The microcanonical barrier and the ensemble tailoring framework

Philipp Schierz, Johannes Zierenberg, Prof. Wolfhard Janke

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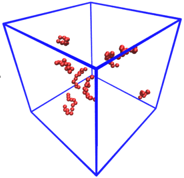

Condensation/Evaporation

Phase coexistence

Sampling problem:

- Phase coexistence
- Exponential critical slowing down

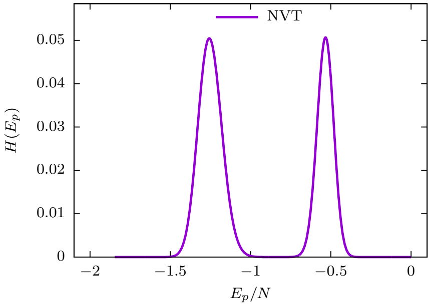

Figure : Potential-energy histogram at equal height for pseudo first-order phase coexistence and alternative sampling.

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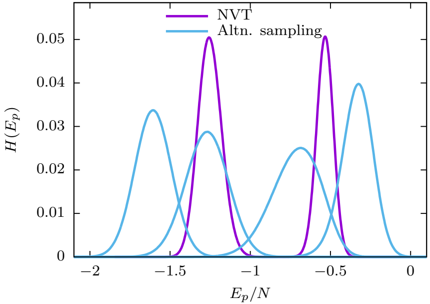

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Phase coexistence

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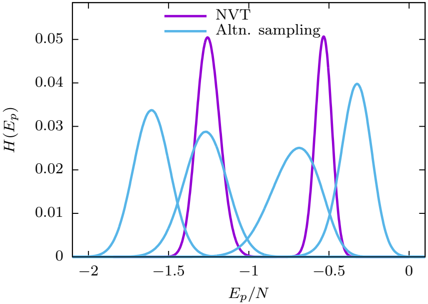
Recover NVT behavior with reweighting:

$$\langle O \rangle_{\mathrm{NVT}} = \frac{\left\langle O \frac{\exp(-\beta E_p)}{W(E_p)_{\mathrm{samp}}} \right\rangle_{\mathrm{samp}}}{\left\langle \frac{\exp(-\beta E_p)}{W(E_p)_{\mathrm{samp}}} \right\rangle_{\mathrm{samp}}}$$



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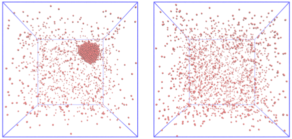
Barrier definition

Example: Droplet condensation of the $N = 2048$ particle Lennard-Jones system.



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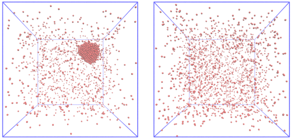

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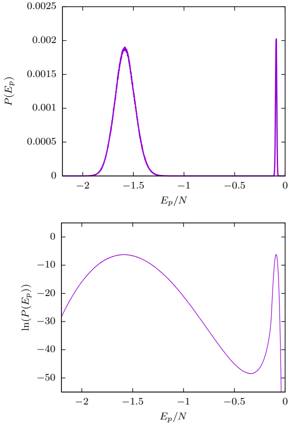

Figure : Canonical equal-height histogram in non-logarithmic and logarithmic display for the $N = 2048$ Lennard-Jones particle system.

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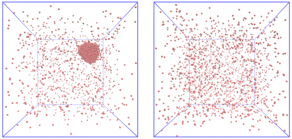

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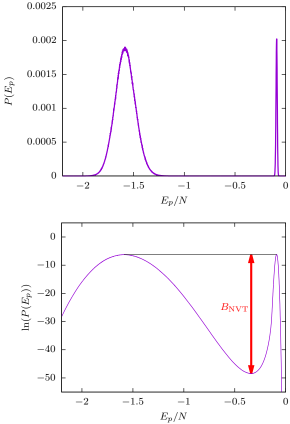
What is the barrier?

