Systematic Microcanonical Analyses of Polymer Adsorption Transitions

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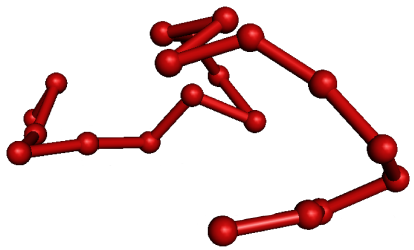
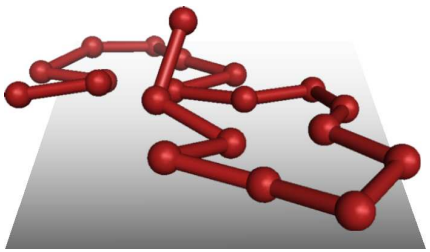
SOFT MATTER SYSTEMS RESEARCH GROUP

November 26, 2009





$\Leftrightarrow$

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10th International NTZ-Workshop on New Developments in Computational Physics

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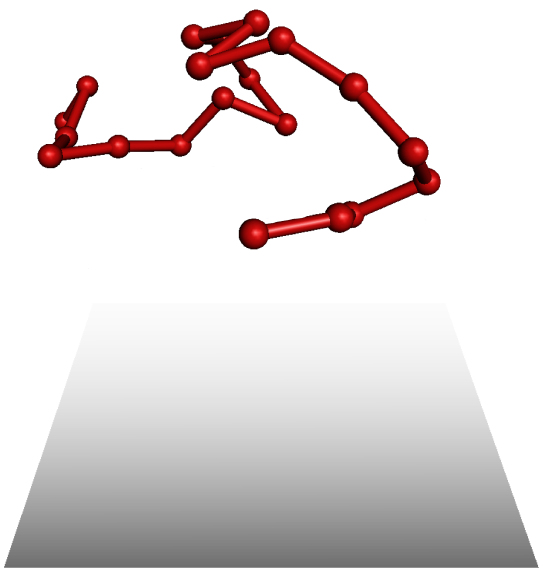
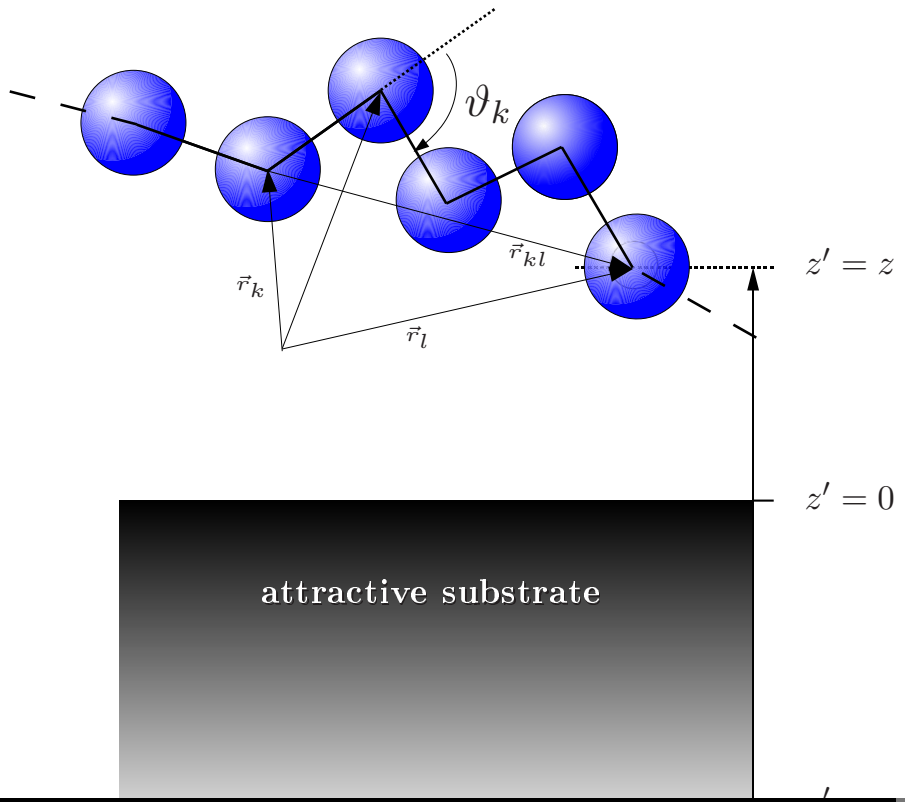


Semiflexible $3D$-Coarse-Grained Polymer near a Substrate

$$E_{\text{total}} = E_{\text{LJ}} + E_{\text{bend}} + E_{\text{sur}}$$



Lennard-Jones Potential

$$E_{\text{LJ}} = 4 \sum_{i=1}^{N-2} \sum_{j=i+1}^{N} \left(\frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}} \right)$$

Bending Energy

$$E_{\text{bend}} = \frac{1}{4} \sum_{k=1}^{N-2} \left(1 - \cos\left(\vartheta_k\right)\right)$$

Surface Attraction

$$E_{\text{sur}} = \epsilon_s \sum_{i=1}^{N} \left(\frac{2}{15} \frac{1}{z_i^9} - \frac{1}{z_i^3} \right)$$

