Enhanced screening in polymer melts with periodic boundary conditions

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Dense polymer systems

- Joint work with Burkhard Dünweg of MPI for Polymer Research, Mainz.
- Polymer melt: very dense system of polymers where each polymer interacts with many other polymers.
- Two competing effects: self-repulsion causes the walk to spread out (like for the self-avoiding walk), while crowding from neighbouring polymers compresses the polymer.
- Remarkably, to leading order these effects cancel, and in a polymer melt each individual chain behaves like a simple random walk and obeys Gaussian statistics.[1] This is known as "Flory screening".

[1] de Gennes, P. G., *Scaling Concepts in Polymer Physics*, Cornell University Press: 1979.

Dense polymer systems

- We measure correlations in the chain via the bond correlation function:

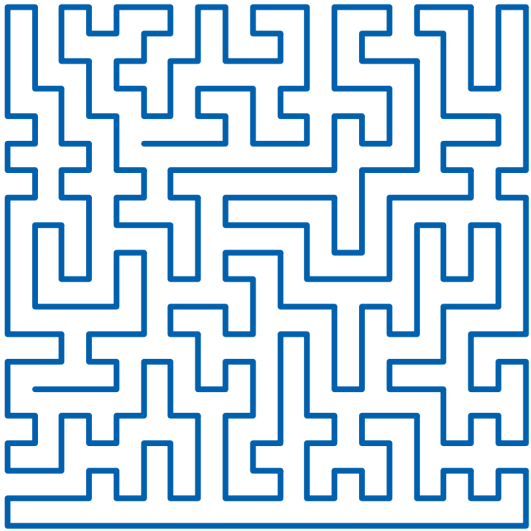
$$C(s) = \frac{1}{b^2} \left\langle \vec{l}_i \cdot \vec{l}_{i+s} \right\rangle$$

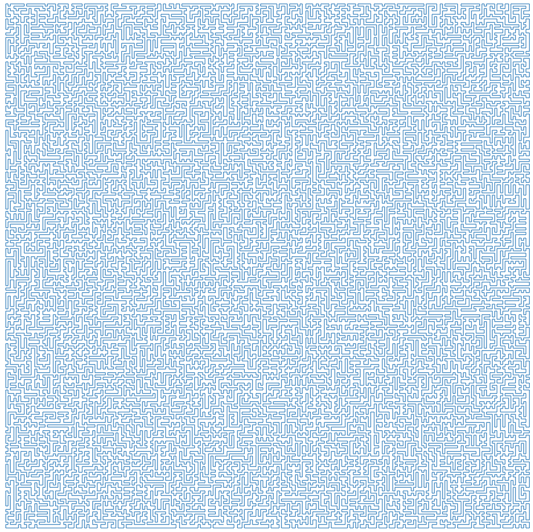
- For a random walk / Brownian motion, $C(s)$ decays exponentially rapidly.
- In a melt, the leading-order correction causes $C(s)$ to decay with a power law[2]: $C(s) \sim s^{-3/2}$.
- We wish to study within chain correlations and other phenomena, e.g. knotting.
- Difficult, because dynamics (including molecular dynamics) for long polymers very slow due to entanglement.

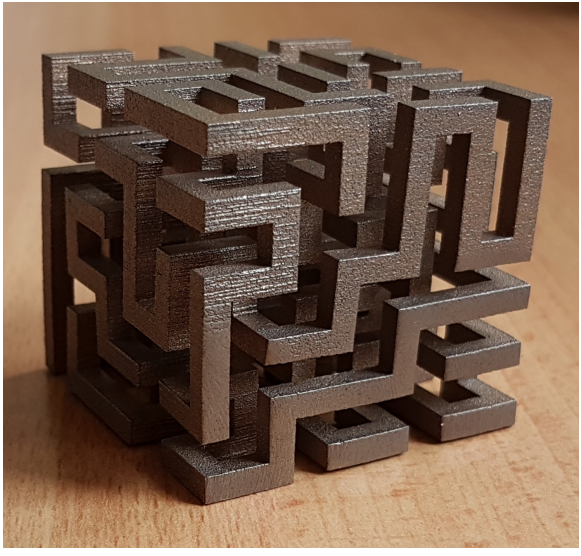
[2] Wittmer, J. P. et al. *EPL (Europhysics Letters)* **2007**, *77*, 56003.

