parQ - A Transition Matrix Method to Calculate the Density of States

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Outline

1. Methods
2. Models
3. Results
4. Conclusion

par$Q$ Method

- par$Q$ is a transition matrix approach utilising an infinite temperature transition matrix
  - it is independent of Monte Carlo scheme
    - e. g. can use standard Metropolis, Wang-Landau or even Threshold Accepting, as well as other methods
  - uses all available data

- Master equation of a random walker being in state E_j:

$$p(E_j, t+1) = \sum_{i=1}^{N} \Gamma_{ji}(T) \cdot p(E_i, t)$$

- Γ temperature dependent TM $\quad \sum_k \Gamma_{ki}(T) = 1 \quad \forall i$

- right eigenvector to eigenvalue 1 of the stationary solution $p^*(E_j)$ has to be the Boltzmann distribution

$$p^*(E_j) = \frac{1}{Z(T)} \Omega(E_j) \mathrm{e}^{-\beta E_j}$$

- for $t \to \infty$ we get:

$$\Omega(E_j) \mathrm{e}^{-\beta E_j} = \sum_{i=1}^{N} \Gamma_{ji}(T) \Omega(E_i) \mathrm{e}^{-\beta E_i}$$

- taking the limit $T \to \infty$

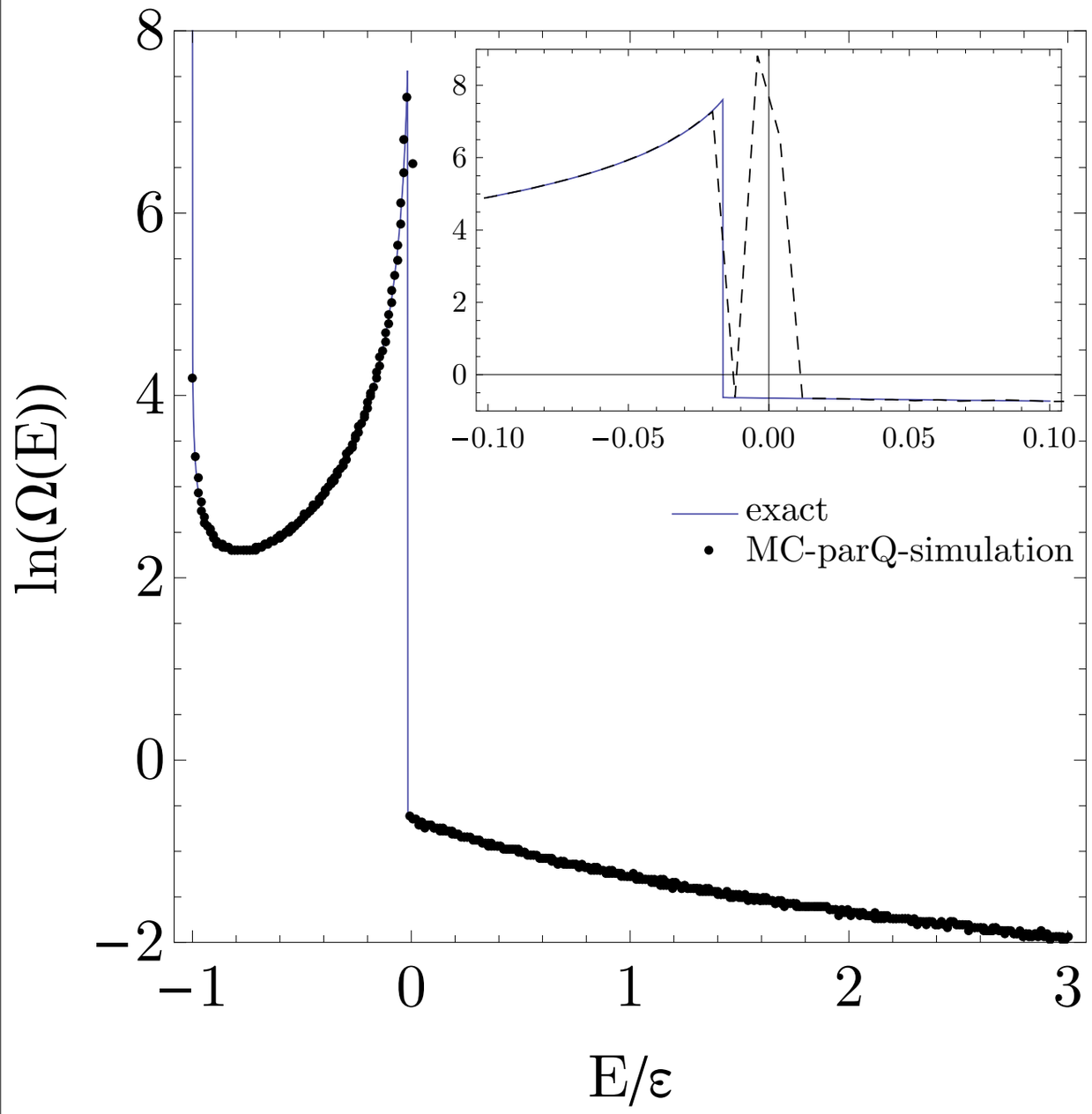
  $$\Omega(E_j) = \sum_i Q_{ji} \Omega(E_i)$$