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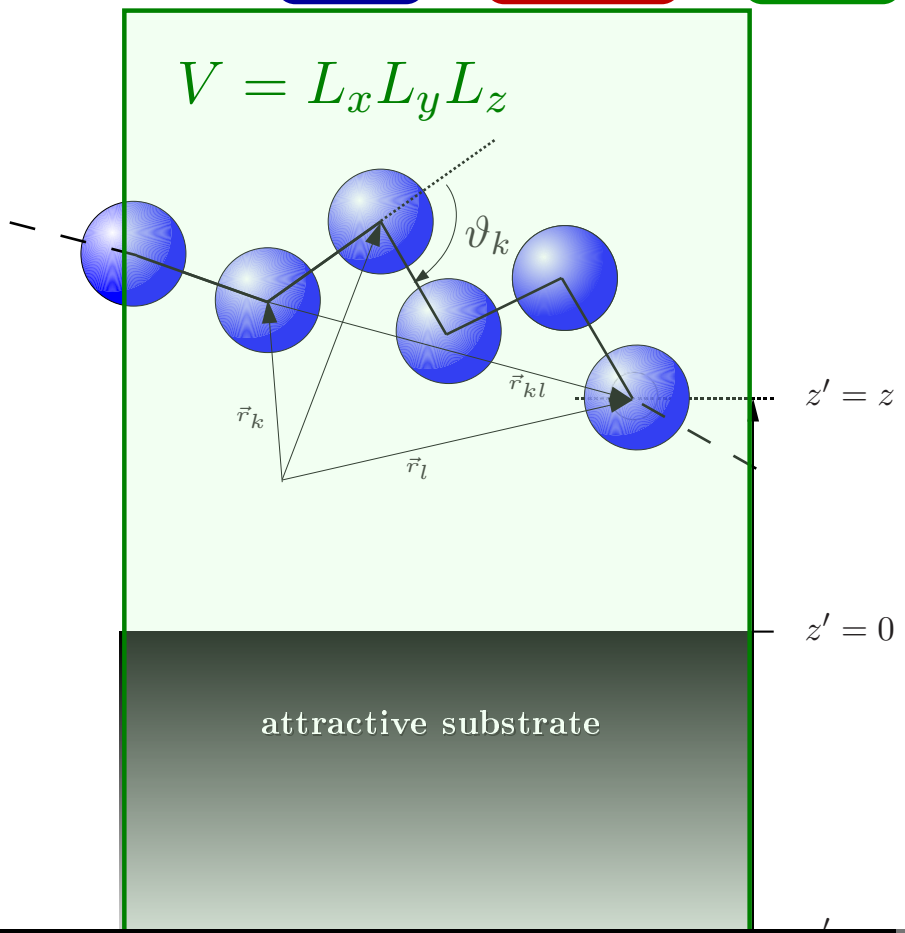

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Canonical vs. Microcanonical Approach

canonical ensemble (controlled by intensive parameter T)

Def.: NVT-ensemble: statistical equilibrium ensemble, where the number of particles (N) and the volume (V) of each microstate are the same. The temperature (T) is the one of a common heat bath.

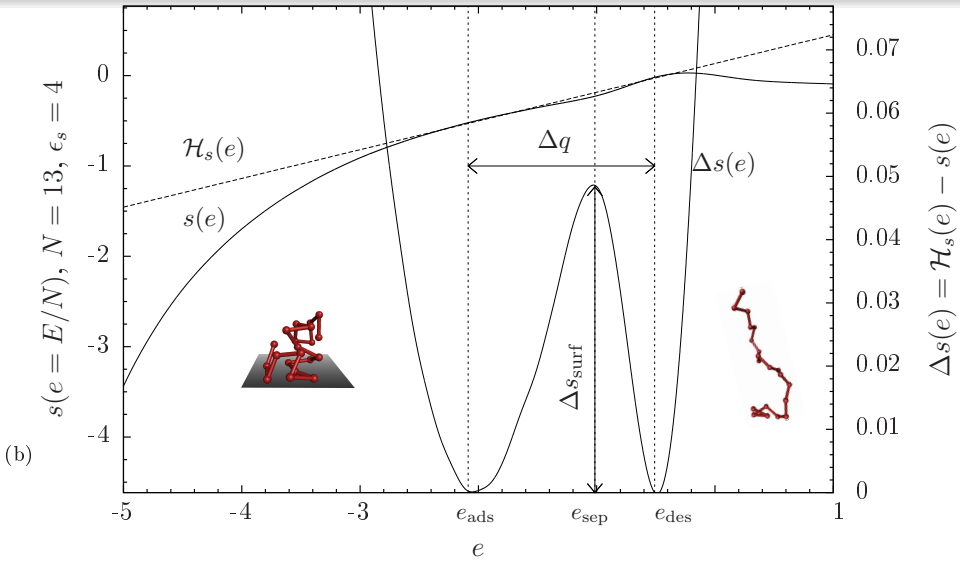
- resultant energy distribution: Boltzmann distribution $p(E) = g(E)e^{-E/k_BT}$

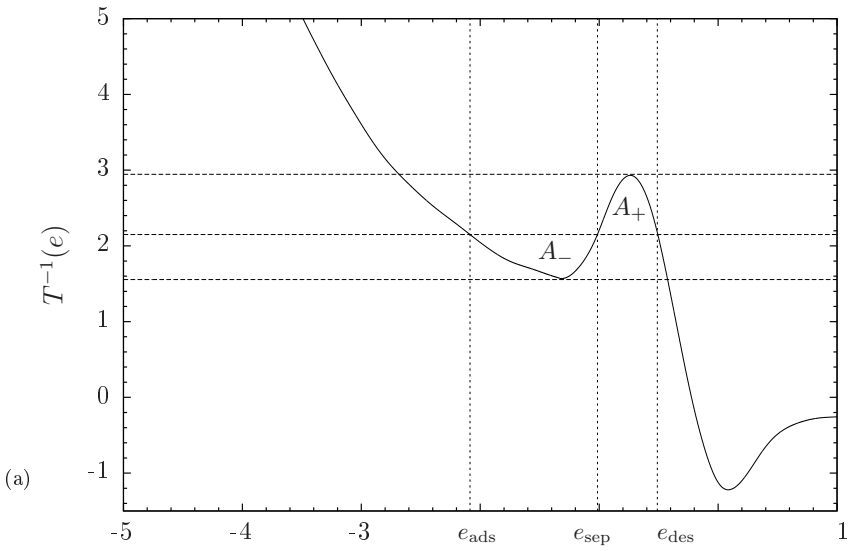
microcanonical ensemble (controlled by extensive parameter E)