$$B = \ln\left[\frac{P^{\mathrm{eqh}}\left(E_p^{\max}\right)}{P^{\mathrm{eqh}}\left(E_p^{\min}\right)}\right]$$

- Indicates how unlikely it is to observe the transition between the coexisting phases



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Correspondences in the NVT and NVE ensemble

	Canonical ensemble	**Microcanoical ensemble**
Full phase space partition function	$\tilde{Z}(\beta) = \int_{\mathbf{X}} \int_{\mathbf{P}} dRdP \; e^{-\beta E},$	$\tilde{\Gamma}(E) = \int_{\mathbf{X}} \int_{\mathbf{P}} dRdP \; \delta\left(E - (E_k + E_p)\right)$

M. Mayor, Phy. Rev. Let. 98 (2007) 137207

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Configurational partition function	$Z(\beta) = \int_{\mathbf{X}} dR\ e^{-\beta E_p}$	$\Gamma(E) = \int_{\mathbf{X}} dR\ \ (E - E_p)^{\frac{3N-2}{2}}\ \Theta(E - E_p)$

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Configuration weight	$W(R, \beta) = e^{-\beta E_p}$	$W(R, E) = \left(E - E_p\right)^{\frac{3N-2}{2}} \Theta(E - E_p)$

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The expressions for the configuration weights allow for an easy adaptation of canonical simulation methods and simplify analytical considerations.

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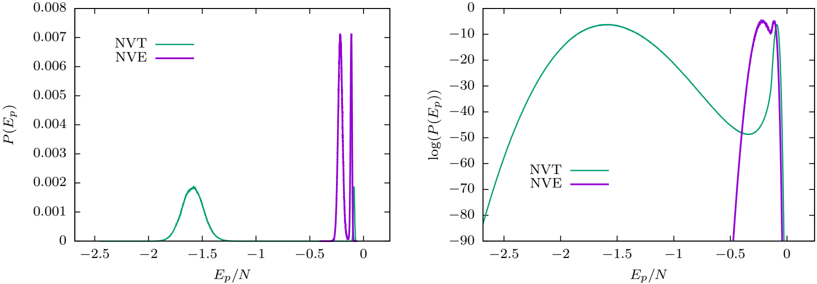
Sampling phase transitions:

Equal height histograms



P. Schierz, J. Zierenberg and W. Janke, Phys. Rev. E 94 (2016) 021301

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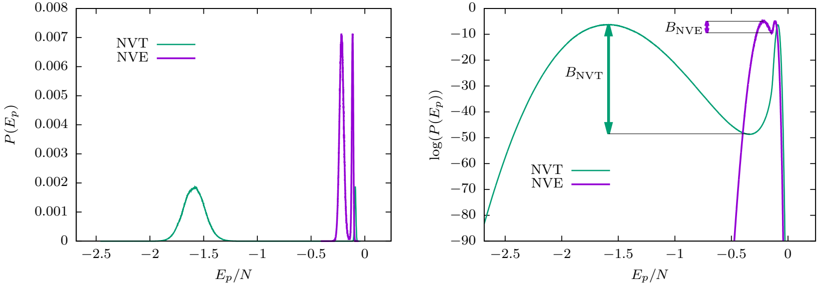

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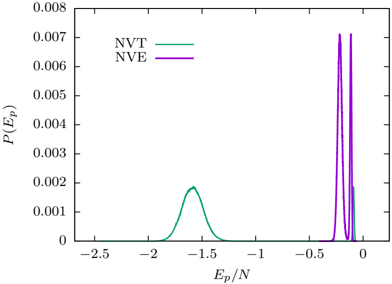

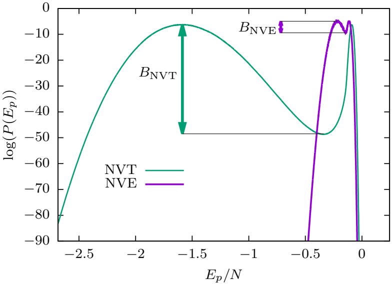

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The energy-driven phase transition in the NVE ensemble shows a much smaller barrier than the equivalent temperature-driven transition in the NVT ensemble.