  where Q is the infinite temperature transition matrix

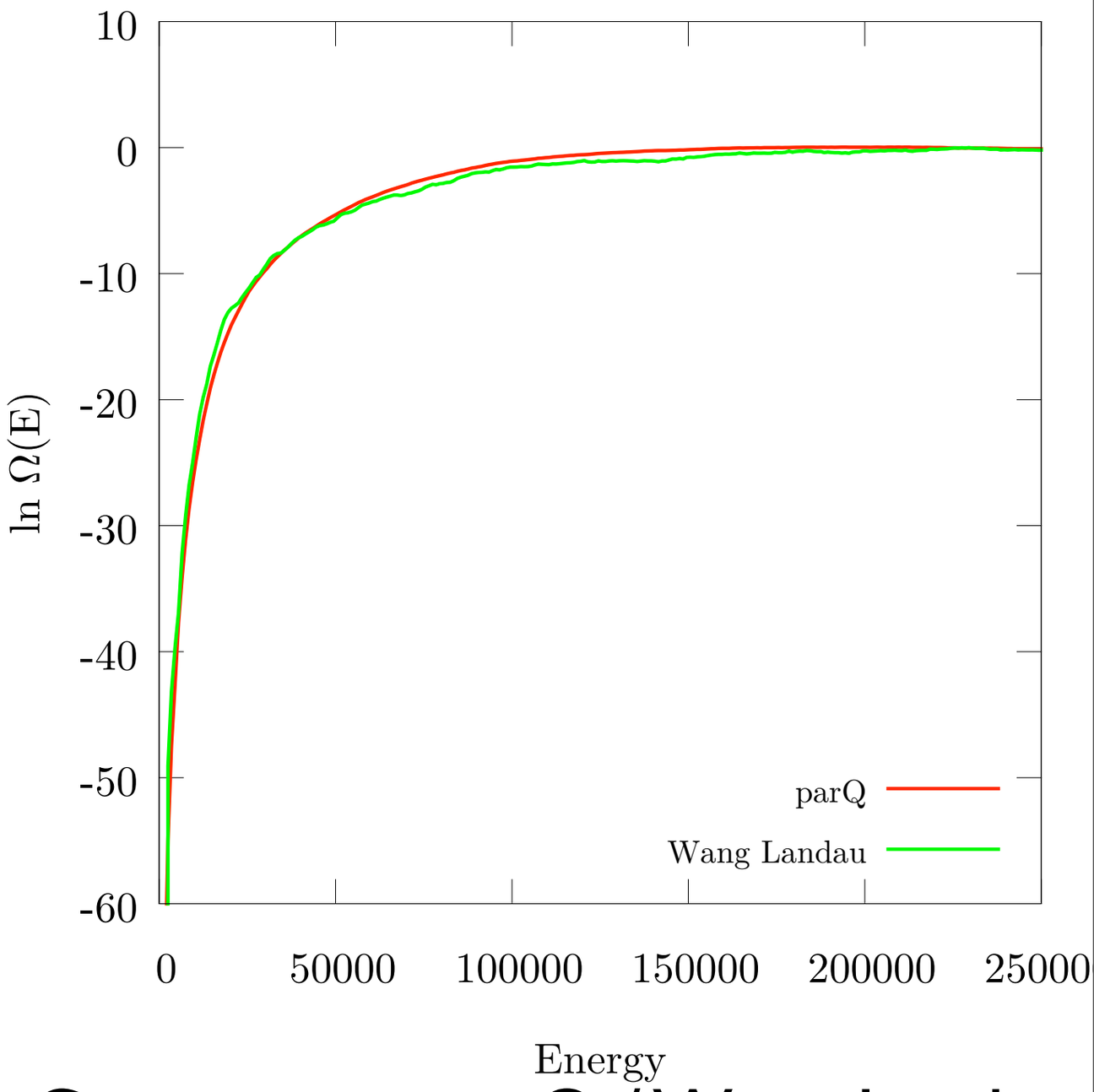
- algorithm:

1. execute Monte Carlo step
2. count *proposed* transitions from E_{old} to E_{proposed} in a matrix $\tilde{Q}_{ji} = \tilde{Q}_{ji} + 1$
   - accept according to underlying Monte Carlo scheme
3. go to 1. until abort condition
4. normalize the matrix $Q_{ji} = \frac{\tilde{Q}_{ji}}{\sum_k \tilde{Q}_{ki}}$
5. calculate eigenvector belonging to eigenvalue 1

Density of states of a simple systems



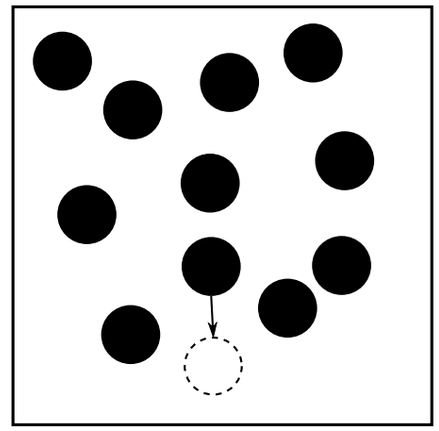
Comparison exact / parQ data of two particle LJ system



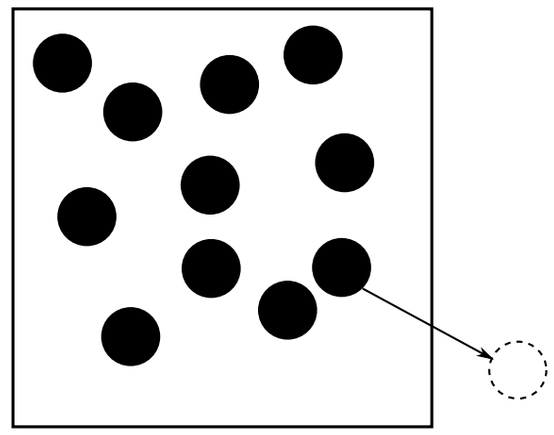
Comparison parQ / Wang-Landau data from simulation of a single hexadecan molecule

par$Q$ in the Grand Canonical Ensemble

- two types of transitions:
  - changes in energy
    (e. g. molecule move or rotation)