Hamiltonian paths

- Hamiltonian paths are self-avoiding walks which visit every vertex in a graph.
- Generally take the graph to be a region of the square or simple cubic lattices.
- Model of the crystal phase of polymers.
- Can extend to polymer melts which involve many paths.
- Universality implies that these lattice models capture essential physics of dense polymer systems.
- What do they look like?







Sampling dense polymer systems

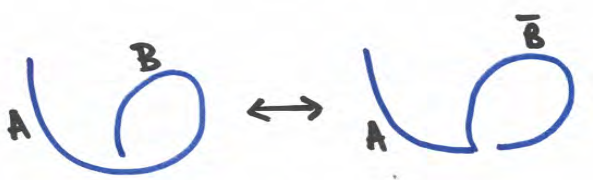
- Connectivity changing Monte Carlo moves, in particular backbite moves, very effective.
- Due to slow equilibration of polymer melts, the quest for efficient Monte Carlo moves has been of interest for a long time.
- For system size N, equilibration in $O(N)$ Markov chain time steps.

Partial history of connectivity changing moves

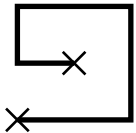
- Early work in 1980s by Olaj and Lantschbauer[3], Mansfield[4].
- Later: Deutsch[5], Theodorou and collaborators[6], Jacobsen and collaborators[7].

[3] Olaj, O. F.; Lantschbauer, W. *Macromolecular Rapid Communications* **1982**, *3*, 847–858.
[4] Mansfield, M. L. *J. Chem. Phys.* **1982**, *77*, 1554–1559.
[5] Deutsch, J. M. *J. Chem. Phys.* **1997**, *106*, 8849–8854.
[6] Karayiannis, N. C. et al. *J. Chem. Phys.* **2002**, *117*, 5465–5479.
[7] Jacobsen, J. L. *Phys. Rev. Lett.* **2008**, *100*, 118102.

Backbite move: choose an end, extend by a single step which will form a loop, traverse loop in opposite direction and delete last bond.



Backbite moves for sampling Hamiltonian paths.



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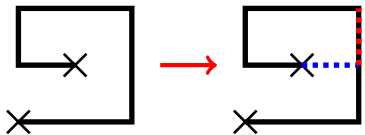

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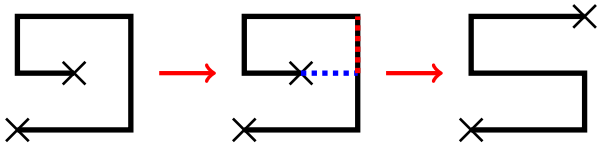

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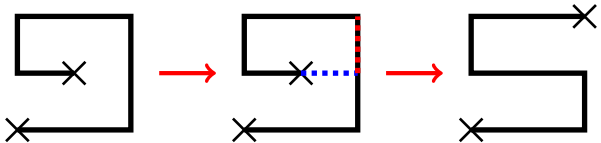
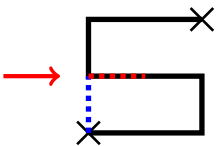
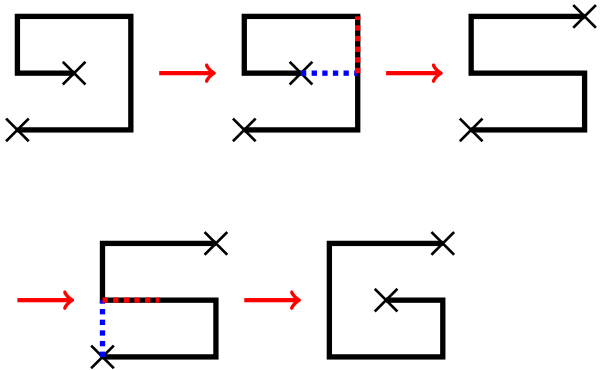




Backbite moves for sampling Hamiltonian paths.