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Equal-area Framework:

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$$K(E_p) = \frac{\partial \ln \Omega(E_p)}{\partial E_p}$$

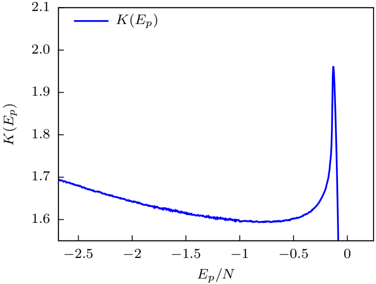

Figure : $K(E_p)$ from the $N = 2048$ Lennard-Jones system and $D(E_p)$ at the equal-area point.

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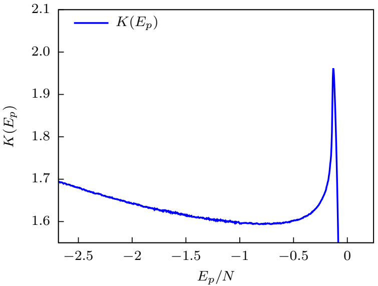

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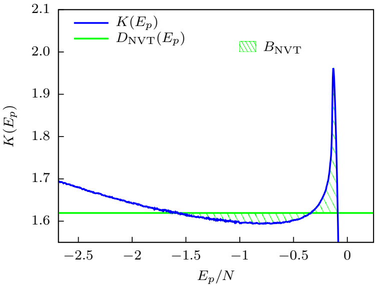

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For the NVT ensemble we obtain:

$$D_{\mathrm{NVT}}(E_p) = -\frac{\partial}{\partial E_p} \ln(e^{-\beta E_p}) = \beta$$

and choose $\beta = \beta_{\mathrm{eqh}}$.

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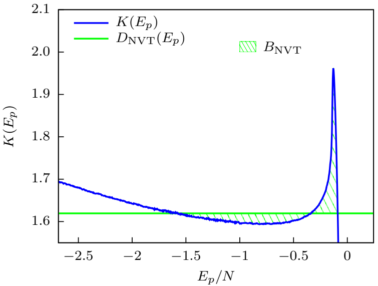
It can be shown that the amount of enclosed area between $K(E_p)$ and $D(E_p)$ equals the barrier B of the ensemble.



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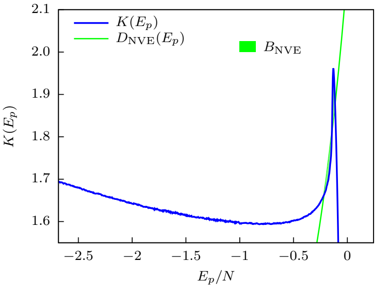

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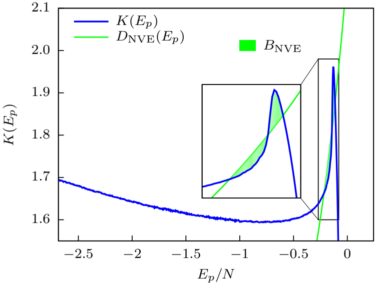

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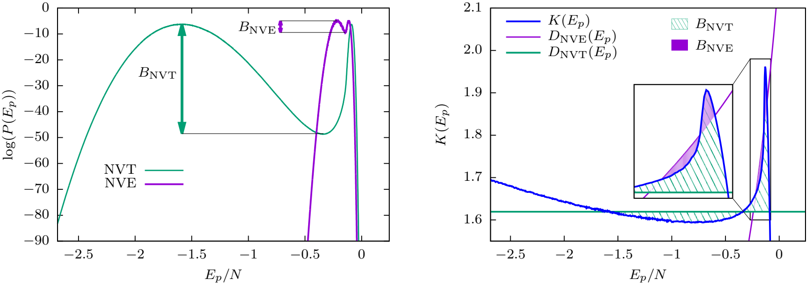