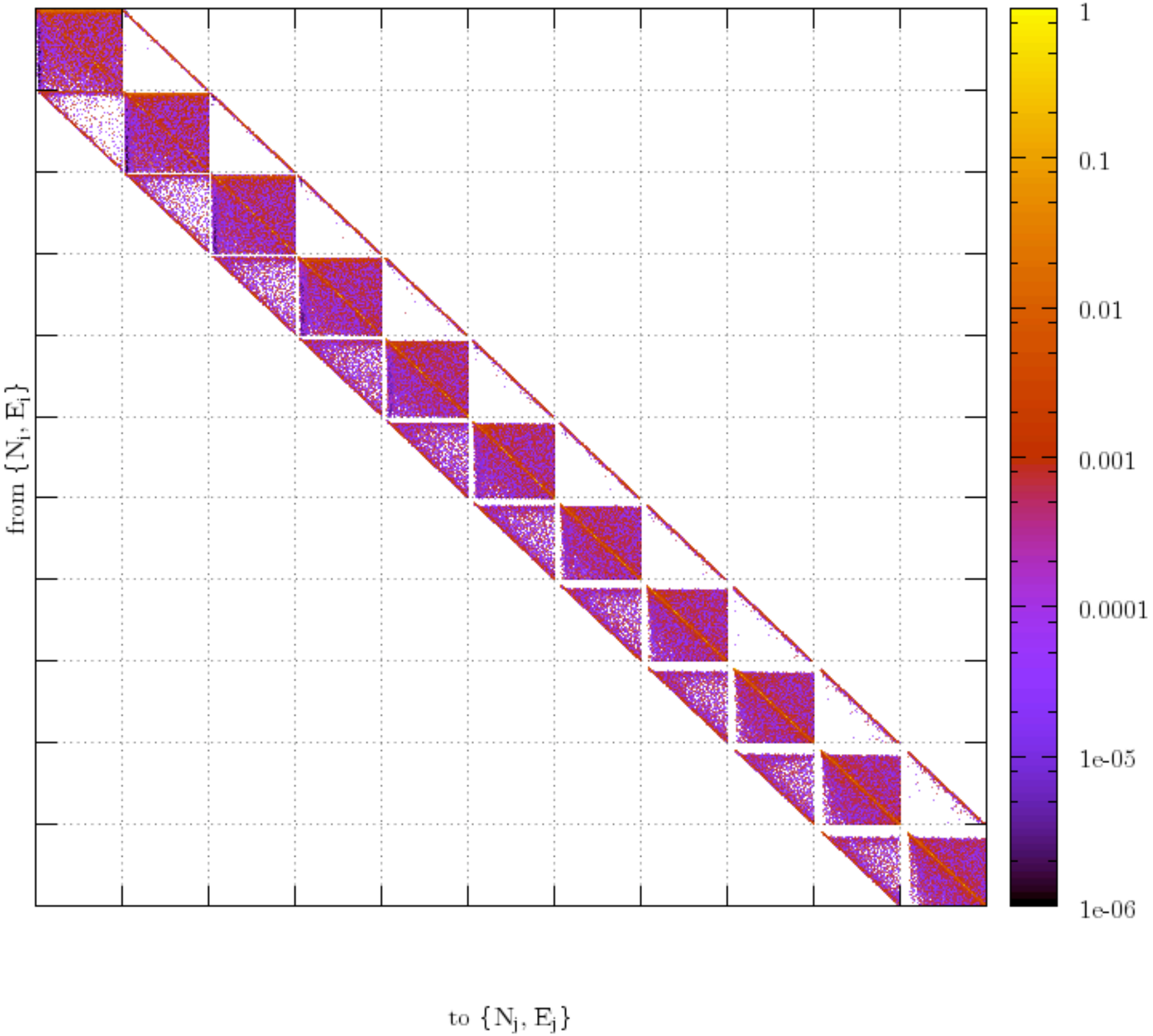


  - changes in particle number
    (e. g. particle insertion or removal,
    changes energy as well)



- structure: three band block matrix

Q matrix of hexadecan



Wang-Landau algorithm

- generalized ensemble Monte Carlo algorithm
- estimates the density of states without having an initial guess
- DoS is constantly modified during simulation while being used as control measure
- detailed balance is not satisfied, especially at beginning of simulation

F. Wang and D. P. Landau. Physical Review E, 64(5):056101, 2001.
F. Wang and D. P. Landau. Physical Review Letters, 86(10):2050-2053, 2001.

- algorithm:

1. initialize $H(E) = 0, \Omega(E) = 1 \; \forall E, f = \mathrm{e}^1$
2. execute Monte Carlo step
3. accept according to $p_{\mathrm{acc}} = \min\left[1, \frac{\Omega(E_{\mathrm{old}})}{\Omega(E_{\mathrm{new}})}\right]$
4. if accepted: $\Omega(E_{\mathrm{new}}) = \Omega(E_{\mathrm{new}}) \cdot f$
   else: $\Omega(E_{\mathrm{old}}) = \Omega(E_{\mathrm{old}}) \cdot f$
5. check flatness of histogram $H(E)$
   - if histogram is flat reset H and $f := \sqrt{f}$
6. proceed with 2 until f is small enough

- grand canonical enhancements:
  - Ω is a function of energy E and particle number N
  - two possible acceptance criterions for particle insertion / deletion moves:

$$p_{\mathrm{acc}}(E_{\mathrm{old}}, N \to E_{\mathrm{new}}, N+1) = \min\left[1, \frac{V}{(N+1)\Lambda^3}\frac{\Omega(E_{\mathrm{old}}, N)}{\Omega(E_{\mathrm{new}}, N+1)}\right]$$

$$p_{\mathrm{acc}}(E_{\mathrm{old}}, N \to E_{\mathrm{new}}, N-1) = \min\left[1, \frac{N\Lambda^3}{V}\frac{\Omega(E_{\mathrm{old}}, N)}{\Omega(E_{\mathrm{new}}, N-1)}\right]$$

$$p_{\mathrm{acc}}(E_{\mathrm{old}}, N \to E_{\mathrm{new}}, N\pm 1) = \min\left[1, \frac{\Omega(E_{\mathrm{old}}, N)}{\Omega(E_{\mathrm{new}}, N\pm 1)}\right]$$

M. S. Shell et al. Physical Review E, 66(5):056703, 2002.

Q.Yan et al. Physical Review Letters, 90(3):035701, 2003.