Def.: NVE-ensemble: ensemble of microstates with (N, V and E conserved), e.g., the system is isolated from any environment

- based on density of states $g(E)$, that is still well-defined for non-extensive systems
- $g(E)$ obtained by multicanonical Monte Carlo sampling

Important Definitions





microcanonical entropy

$s(e) = N^{-1} k_B \ln g(e)$, with $k_B = 1$ and $e = E/N$

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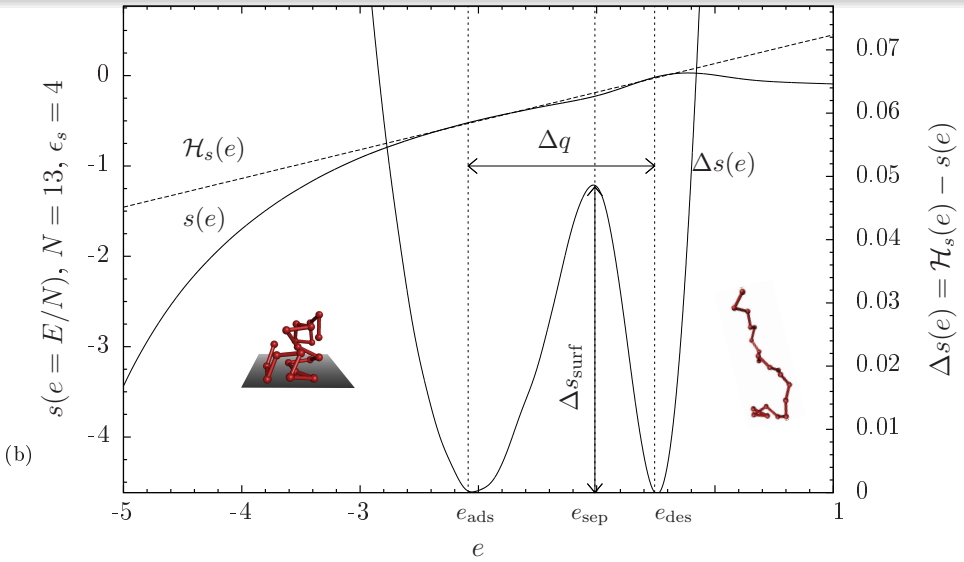

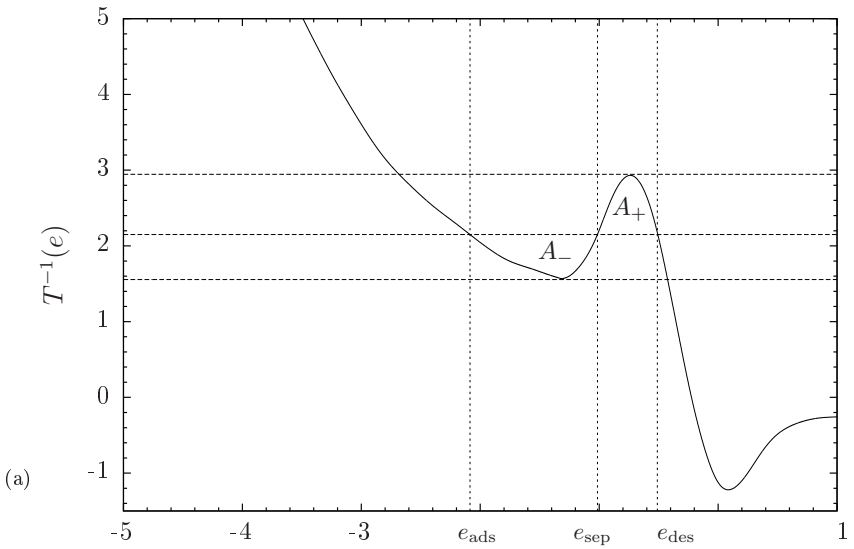

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$T(e) = (\partial s(e)/\partial e)^{-1}_{N,V}$

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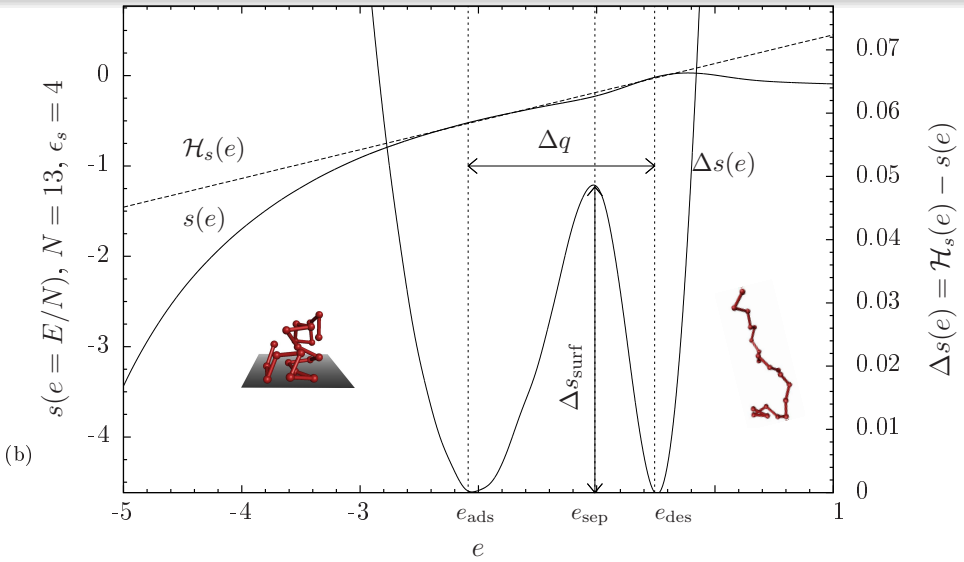