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[2] P. Schierz, J. Zierenberg and W. Janke, Phys. Rev. E 94 (2016) 021301

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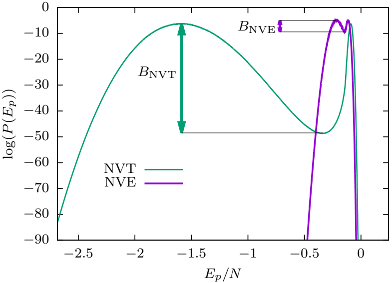

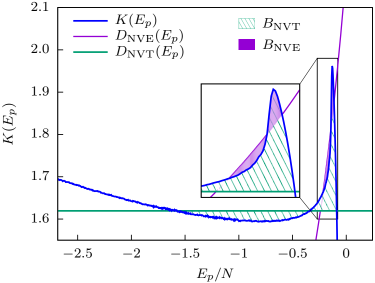

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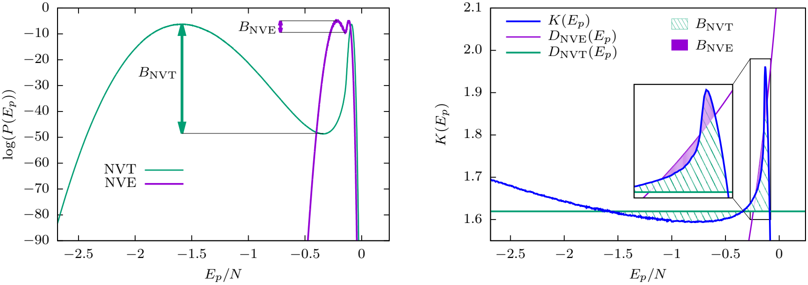

- $K(E_p)$ has always an S-shape [1] if a system shows canonical phase coexistence at the phase transition (first-order transitions).
- For such general first-order transitions it can be shown that the NVE barrier always has to be smaller or may even vanish [2].

$$B_{\mathrm{NVE}} < B_{\mathrm{NVT}}$$

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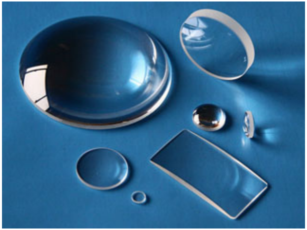
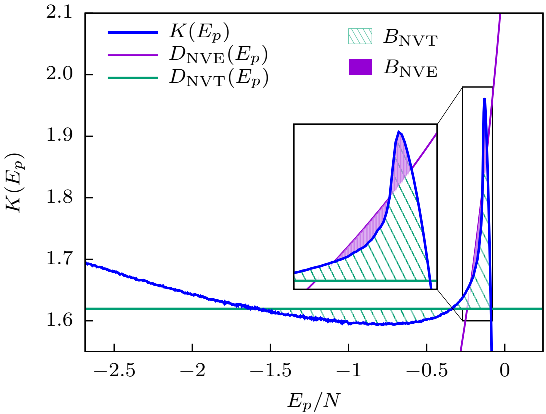
- Possible applications for industrial processes where phase transitions are crucial (steel production, glass production, ...)?



Ensemble Tailoring:



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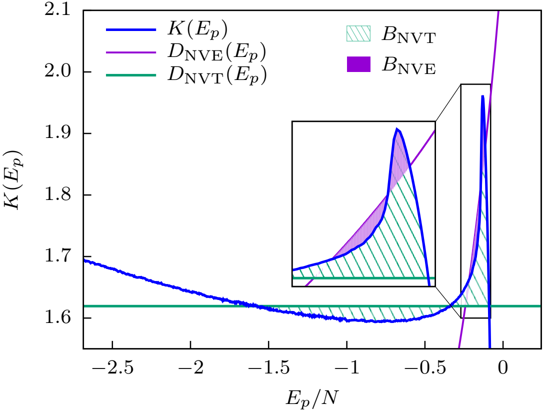

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How to tailor an ensemble with a specific or even vanishing barrier?