- different acceptance schemes correspond to difference between excess contribution and configurational density of states:

$$\Omega_{\mathrm{ex}}(N,V,E) \propto \frac{N!}{V^N}\Omega_{\mathrm{config}}(N,V,E)$$

M. S. Shell et al. Physical Review E, 66(5):056703, 2002.

Eigenvector calculation

- Power iteration:

$$b_{k+1} = \frac{Qb_k}{||Qb_k||}$$

- pros:
  - easy to implement
  - stable
  - easy to parallelize, even on GPU
- cons:
  - slow if largest eigenvalues λ_1 and λ_2 are of same magnitude

- other methods possible?:
  - GTH method (M. Fenwick, J. Chem. Phys 125, 2006)
    pro: solves directly in one step
    cons: does not work with sparse matrices, not always stable
  - partial LU decomposition + invers iteration
    con: gives very inaccurate results
  - Arnoldi, Lanczos or Krylov-Schur methods: tried methods available in SLEPc package

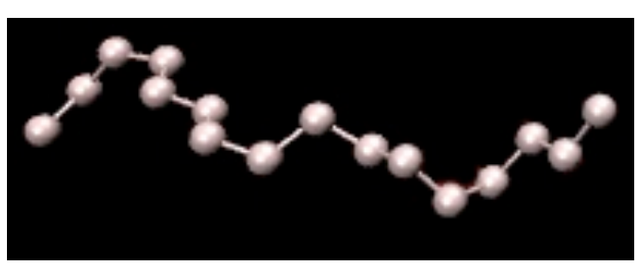
Models

- Lennard-Jones system:

$$V(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\}$$

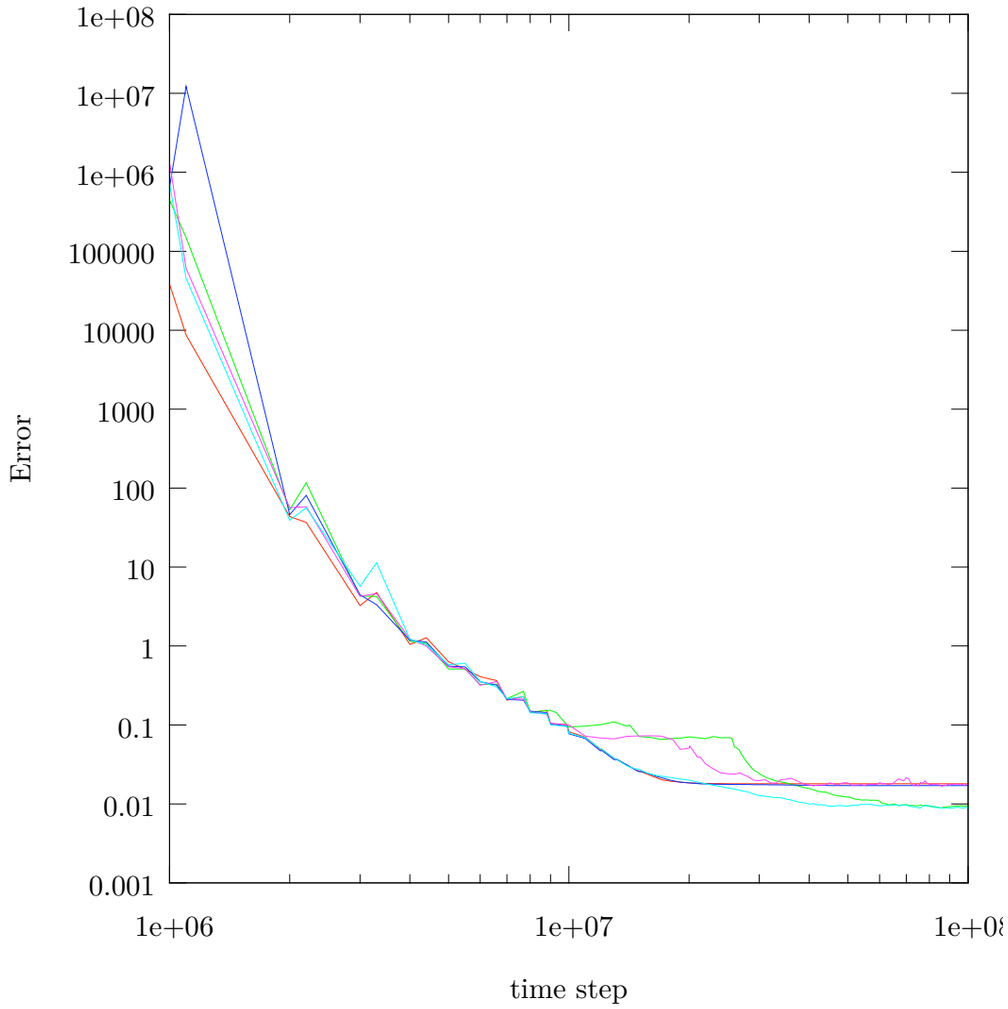
with cut-off at 2.5σ

- Hexadecan $\mathrm{C_{16}H_{34}}$ system of 16 beads:
  - TraPPE-UA (united atom) forcefield (hydrogens are lumped into neighbouring carbon atoms)