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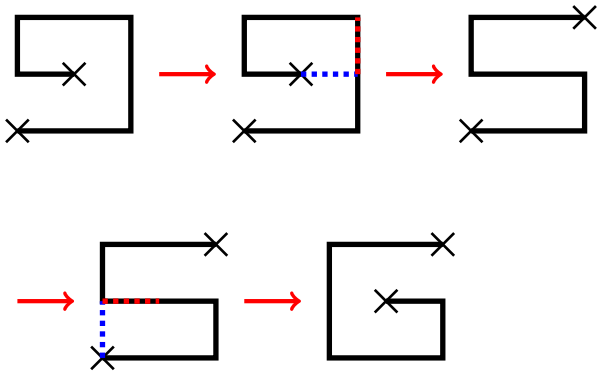
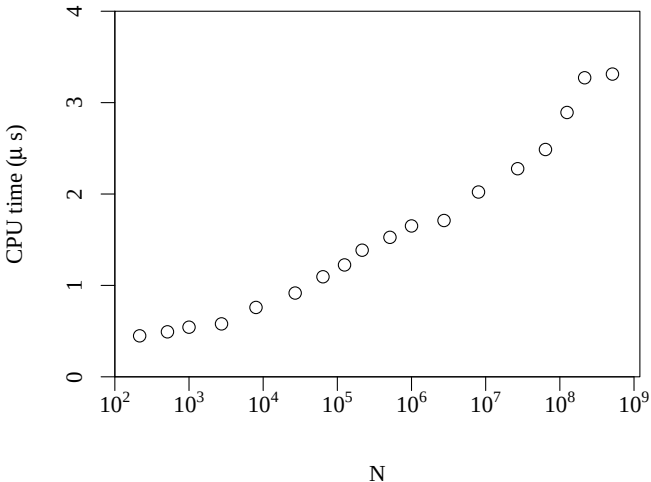


Each time we make a backbite move we create a loop, delete the edge that completes the loop, and *reverse* the orientation of the remaining edges of the loop.

Backbite implementation

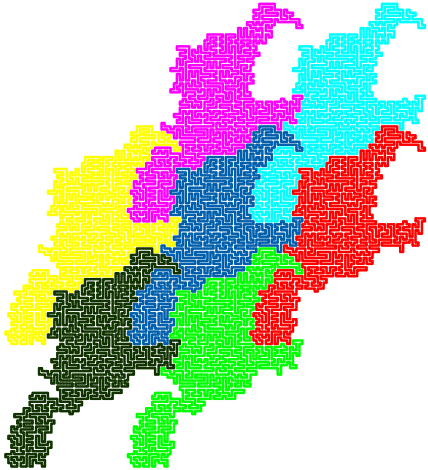
- For the simple cubic lattice, loops are of mean size $O(N)$.
- $\Rightarrow$ mean CPU time per backbite move $O(N)$?
- Binary tree implementation: to reverse $O(N)$ steps requires $O(\log N)$ operations ("tree rotations").
- For simple cubic lattice, mean size of loops is $O(N)$.
- $L = 800$, $N = 512$ million:
  - Reverse 178 million steps, $\cdots$
  - $\cdots$ or perform 18.7 tree rotations.
- Very fast in practice.