Ensemble Tailoring:

Multicanonical method (MUCA) [1,2]:

$$W_{\mathrm{MUCA}}(E_p) = \frac{1}{\Omega(E_p)}$$

[1] B. A. Berg and T. Neuhaus, *Phys. Lett. B* **267** (1991), *Phys. Rev. Lett.* **68** (1992)
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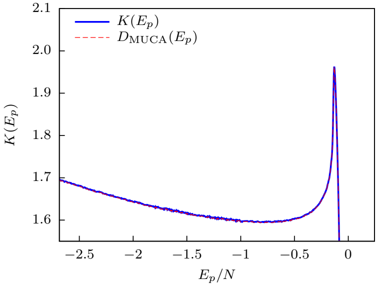
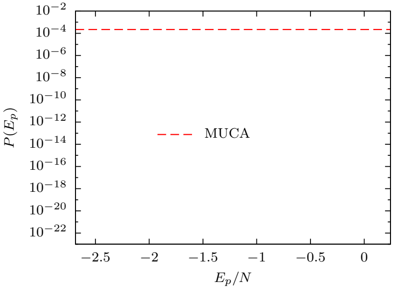
No enclosed area and hence no transition barrier.





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Ensemble Tailoring:

Gaussian modified ensemble (GME):

$$W_{\mathrm{GME}}(E_p) = e^{-(A/2)E_p^2 - BE_p},\ \ D_{\mathrm{GME}}(E_p) = AE_p + B$$

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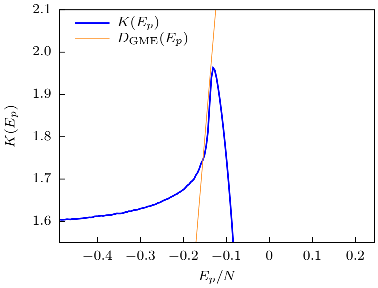
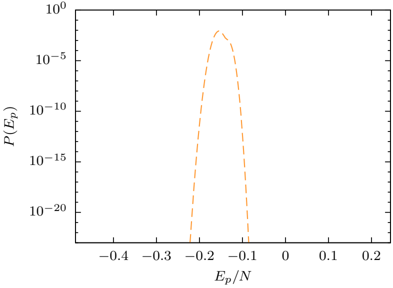
Barrier vanishes with a large enough slope parameter A.





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Ensemble Tailoring:

Artificial polynomial ensemble:

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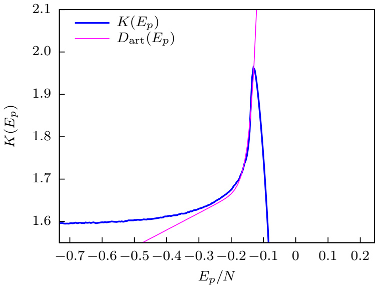
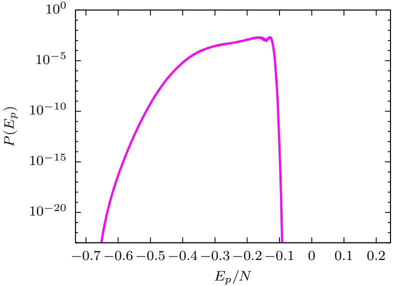
Artificial ensemble with a large histogram width and a small barrier.





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- The transition barrier of the NVE ensemble is always lower than in the corresponding first-order NVT transition.
- A lower barrier leads to fast simulations for phase transitions.
- The proposed analytical framework may be used to tailor artificial ensembles for computational purposes by an educated guess of $D(E_p)$.