Comparison of microcanonical MD and MC simulations for liquid-gas like phase transitions

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November 27, 2014

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Introduction:

Molecular dynamics (MD):

- Based on Newtons equations of motion
- We do constant energy simulations with the Velocity Verlet integrator

Monte Carlo (MC):

- Based on ensemble formulation
- Applied methods: MUCA, Metropolis-Hastings

Motivation:

- Recently mesoscopic system are studied with a moderate number of degrees of freedom
- How comparable are MD and MC in the microcanonical ensemble?

Introduction:

Microcanonical (NVE) ensemble:

- Motivated by Newtons equations of motion $\rightarrow$ MD should be the native simulation technique
- Temperature is only an observable in the NVE ensemble
- Monte Carlo simulations can also produce NVE ensemble data (MUCA [1], NVE Metropolis [2])

Our aim:

- Reproduce quantitative microcanonical MC result by developing MD analysis techniques
- Implement a multi histogram reweighting method for MD

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[1] B.A. Berg and T. Neuhaus, Phys. Lett. B 267 (1991) 249; Phys. Rev. Lett. 68 (1992) 9; W. Janke, Int. J. Mod. Phys. C 03 (1992) 1137; Physica A 254 (1998) 164

[2] J.R. Ray, Phys. Rev. A 44 (1991) 4061

Ensembles:

Microcanonical NVE ensemble:

$$\Gamma = \int_{\mathbf{X}} \int_{\mathbf{P}} \mathbf{dx^N dp^N} \delta \left(E - (E_{kin}(p) + E_p(x)) \right)$$

[1] R. Lustig, J. Chem. Phys 100 (1994) 3048

[2] F. Calvo,J.P. Neirotti,D.L. Freemann and J.D. Doll, J. Chem. Phys 112 (2000) 10350

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NVEP ensemble [1]:

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Molecular dynamics or NVEPJ ensemble [2]:

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[2] F. Calvo,J.P. Neirotti,D.L. Freemann and J.D. Doll, J. Chem. Phys 112 (2000) 10350

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Molecular dynamics or NVEPJ ensemble [2]:

$$\Gamma = \int_{\mathbf{X}} \int_{\mathbf{P}} \mathbf{dx^N dp^N} \delta \left(E - \left(E_{kin} + E_p \right) \right) \cdot \delta \left(\mathbf{P} - \sum \mathbf{p_i} \right) \delta \left(\mathbf{J} - \sum \mathbf{j_i} \right)$$

For a high number of degrees of freedom the differences should vanish.

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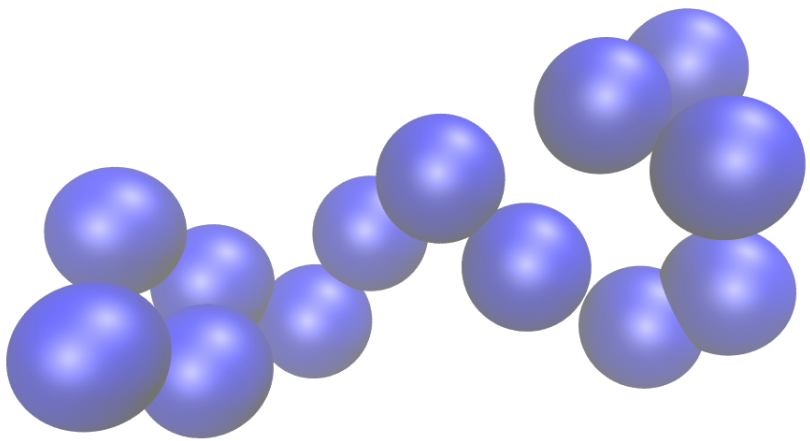
[1] R. Lustig, J. Chem. Phys 100 (1994) 3048

[2] F. Calvo,J.P. Neirotti,D.L. Freemann and J.D. Doll, J. Chem. Phys 112 (2000) 10350

Single polymer with 13 monomers:



NVE vs. NVEPJ problem:

Number of degrees of freedom f=33

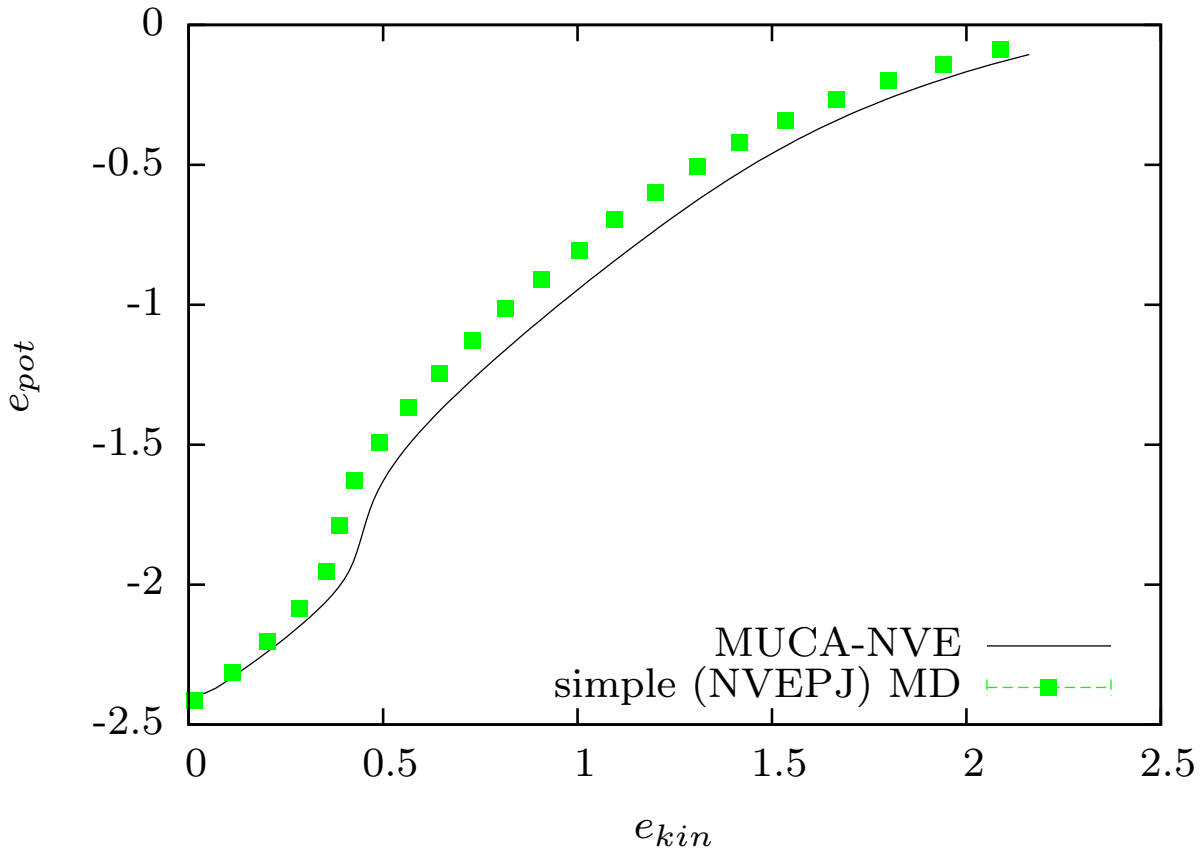


Figure : Kinetic energy-potential energy plot for a 13mer

Reweighting:

Reweighting between NVEPJ and NVE ensemble:

$$\langle O \rangle_{NVE} = \frac{\left\langle O \frac{W_{NVE}(E_p)}{W_{NVEPJ}(E_p,P,J,I)} \right\rangle_{NVEPJ}}{\left\langle \frac{W_{NVE}(E_p)}{W_{NVEPJ}(E_p,P,J,I)} \right\rangle_{NVEPJ}}$$

Reweighted data:

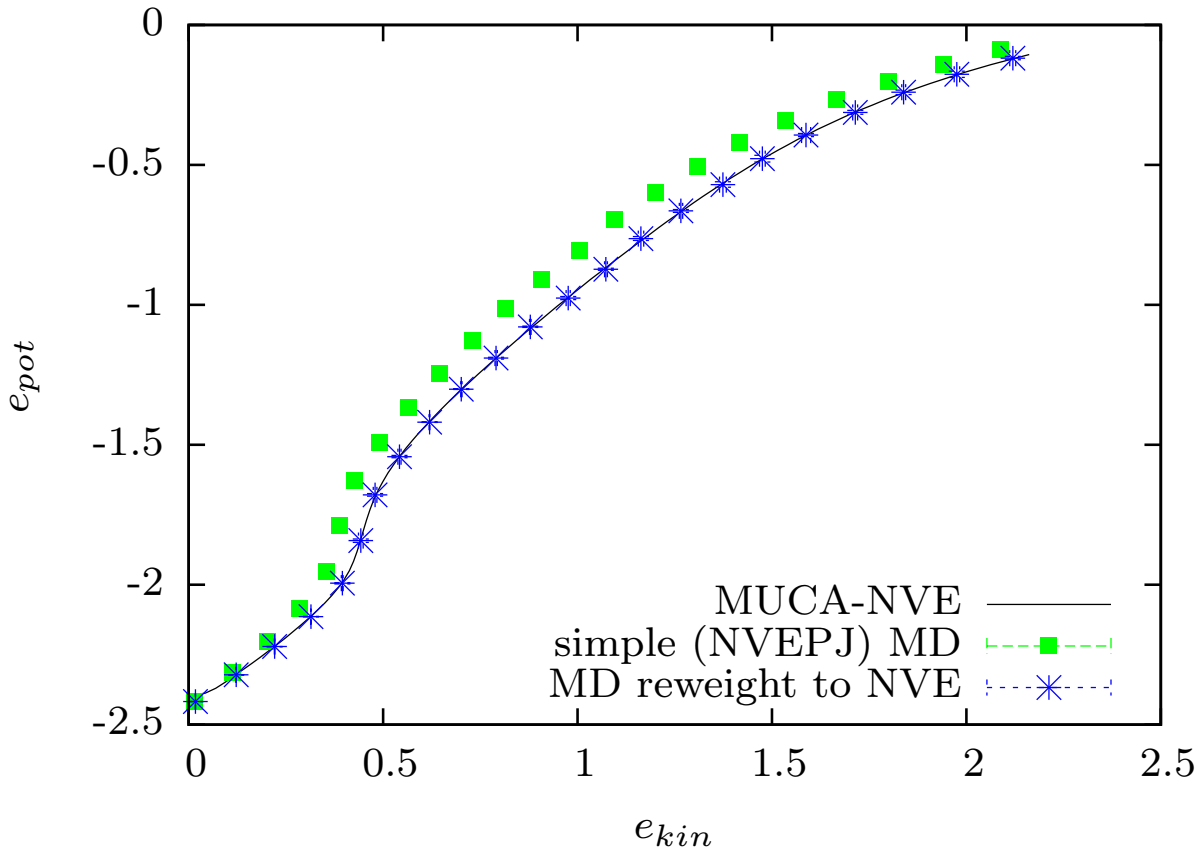
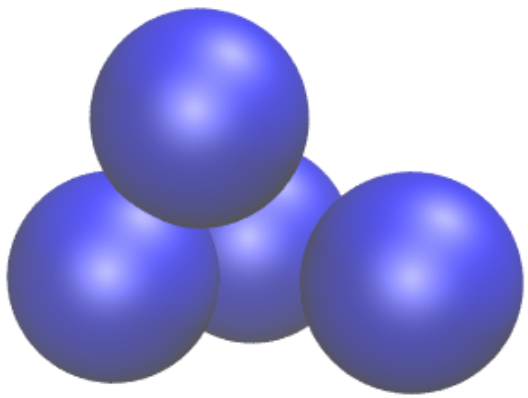