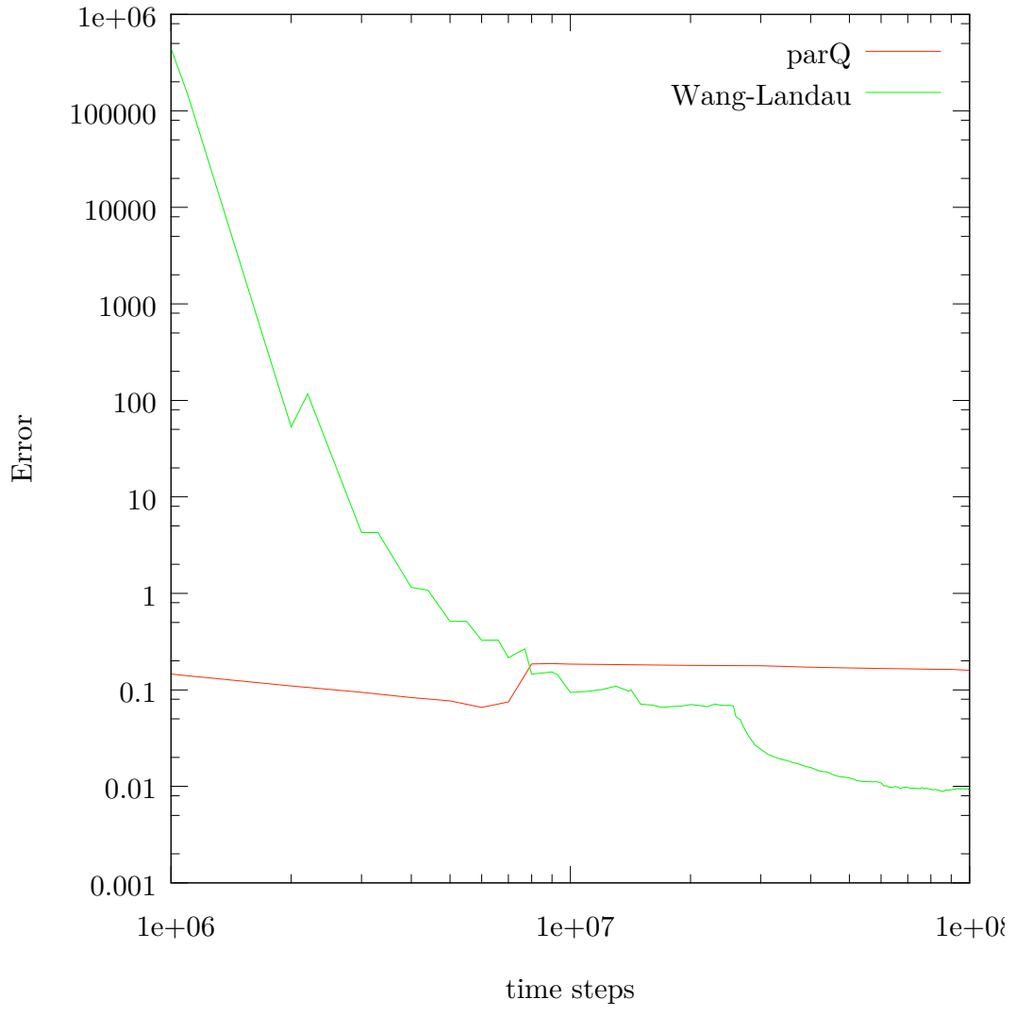


Results

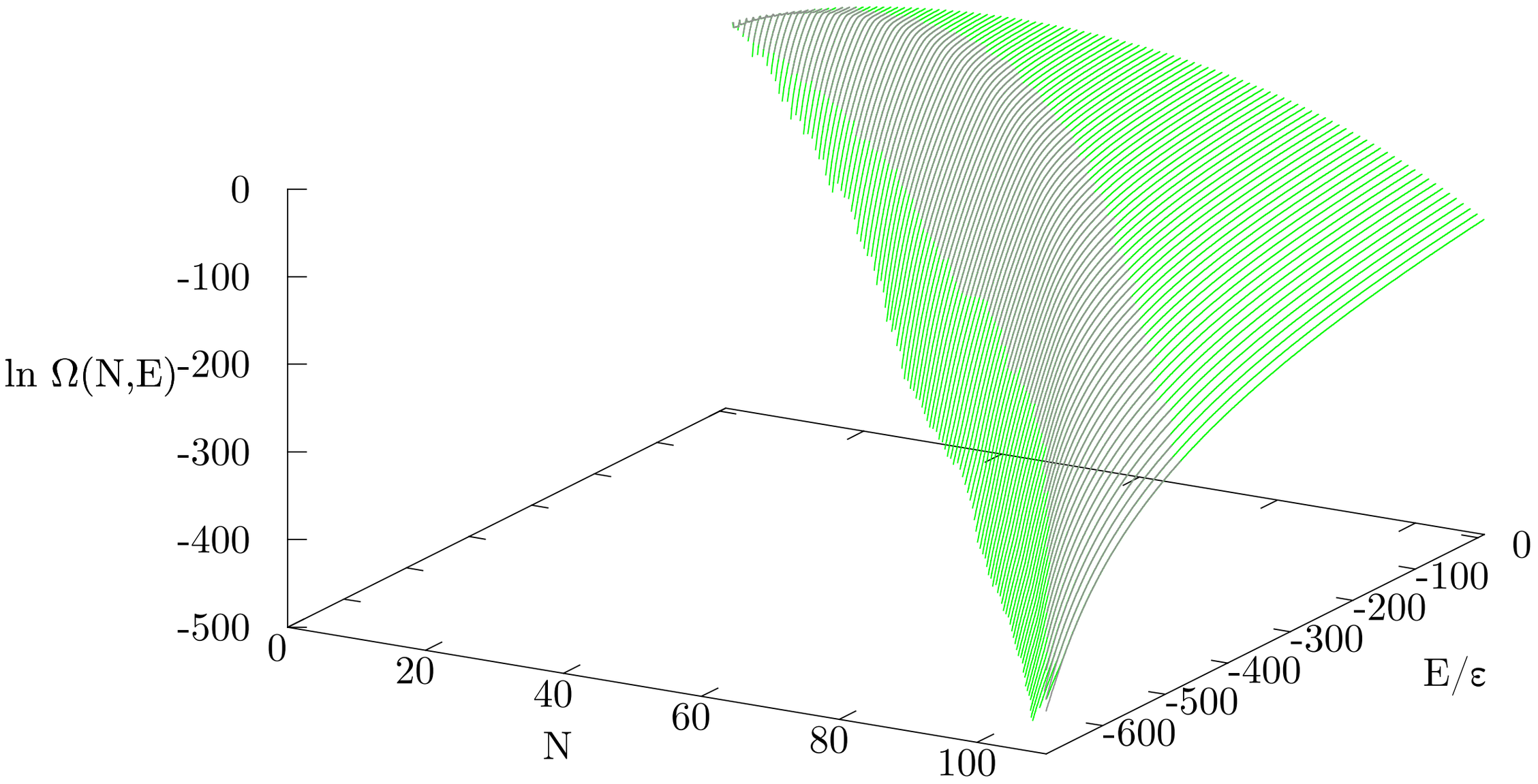
- Wang-Landau simulations typically exhibit saturation of error