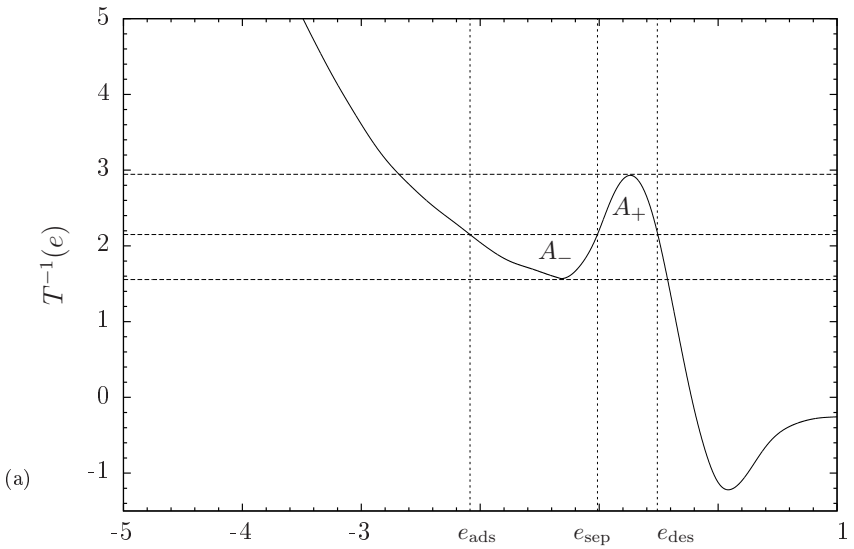

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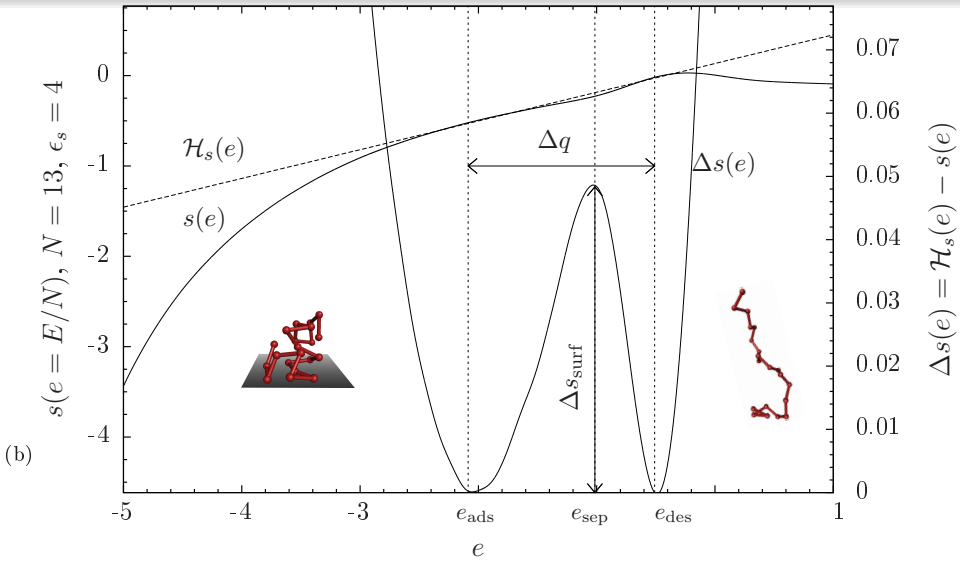

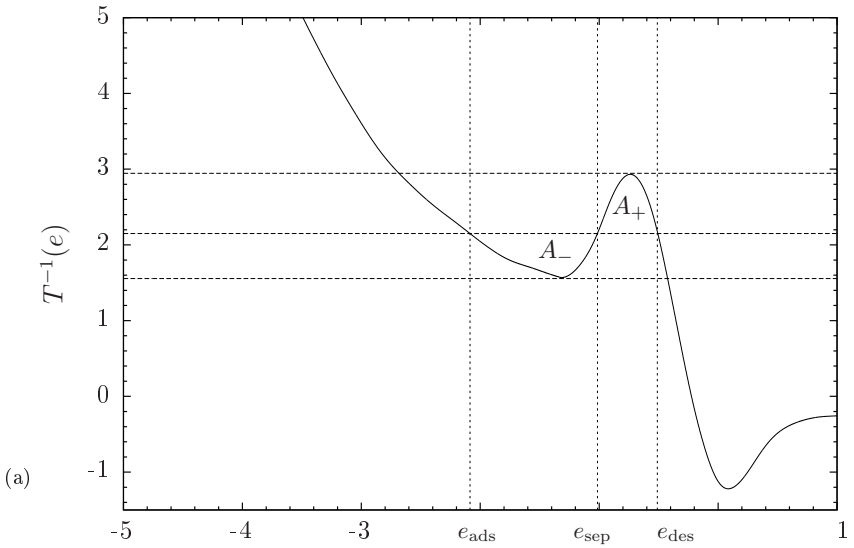

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Latent heat per monomer required to break the surface contacts at $T_{\rm ads}$

$\Delta q = e_{\rm des} - e_{\rm ads} = T_{\rm ads}[s(e_{\rm des}) - s(e_{\rm ads})]$