Figure : Kinetic energy-potential energy plot for a 13mer

Lennard Jones gas:

Lennard Jones gas with 4 particles



NVEPJ reweight attempt:

Number of degrees of freedom f=9 resp. f=6

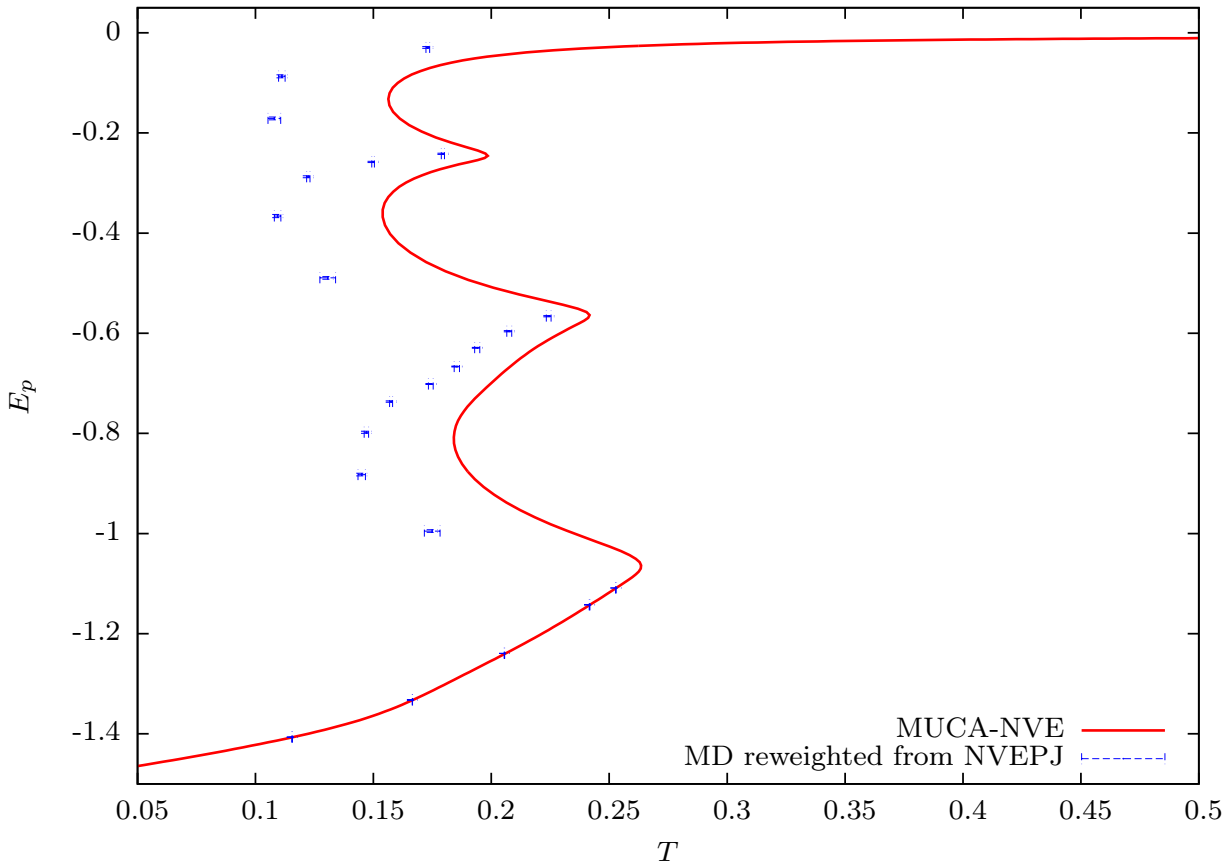


Figure : Temperature-potential energy plot for 4 LJ particles

Reweighting with ensemble determination:

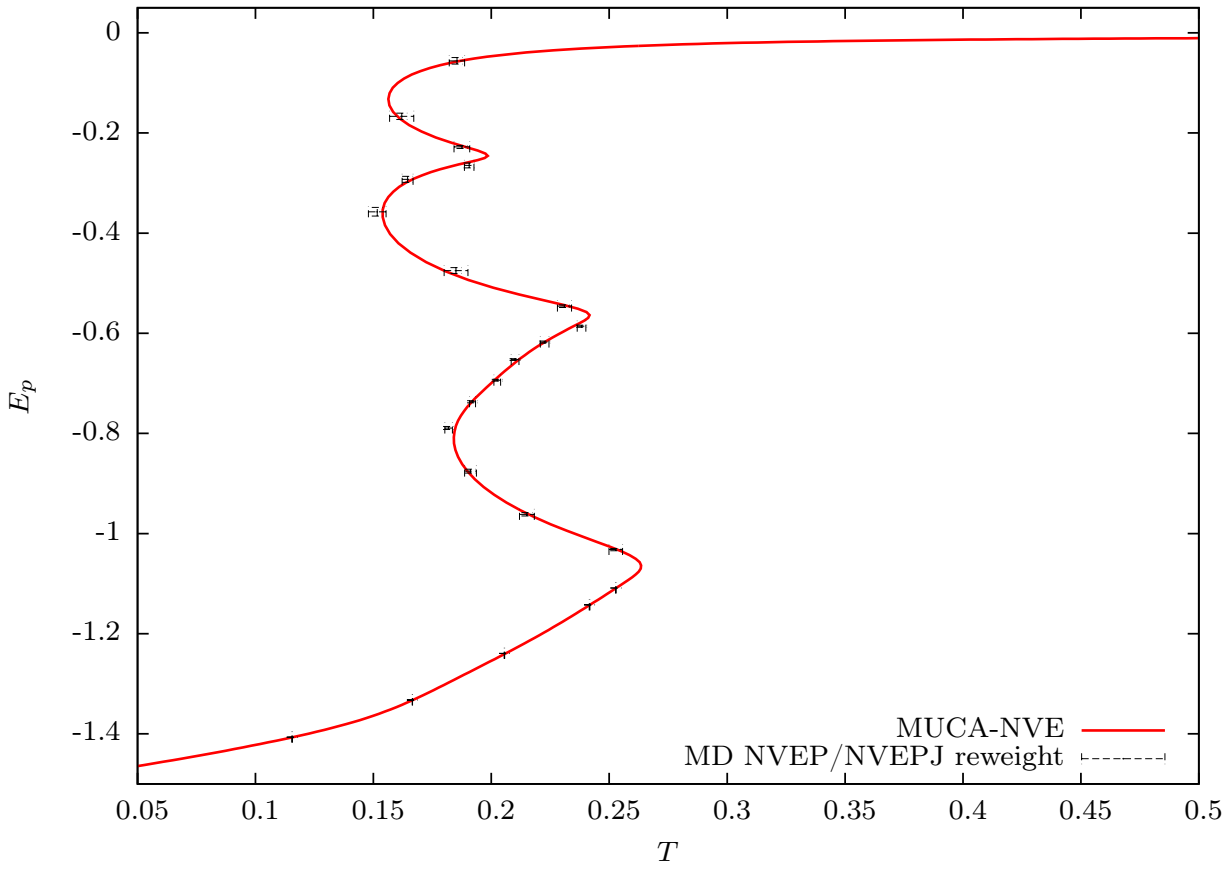
NVEPJ to NVE reweighting for low total energies (condensate):

$$\langle O \rangle_{NVE} = \frac{\left\langle O \frac{W_{NVE}(E_p)}{W_{NVEPJ}(E_p,P,J,I)} \right\rangle_{NVEPJ}}{\left\langle \frac{W_{NVE}(E_p)}{W_{NVEPJ}(E_p,P,J,I)} \right\rangle_{NVEPJ}}$$

NVEP to NVE reweighting for higher total energies (gas):

$$\langle O \rangle_{NVE} = \frac{\left\langle O \frac{W_{NVE}(E_p)}{W_{NVEP}(E_p,P,J,I)} \right\rangle_{NVEP}}{\left\langle \frac{W_{NVE}(E_p)}{W_{NVEP}(E_p,P,J,I)} \right\rangle_{NVEP}}$$

Result:



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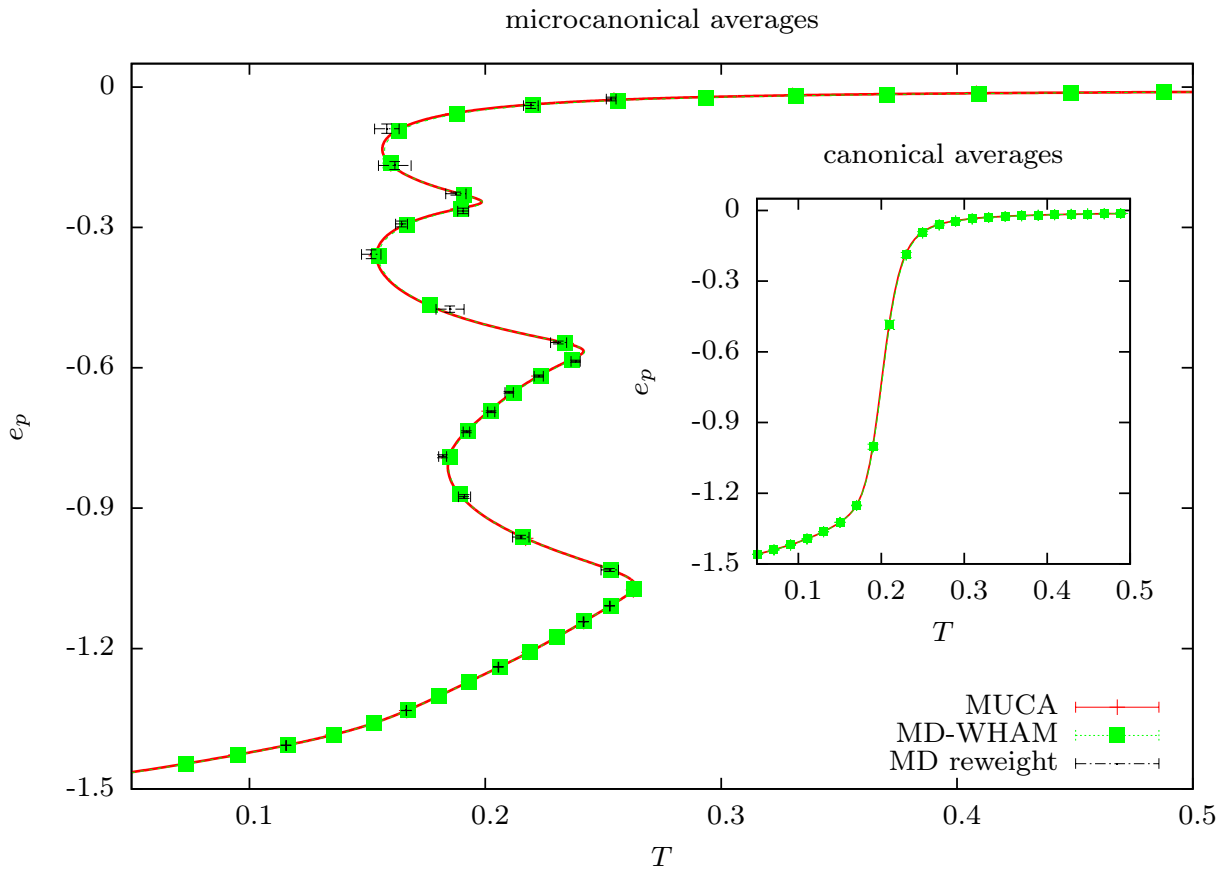
MD WHAM:

Adapted WHAM procedure:

	NVE	**NVT [1]**
$W(E_p) =$	$(E_m - E_p)^{\frac{3N-2}{2}}\,\Theta(E_m - E_p)$	$e^{-\frac{E_p}{T_m}}$
$\Omega(E_p, Z_1, ..., Z_M) =$	$C\,\frac{\sum_m^M H_m(E_p)}{\sum_m^M N_m \frac{1}{Z_m} W_{NVE_m}(E_p)}$	$C\,\frac{\sum_m^M H_m(E_p)}{\sum_m^M N_m \frac{1}{Z_m} W_{NVT_m}(E_p)}$
$Z_m =$	$\sum_{E_p=E_{min}}^{E^m} \Omega(E_p, Z_1, ..., Z_M) W_{NVE_m}(E_p)$	$\sum_{E_p=E_{min}} \Omega(E_p, Z_0, ..., Z_M) e^{-\frac{E_p}{T_m}}$

[1] S. Kumar, J.M. Rosenberg, D. Bouzida, R.H. Swendsen and P.A. Kollman, J. Comput. Chem. 13 (1992) 1011

MD-WHAM result:



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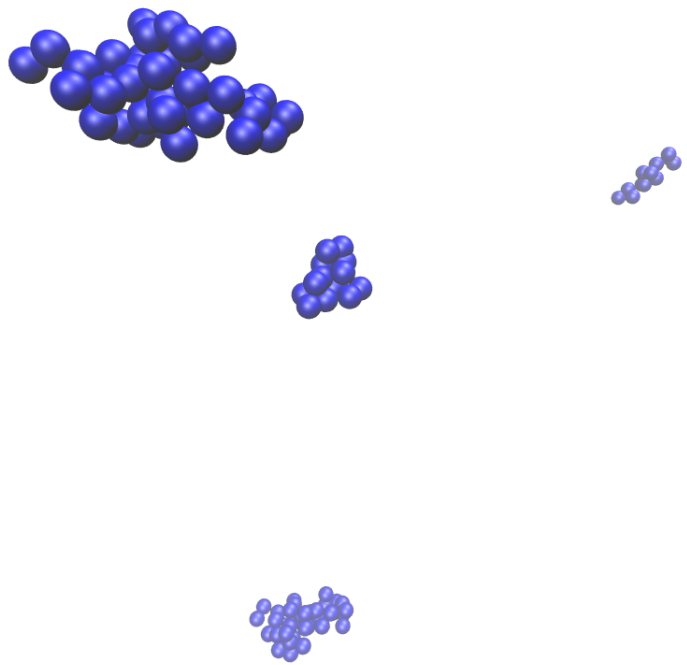
8 x 13 polymer system:



MD-WHAM result:

Number of degrees of freedom f=309 resp. f=303

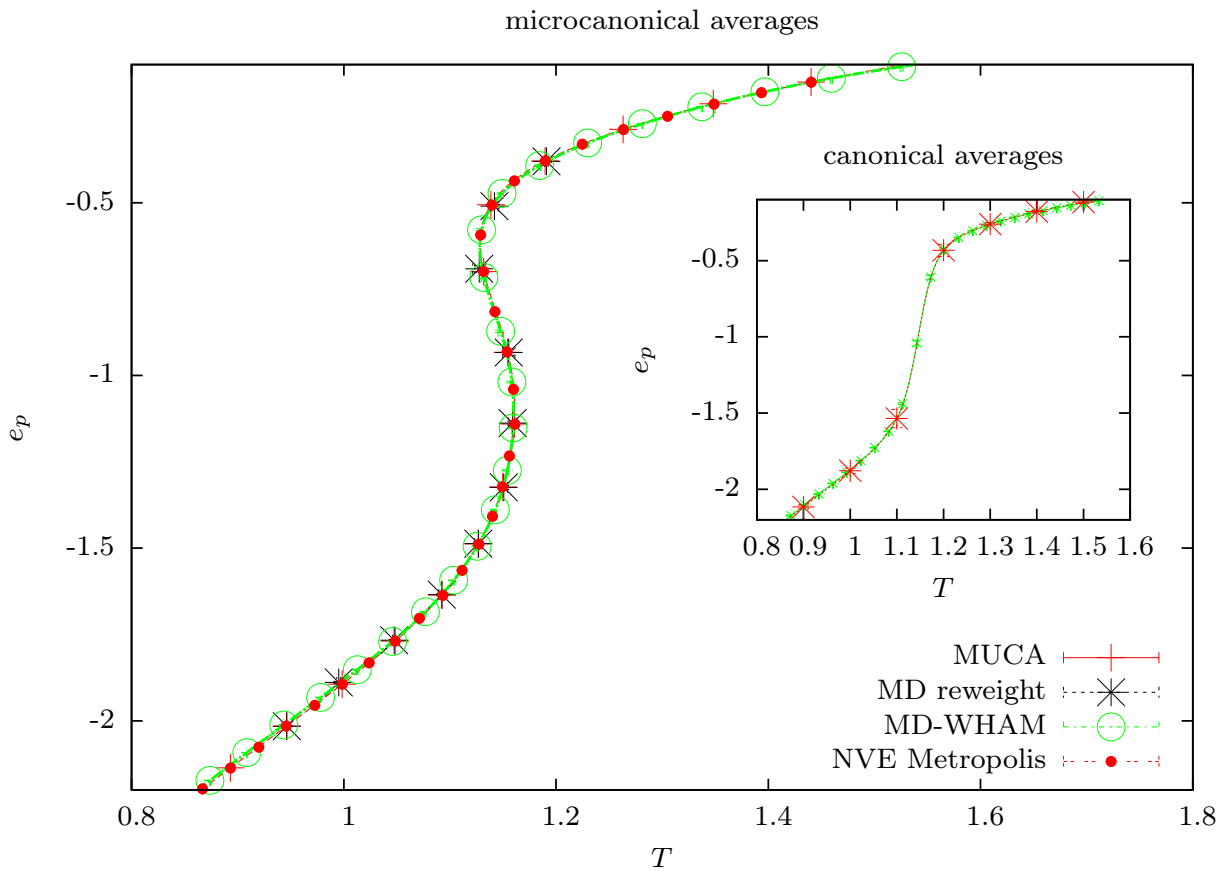


Figure : Temperature-potential energy plot for 8x13mer

Non ergodicity for single MD run:

Differences for separate initial conditions:

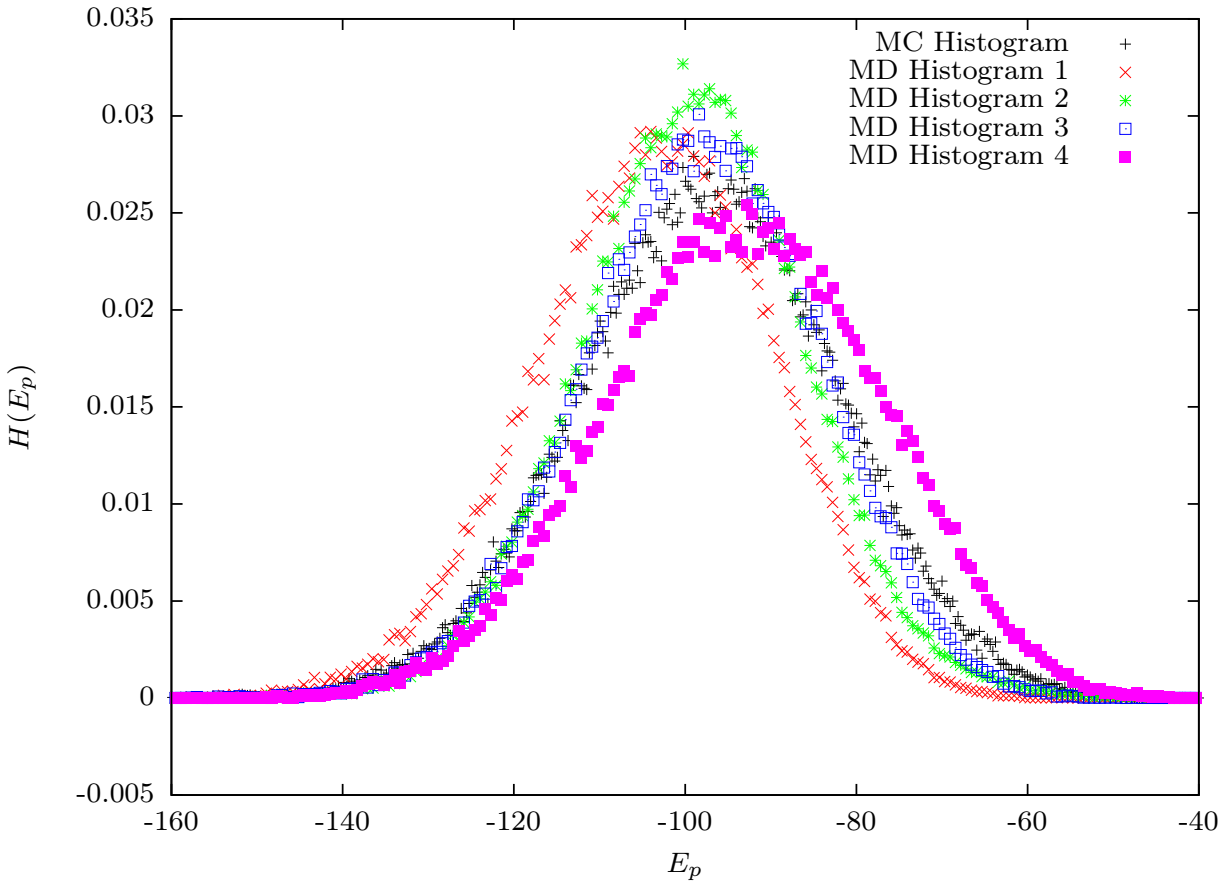
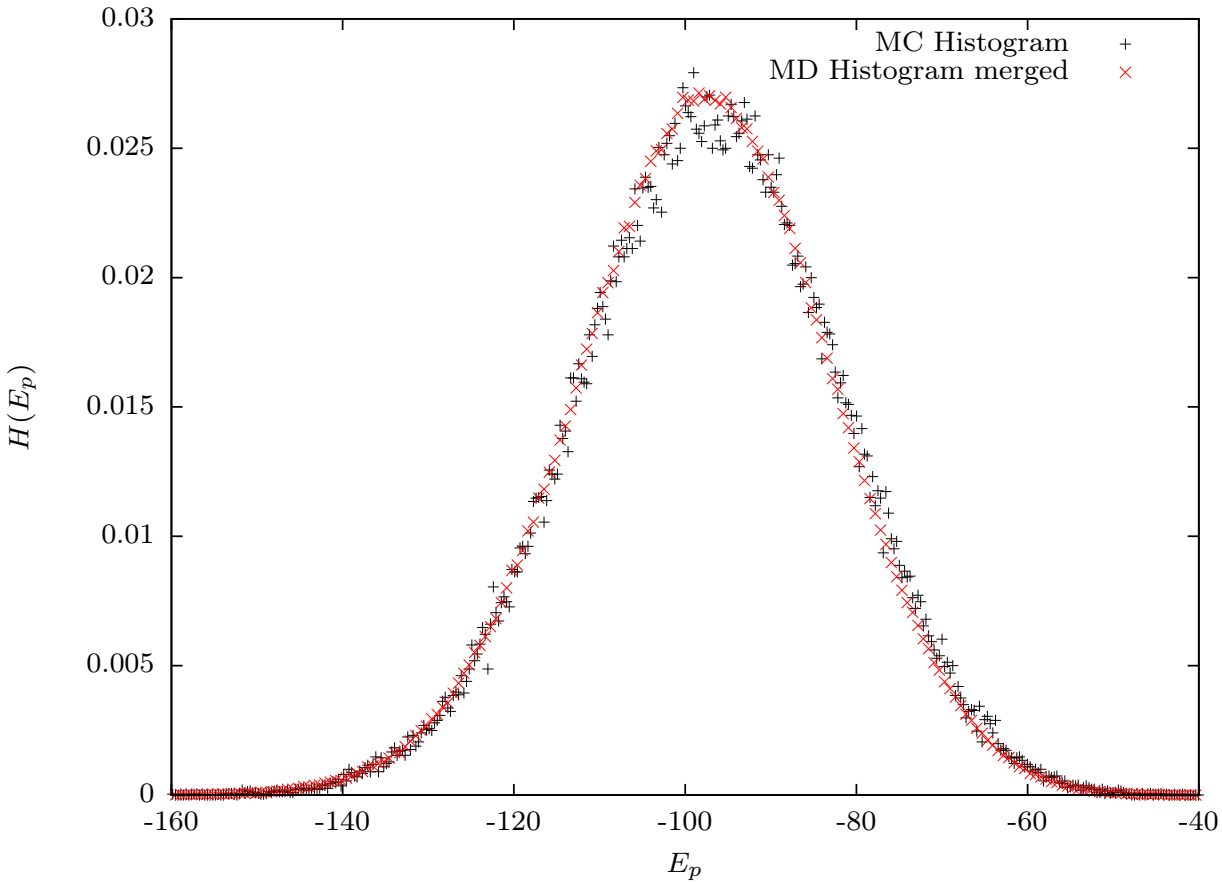