- parQ can be achieve better results, especially in the beginning:

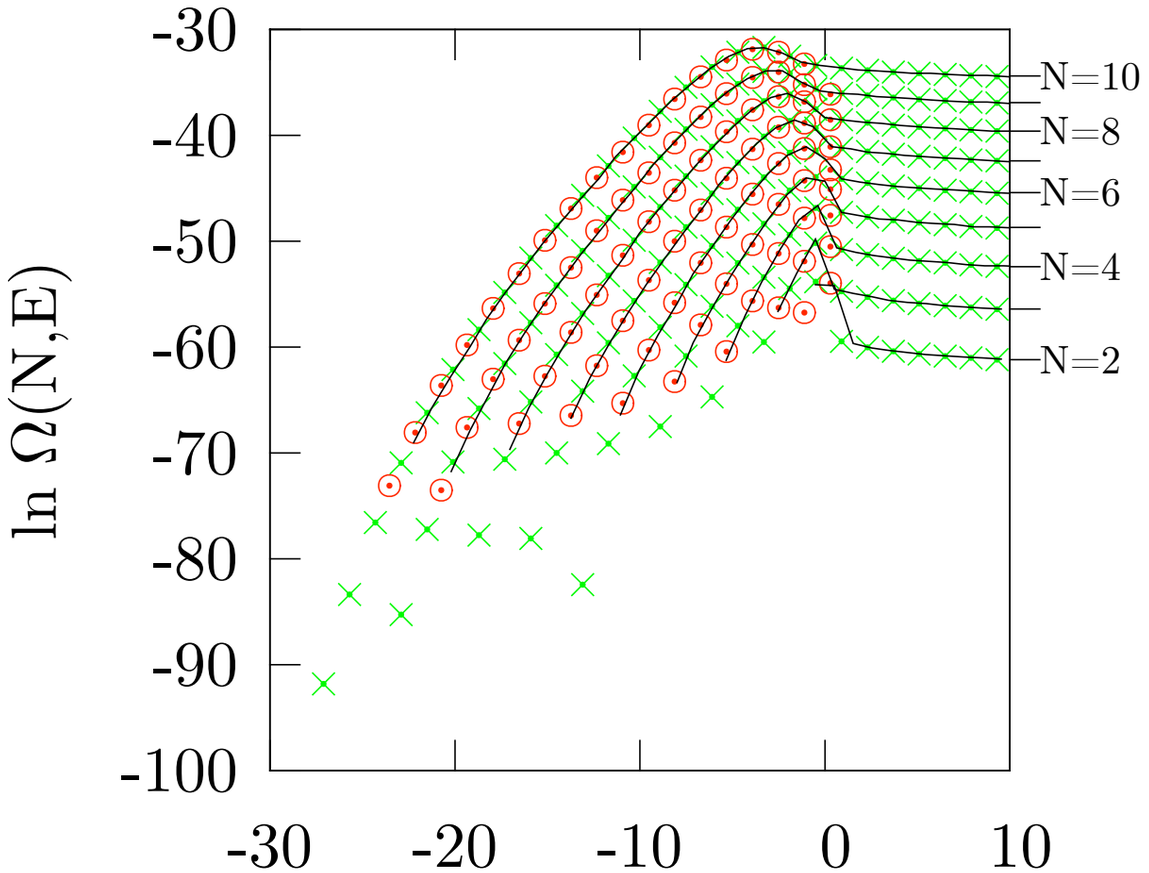


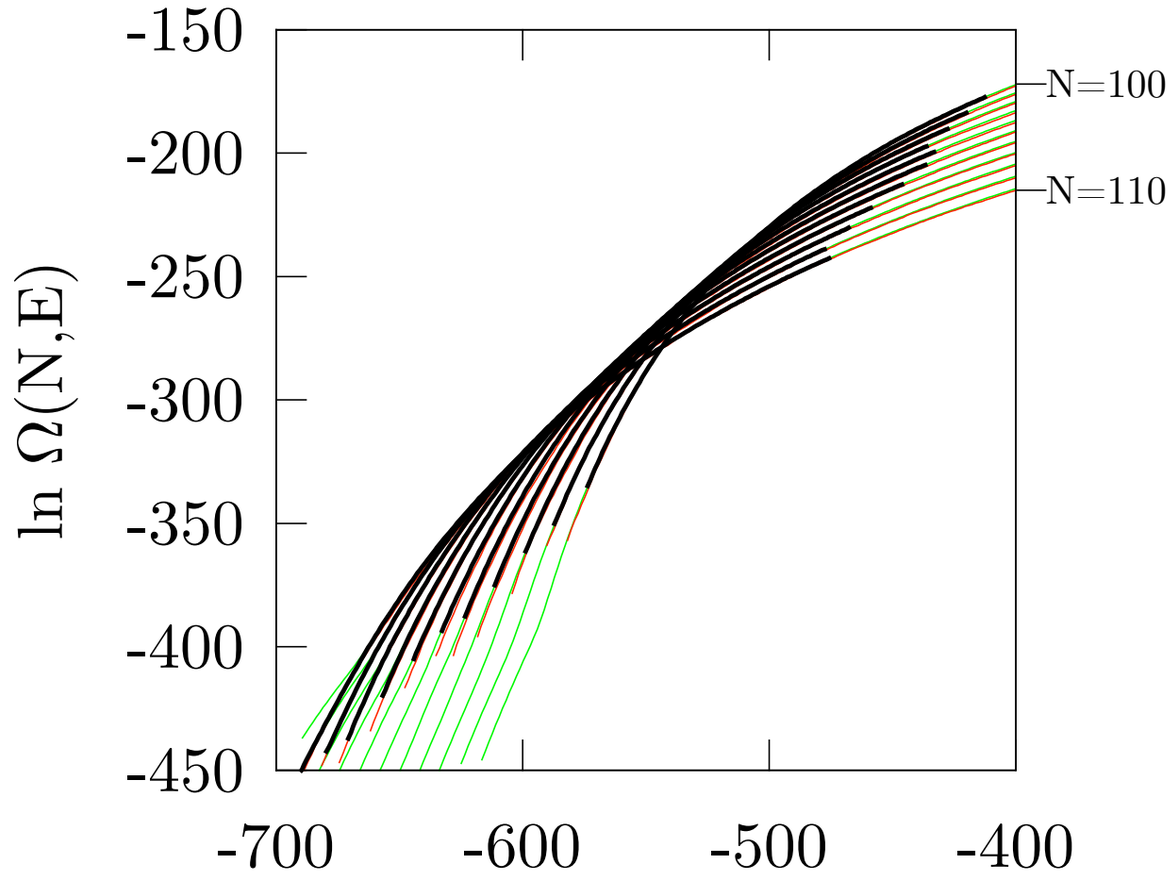
