 7 B
3.0	0.1	0.2	0.1	1.0	1.8	96.8
6.0	7.6	25.5	11.9	27.8	10.7	4.5
7.0	11.0	36.3	16.6	15.9	3.0	0.5
8.0	10.8	41.5	19.6	7.9	0.5	0.0
9.0	13.8	43.5	19.8	3.1	0.1	0.0

- ratio of minima (2:6:3:3) given by symmetry (rotational and vibrational degrees of freedom contribute negligibly); agrees with [E2D] and [M2D]
- populations agree with [E2D] at $\beta\varepsilon_0$ between 6 and 7
- depletion interaction (estimated at ~2 k_BT) might not be dominant

Dynamics

- relaxation times calculated for each pair of topological neighbours
- relaxation times more reliable at lower friction → extrapolation



- kinetic Monte Carlo used to get the number of transitions

	T↔C	T↔P	C↔P
expt.	55	63	140
$\beta\varepsilon_0$=6	300	1000	1800
$\beta\varepsilon_0$=7	130	220	530
$\beta\varepsilon_0$=8	60	80	200

rounded numbers of transitions per 26 hours

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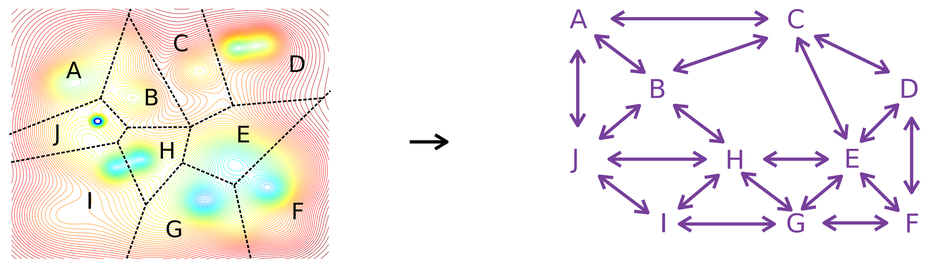
Discrete relaxation path sampling

- links energy landscape methods [EL] with MD sampling. Rare events are studied in 5 steps:

1. space partitioning

- configuration space is fully partitioned (no void typical for reactive flux methods)
- good partitioning: compact cells without significant internal barriers

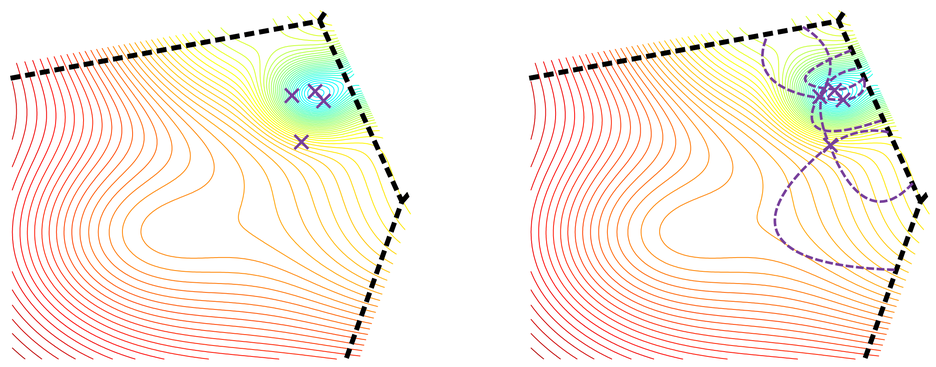


2. sampling thermodynamics

- several configurations are randomly sampled from the equilibrium distribution
- constrained Monte Carlo or any other enhanced sampling method that does not require a progress coordinate (parallel tempering, nested sampling etc.) can be used

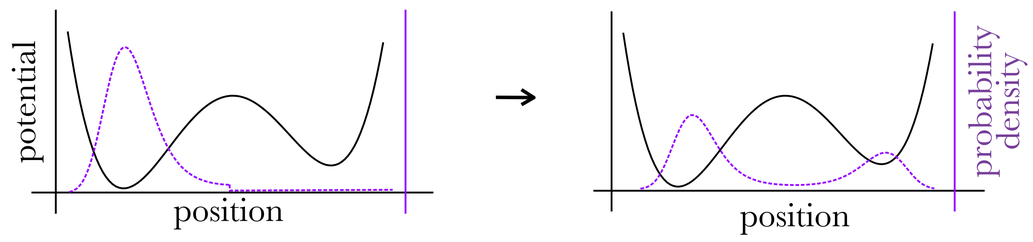
3. constrained MD

- starting from the equilibrium distribution inside cell, random Maxwell-Boltzmann velocities
- stopped after a trajectory leaves the cell; simulation run to both trajectory ends
- four types of quantities are sampled, exit probabilities from cell interior and cell boundaries, mean exit times and mean boundary-to-boundary trajectory lengths



4. solving relaxation equations

- the relaxation rate from one cell to one neighbouring cell is obtained
- the pair of cells is isolated from the rest using *equilibrium* boundary conditions
- derived from decomposition of relaxation into exit and reinitiation at the boundaries
- can be propagated numerically, but an analytical solution exists → solving linear system



5. regrouping

- if an observable state is composed of multiple DRPS states, the DRPS kinetic network must be regrouped and the DRPS states lumped
- the new graph transformation [NGT] uses reactive flux-based equation
- diagonalisation of the rate matrix is used in a relaxation-based lumping formula [RGRP]
- we are currently developing a computationally inexpensive relaxation-based lumping formula

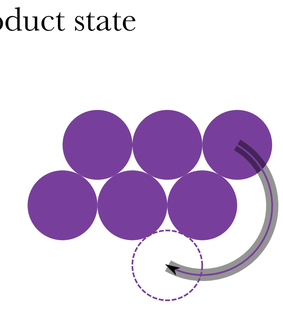
Conclusion

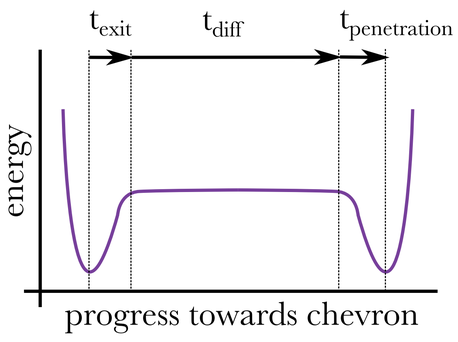
- DRPS provides a hybrid methodology, which includes sampling dynamics and a master equation framework. Simulations can be systematically improved, so that the accuracy can achieve quantitative agreement with experiments.

- the centre of the shifting particle is constrained to a narrow channel (grey below); the diffusion time through this channel is so long that the particle returns back to the original position more frequently than it progresses to the product state

- calculation of the correction factor for transition state theory will be expensive → space partitioning

- the binding energy is probably greater than the one suggested in the original paper [E3D]





References

[DPS] Wales, 2002, Mol. Phys. 100, 3285
[DRPS] Fačkovec et al., 2015, J. Chem. Phys. 143, 044119
[E2D] Perry et al., ArXiV 1411.5680
[E3D] Meng et al., 2010, Science 159, 211
[EL] Wales, 2003, *Energy landscapes*, Camb. Uni. Press
[M2D] Morgan and Wales, 2014, Nanoscale 6, 10717
[NGT] Wales, 2009, J. Chem. Phys. 130, 204111
[RGRP] Hummer and Szabo, J. Phys. Chem. B 119, 9029

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