CPU time per backbite move $\mathbb{Z}^3$

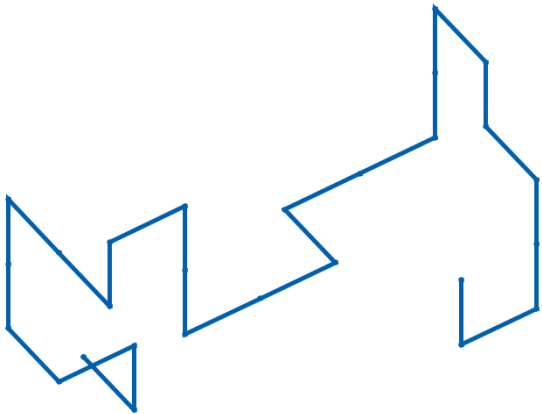


A single dense polymer with PBC

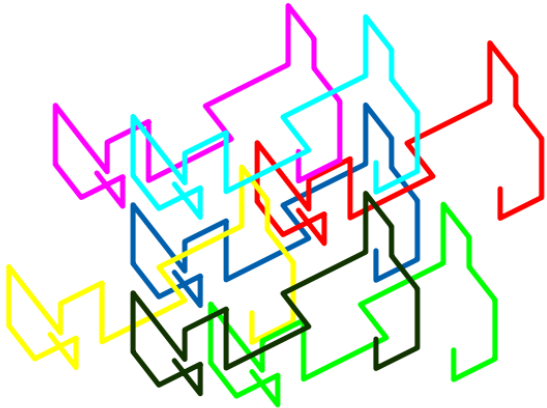
- Can a Hamiltonian path with periodic boundary conditions (PBC) reproduce behaviour of a polymer melt?
- Can explicitly see random walk behaviour for $d = 3$ when we unwind it.
- Multiple copies are space filling, because in reduced coordinates the walk must fill the original grid.
- In the large N limit, do we get the same behaviour as the polymer melt?



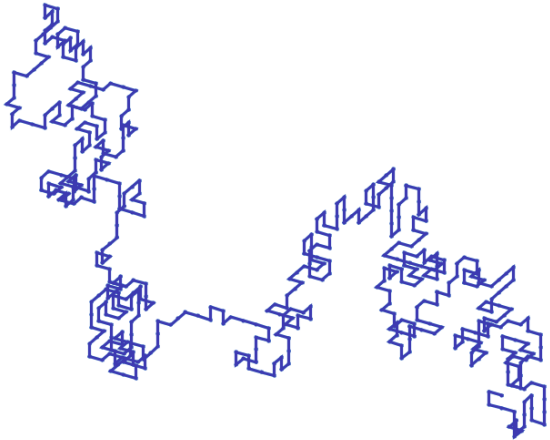
40×40 grid, with copies from winding.
Note that the walk is disc like.



$3 \times 3 \times 3$ grid.



$3 \times 3 \times 3$ grid, with copies from winding around.



$8 \times 8 \times 8$ grid; random walk behaviour clearly observable.

A single dense polymer with PBC

- $N = L^3$; random walk behaviour.
- Subchains of length s do not "feel" the boundary until they wind around the box, that is when

$$s^{1/2} = L = N^{1/3};$$
$$\Rightarrow s = L^2 = O(N^{2/3}).$$

- For $s \ll L^2$ we expect that the subchain will behave as in a melt.
- A priori unclear what will happen for $s \gg L^2$.