Wang-Landau Results for LJ System



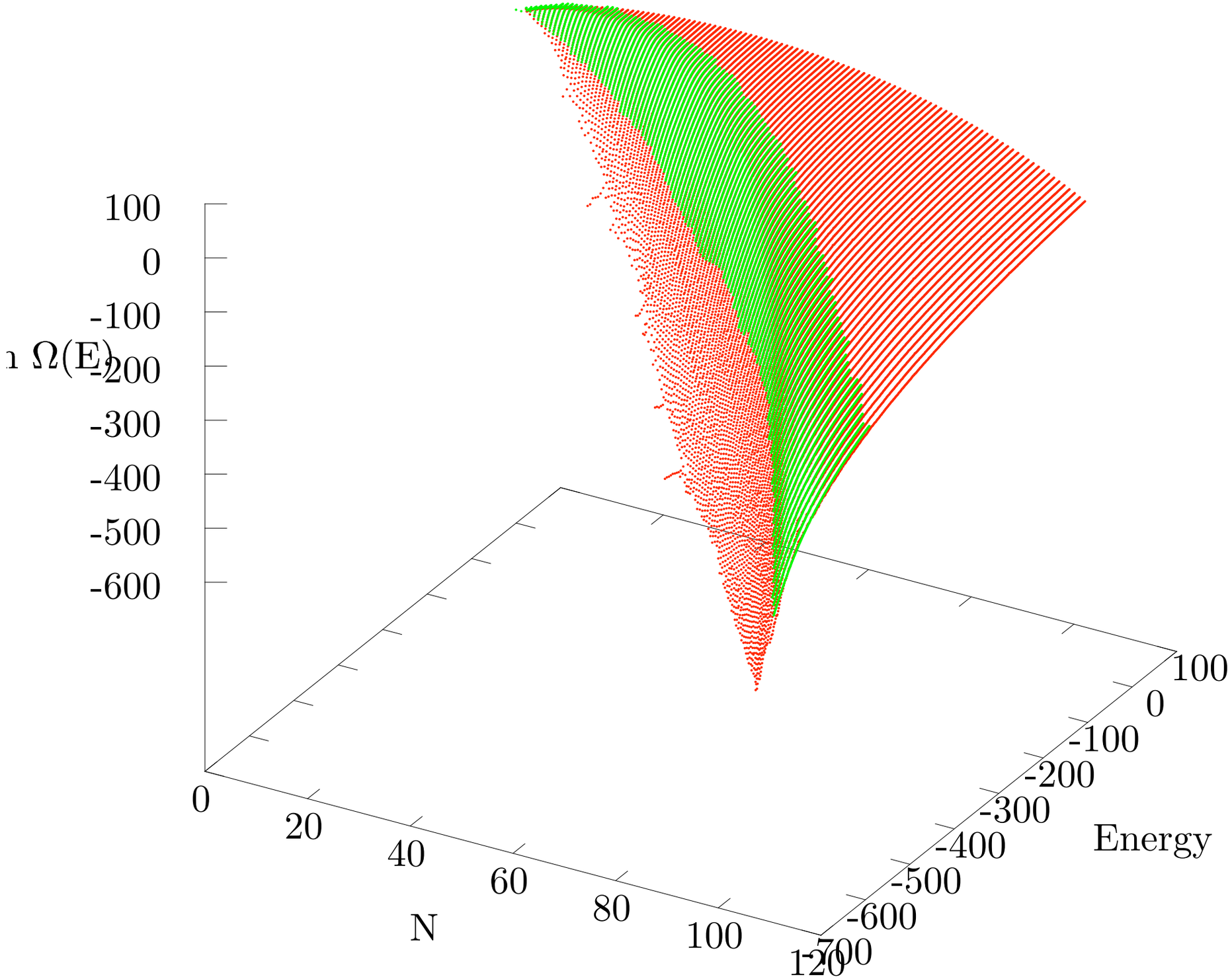
green - WL simulation

black - literature data (cf. Q.Yan et al. Physical Review Letters, 90(3):035701, 2003)