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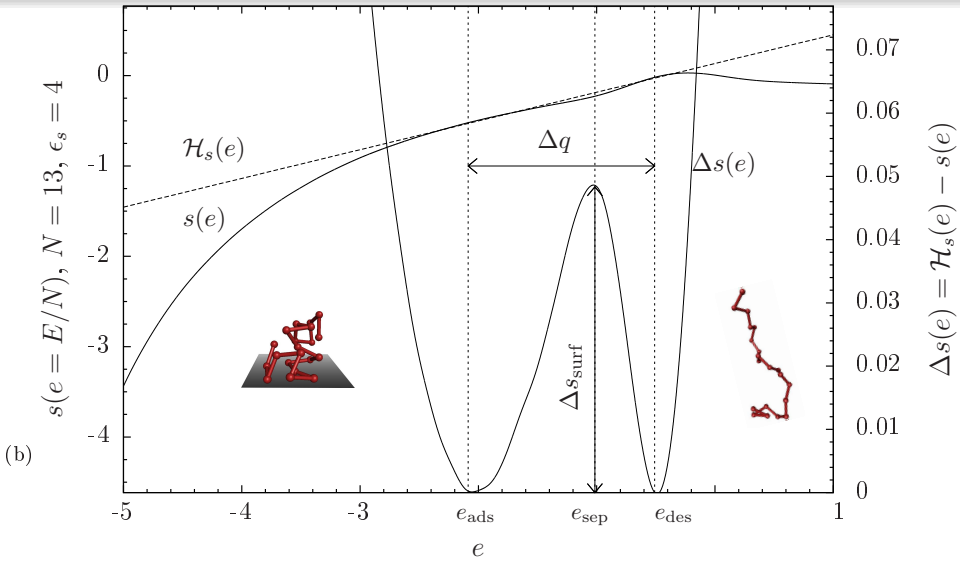

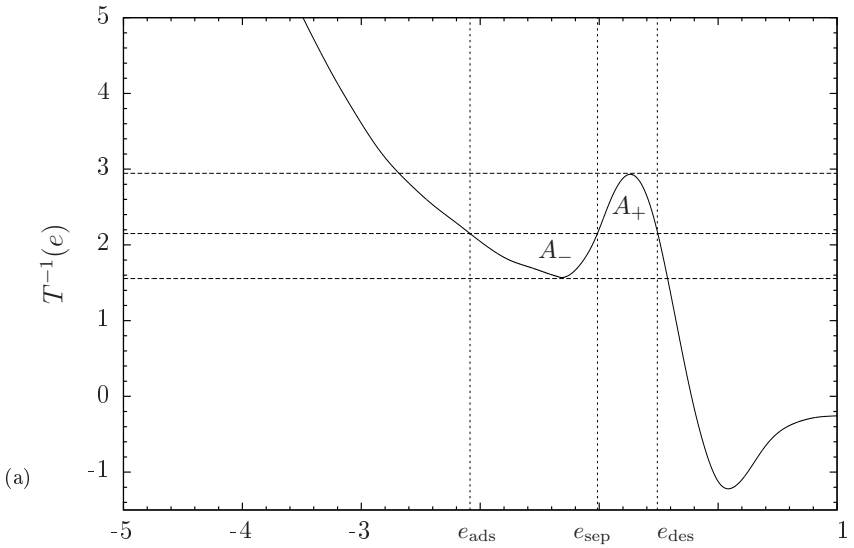

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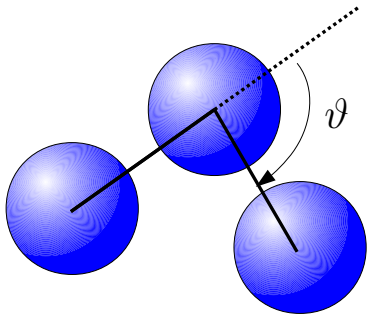
Surface entropy

$\Delta s_{\rm surf} \equiv \Delta s(e_{\rm sep})$, where $e_{\rm sep}$ is the energy with $\Delta s(e) = \mathcal{H}_s(e) - s(e)$ being maximal

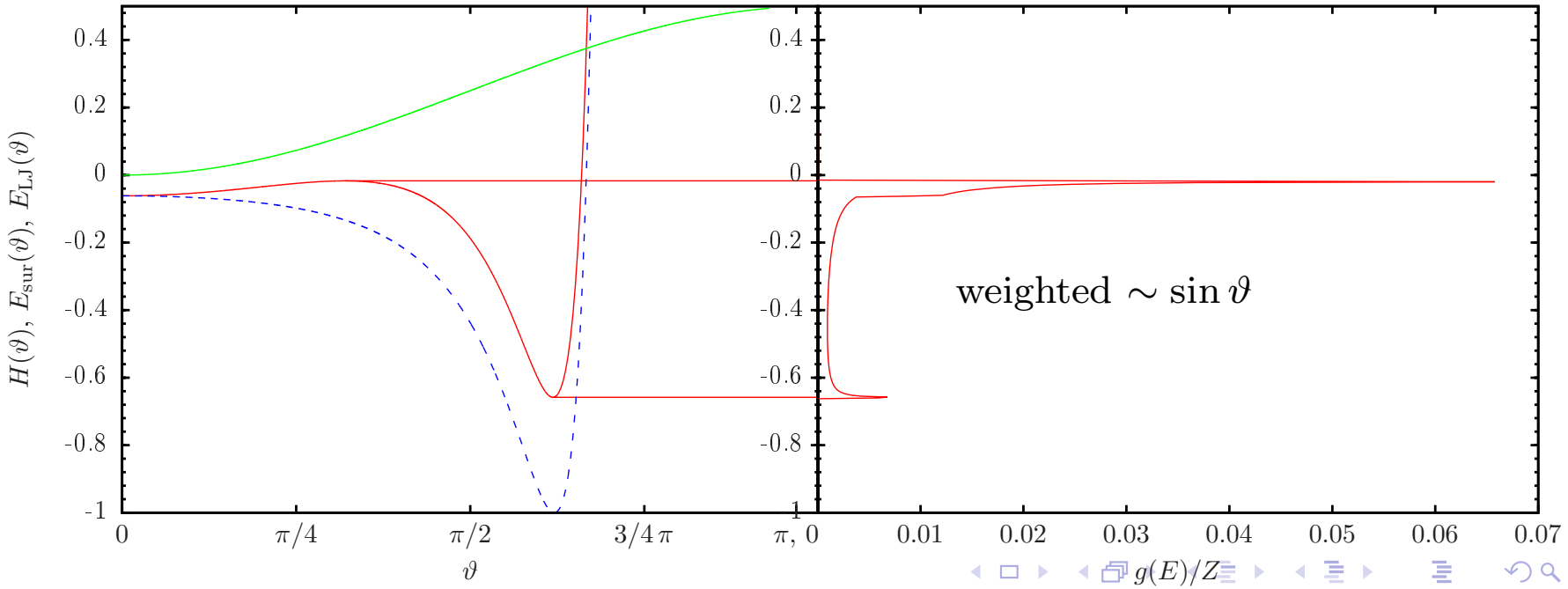
Let's start simple: Density of States $g(E)$ of a Free 3mer