Figure : Histograms at one total energy

Non ergodicity for single MD run:

Merge from ~20 initial conditions:



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Comparison to common MD analysis:

Our method:

- time series reweighting

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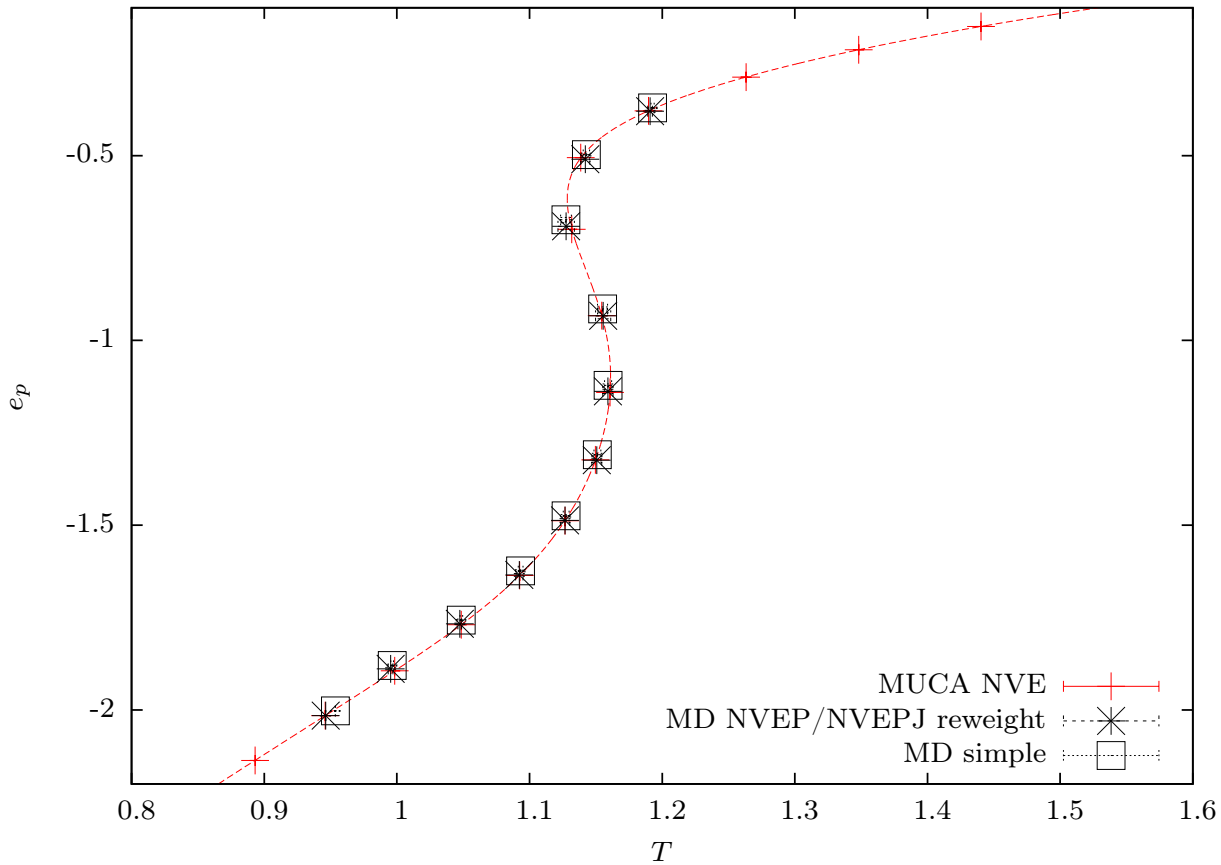
Common method:

- temperature definition via equipartition theorem:

$$\langle T \rangle = \frac{2}{f} \frac{\langle E_{kin} \rangle}{k_B}$$

- the number of degrees of freedom in this formula takes care of the conservation laws

Comparison to common MD analysis:



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Summary:

What we have learned about MD:

- MD samples the NVEPJ or NVEP ensemble for the examples in this work
- MD tends to be non ergodic in a single MD run for more complicated systems
- We can estimate a density of states from MD simulations
- We can estimate NVT averages (losing dynamics) from many MD simulations at different total energies

End

Thank you for your attention!