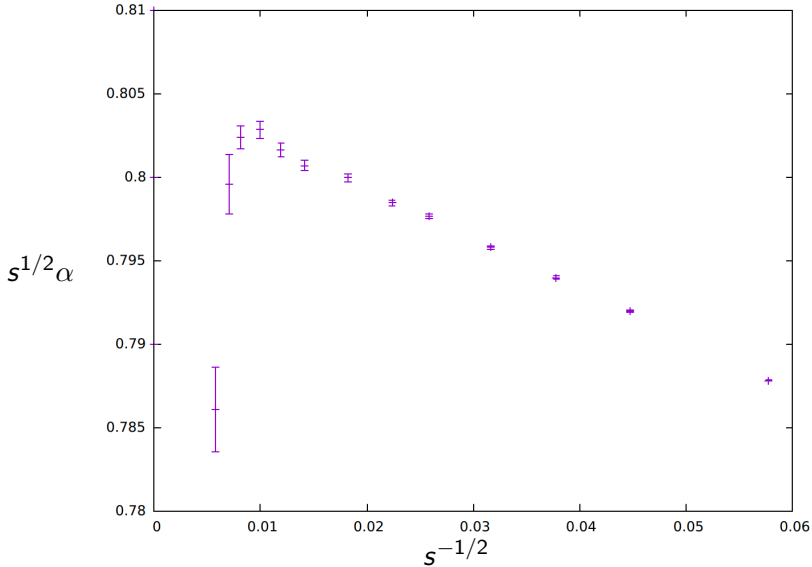
A single dense polymer with PBC

- Wittmer et al. predicted power-law within-chain correlations. This results in leading correction to scaling for $\langle R_E^2 \rangle$ to be $O(s^{-1/2})$ for a chain of length s.
- Expect that universal amplitude ratios assume random walk values.
- Together:

$$\frac{\langle R_E^4 \rangle}{\langle R_E^2 \rangle^2} = \frac{5}{3}\left(1 + \frac{a}{s^{1/2}} + \frac{b}{s} + \cdots\right)$$

- We sample systems with $L = 300$ so $N = 27 \times 10^6$, and expect that subchains of length $s \lessapprox L^2 = 9000$ will behave as if they are in a melt.
- Estimate:

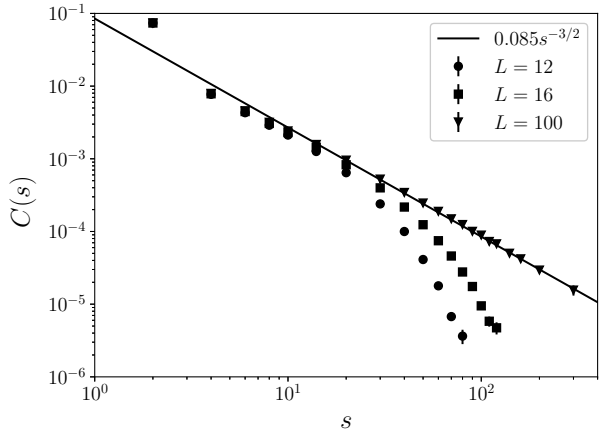
$$\alpha = \frac{\langle R_E^4 \rangle}{\langle R_E^2 \rangle^2} - \frac{5}{3}, \qquad s^{1/2}\alpha = a' + \frac{b'}{s^{1/2}} + \cdots$$


0.81
0.805
0.8
0.795
0.79
0.785
0.78
0
0.01
0.02
0.03
0.04
0.05
0.06
$s^{1/2}\alpha$
$s^{-1/2}$

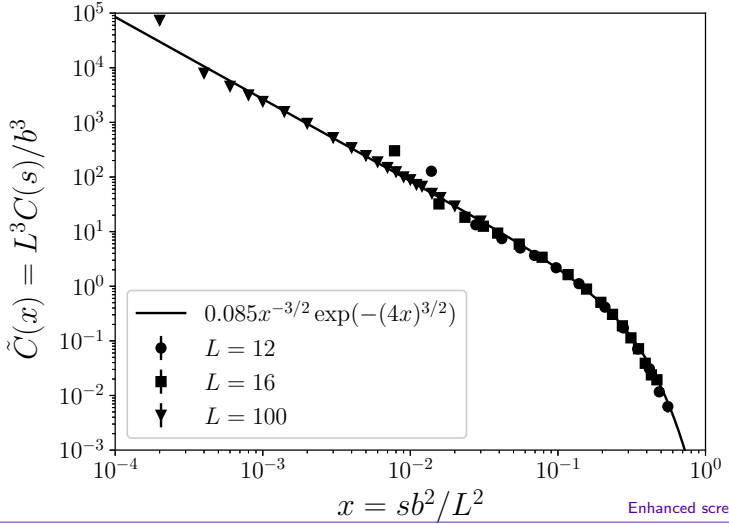
Bond-vector autocorrelation

We study the bond-vector autocorrelation function $C(s)$, where s is the separation along the chain.