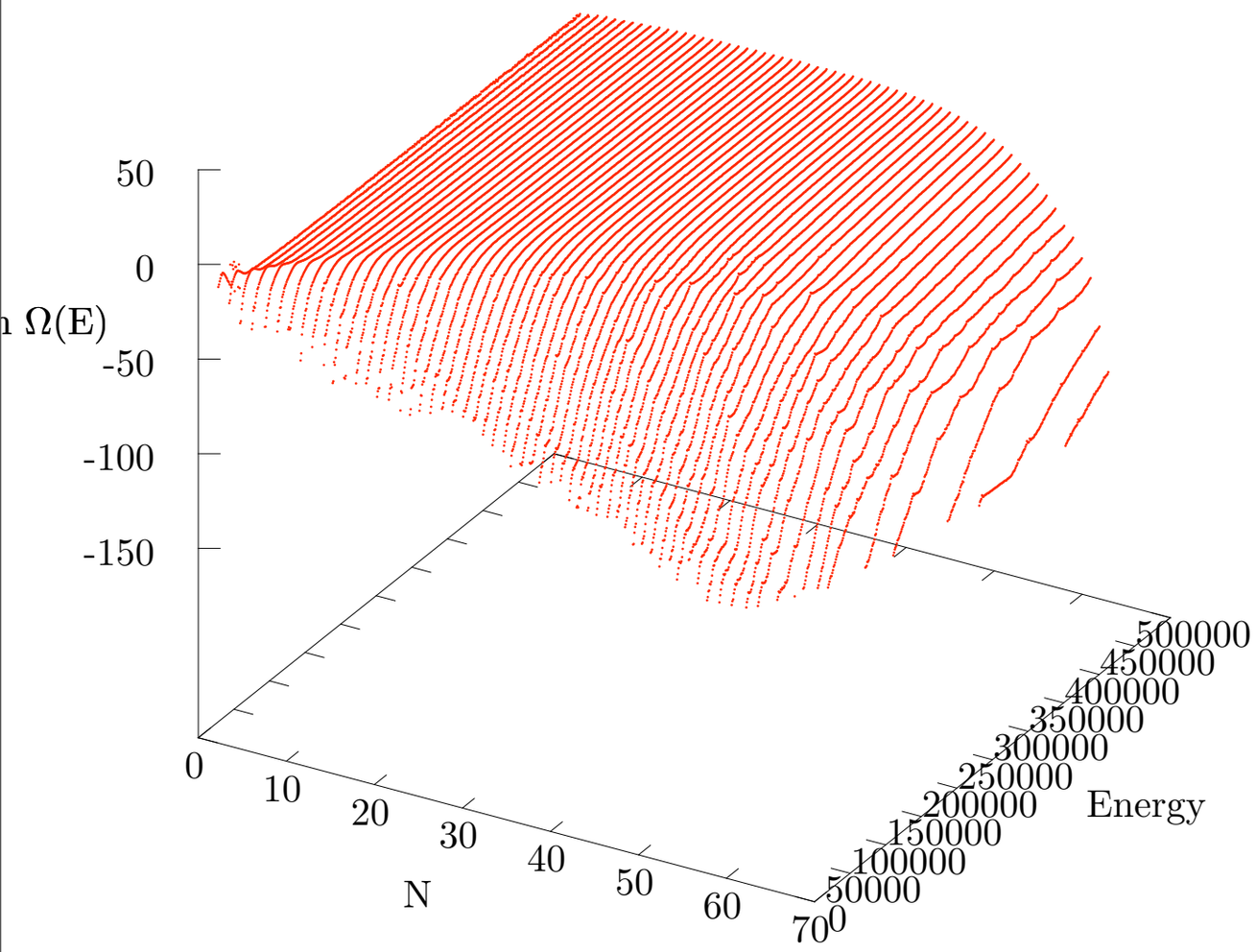


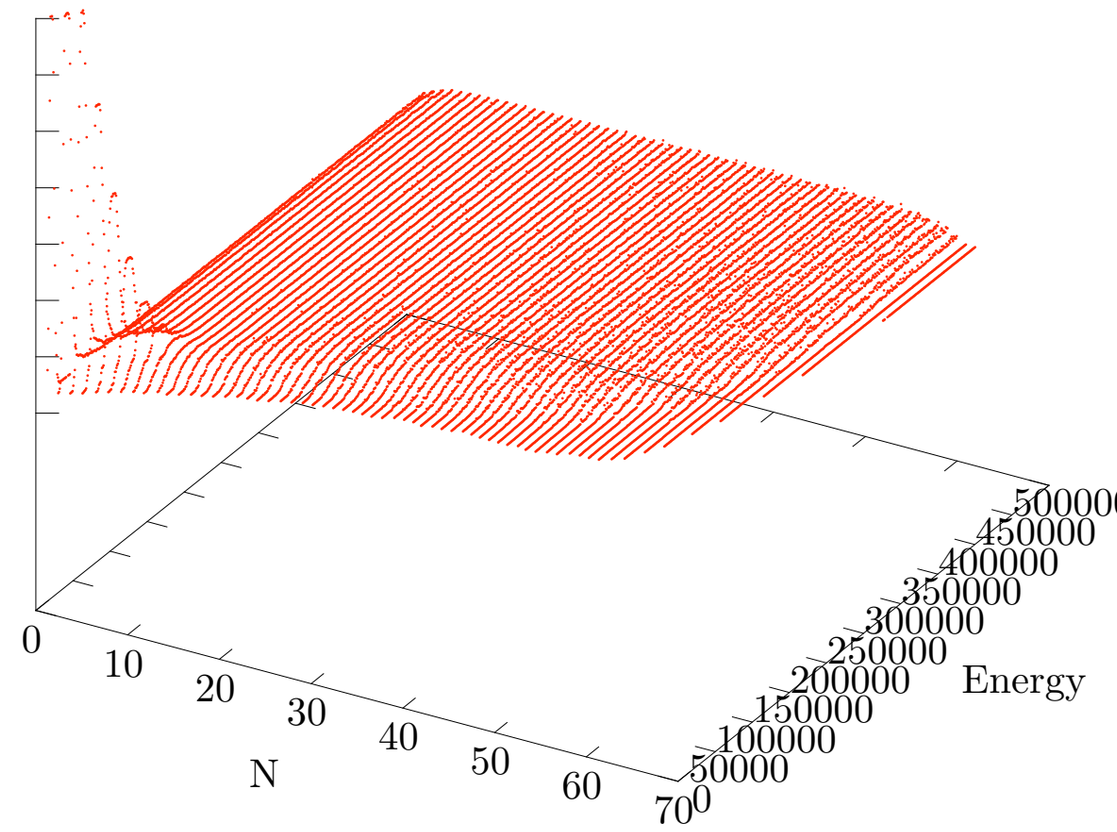


- red - WL simulation with per-particle-number constrained energy range
- green & black as before



- red - parQ
  green - reference





- Hexadecan
  left parQ, right Wang-Landau

Further development

- find optimal sampling scheme for par$Q$
- quality criterion for transition matrix
- faster eigenvector calculation
- direct exchange of data between WL algorithm and parQ data during simulation

Conclusion

- parQ can be used to calculate the density of states
- delivers results equal to or even better than established Wang-Landau method
- easy to parallelize
- easy to adopt to other sampling schemes