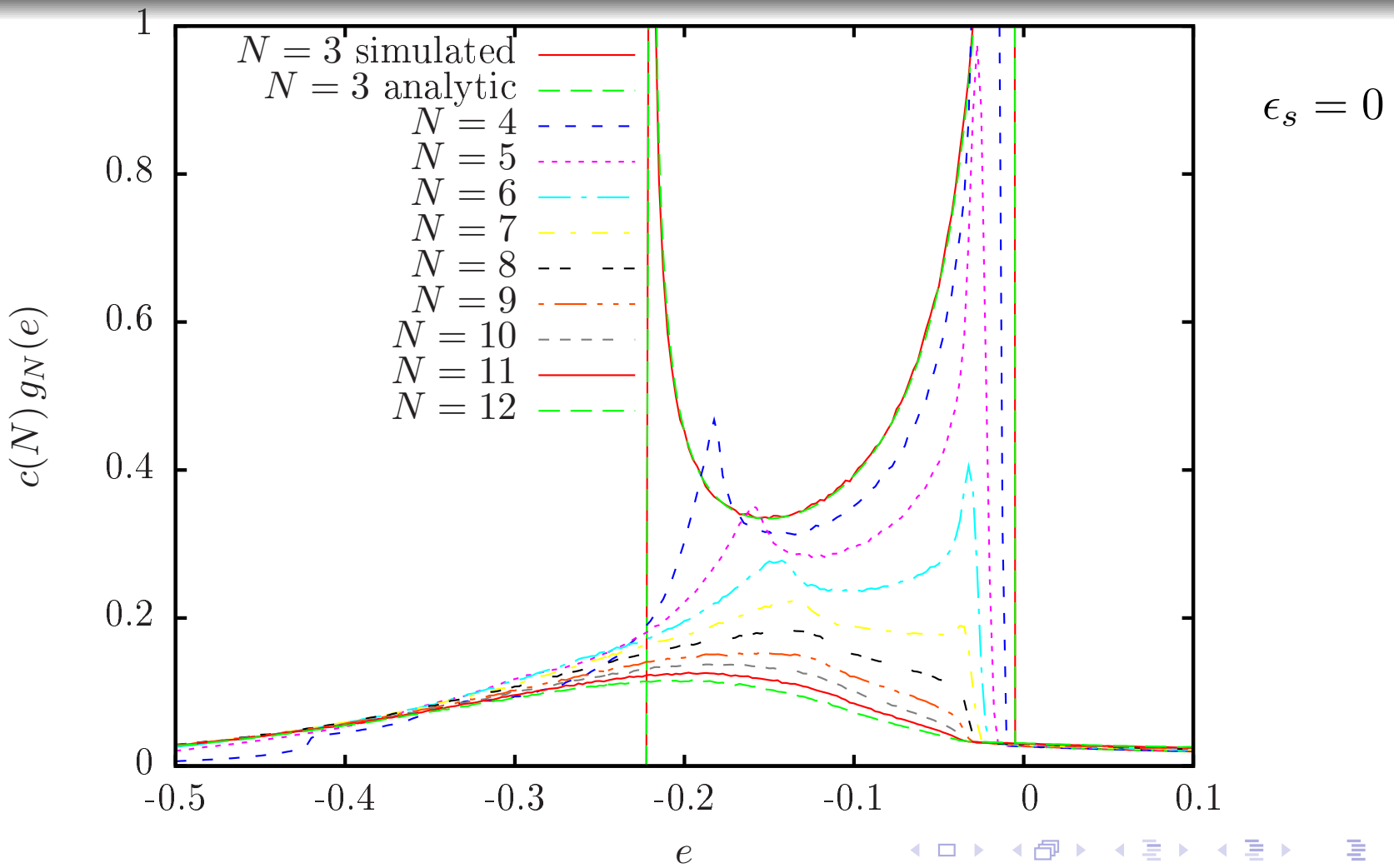
$$N = 3 \text{ and } \epsilon_s = 0$$

Here the hamiltonian can be written as:

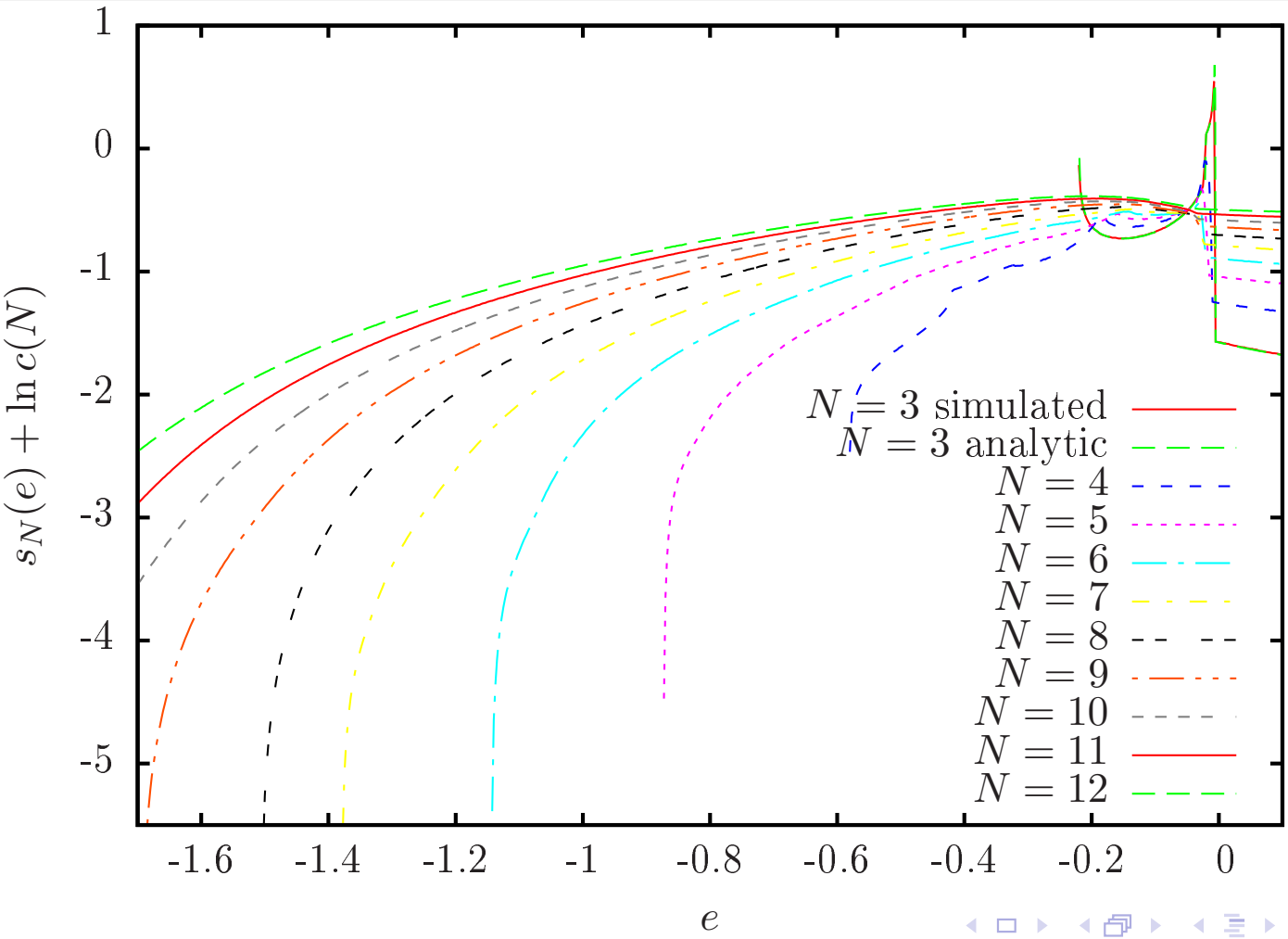
$$\begin{aligned} H(\vartheta) &= E_{\mathrm{LJ}} + E_{\mathrm{bend}} \\ &= 4(2 + 2\cos\vartheta)^{-3}((2 + 2\cos\vartheta)^{-3} - 1) \\ &\quad + (1 - \cos\vartheta)/4 \end{aligned}$$



Density of States $g(e)$ of a Free Polymer increasing the Chain Length



Microcanonical Entropy $s(e) = \ln g(e)$ of a Free Polymer increasing the Chain Length