- Expect $C(s)$ decays as $s^{-3/2}$; this leads to the $s^{-1/2}$ correction term for $\langle R_E^4 \rangle / \langle R_E^2 \rangle^2$.
- But, once $s \sim L^2$ decay is far more rapid! The autocorrelations are screened once the walk wraps around the box.
- Data collapse possible in terms of a scaling variable.



$\tilde{C}(x) = (L^3/b^3)C(s)$ as a function of the finite–size scaling variable $x = sb^2/L^2$.
(Note that the error bars are not visible at this scale.)



Conclusion

- Backbite moves can be implemented very efficiently via a binary tree.
- Working with subchains of single long chain with PBC seems like a viable way to understand melts.
- We verify Wittmer et al.'s prediction of the $s^{-3/2}$ decay in correlations and $s^{-1/2}$ correction to the universal amplitude ratio to high precision.
- Open questions regarding enhanced convergence / Flory screening.
- Numerically well understood, and we have a complete empirical description.
- Paper being written up now ...

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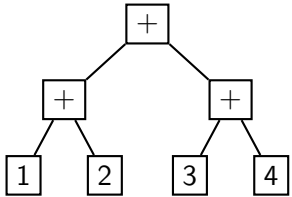
- ... but we are in search of a theory from first principles!

Time reversal symmetry elements in the binary tree nodes.



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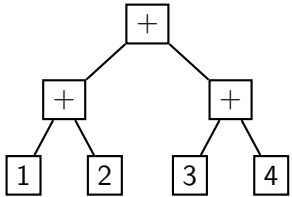

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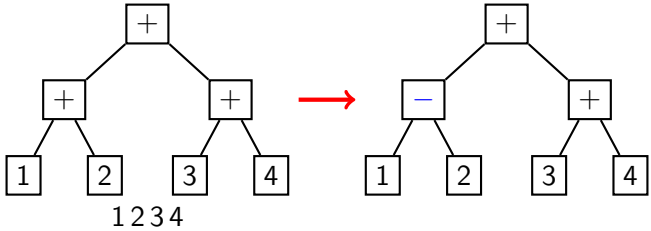

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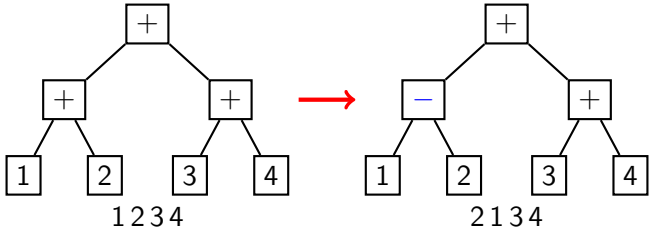

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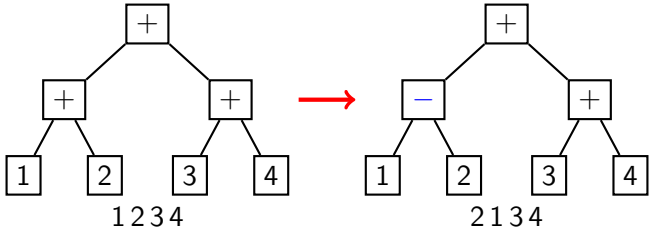

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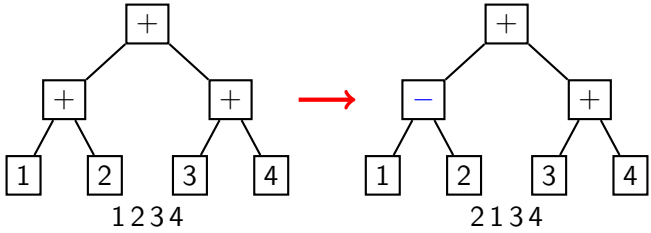
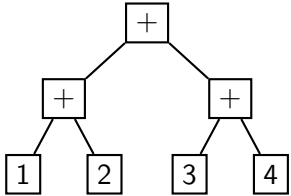


How do we reverse sequences of steps which don't align with the tree?



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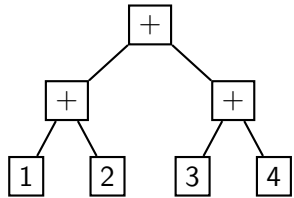

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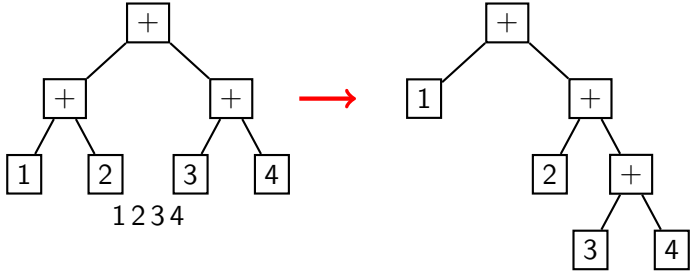

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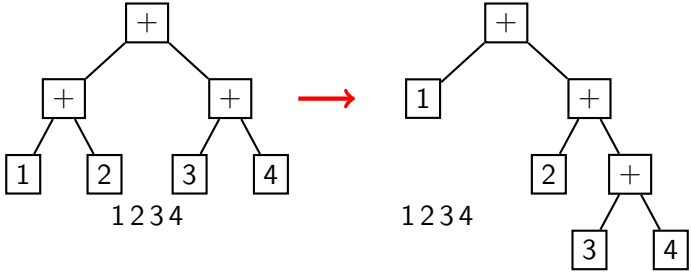

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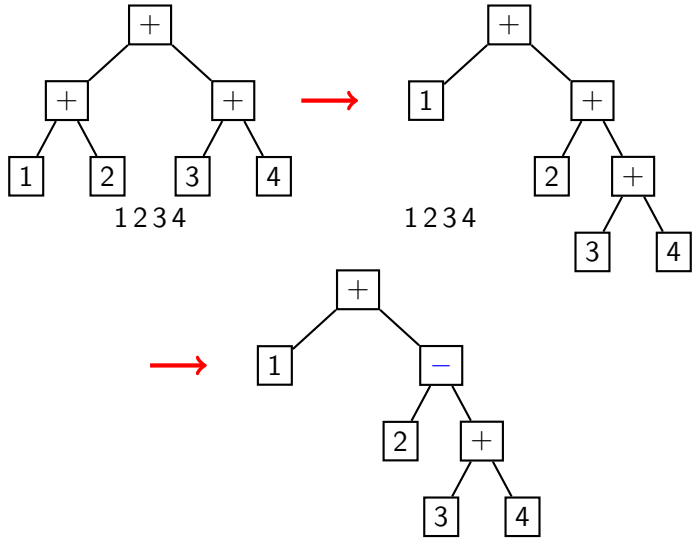
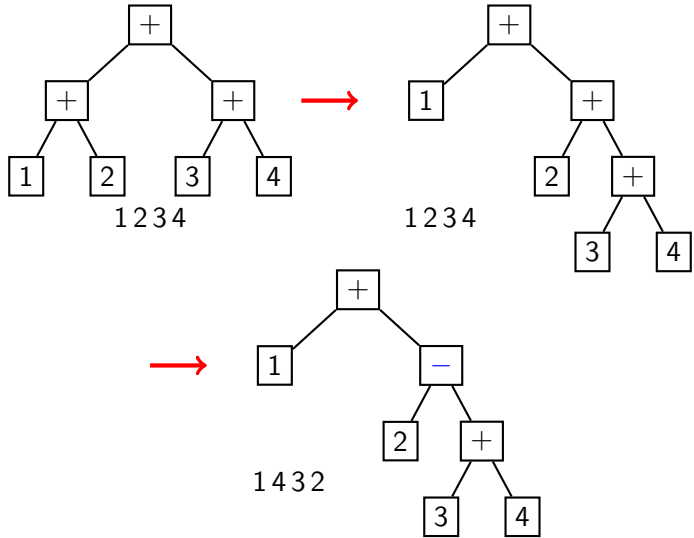
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