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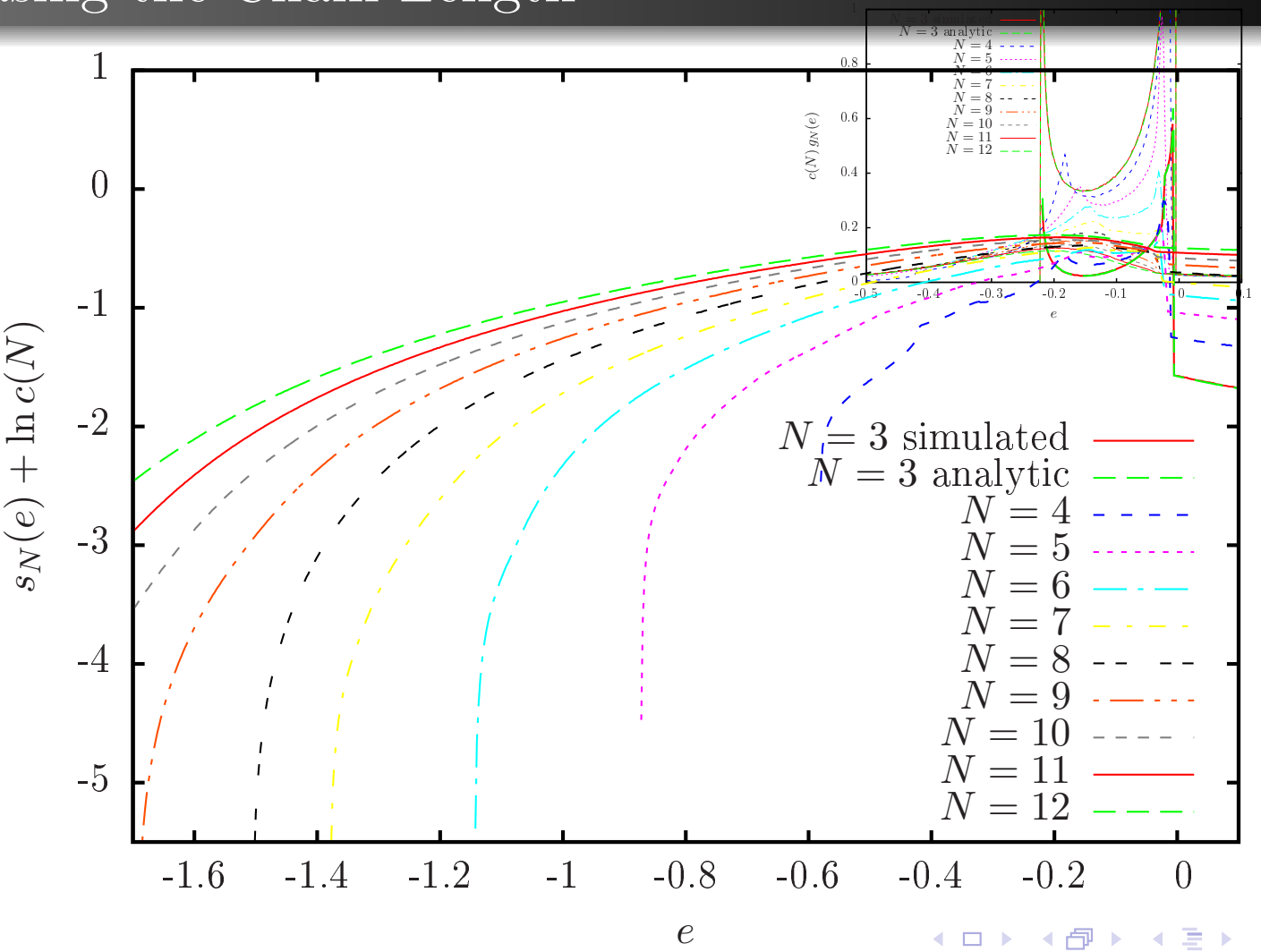
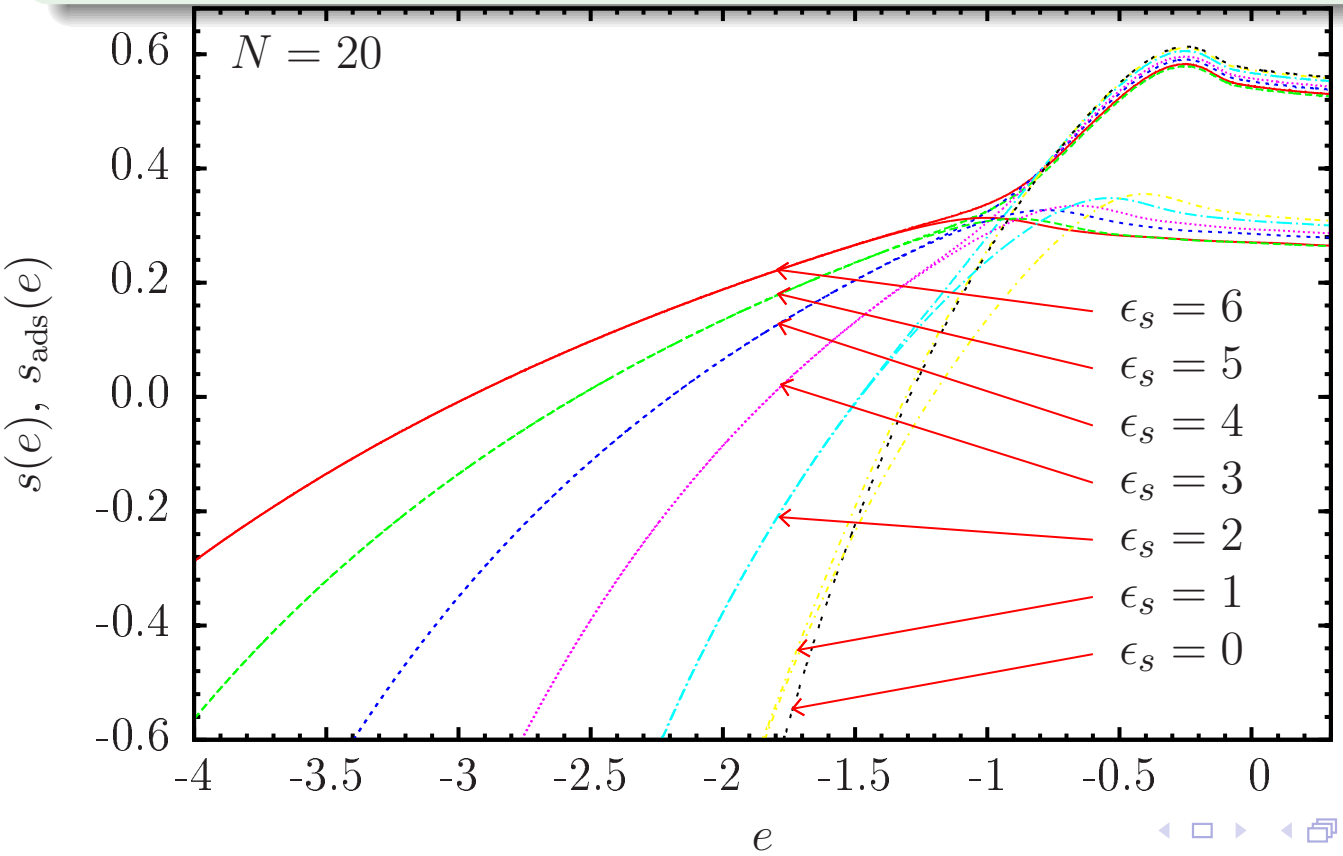


$\epsilon_s = 0$

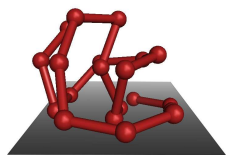
Now add and increase a Substrate Attraction

divide $s(e)$ into adsorbed and desorbed part

- def.: adsorbed if: $e_{\text{surf}} < -0.1\,\epsilon_s$ (some arbitrariness here)
- $s_{\text{des}}(e)$ quite constant while $s_{\text{ads}}(e)$ arises with ϵ_s
- s_{ads}, s_{des} both concave at adsorption transition



small ϵ_s



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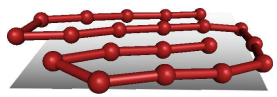
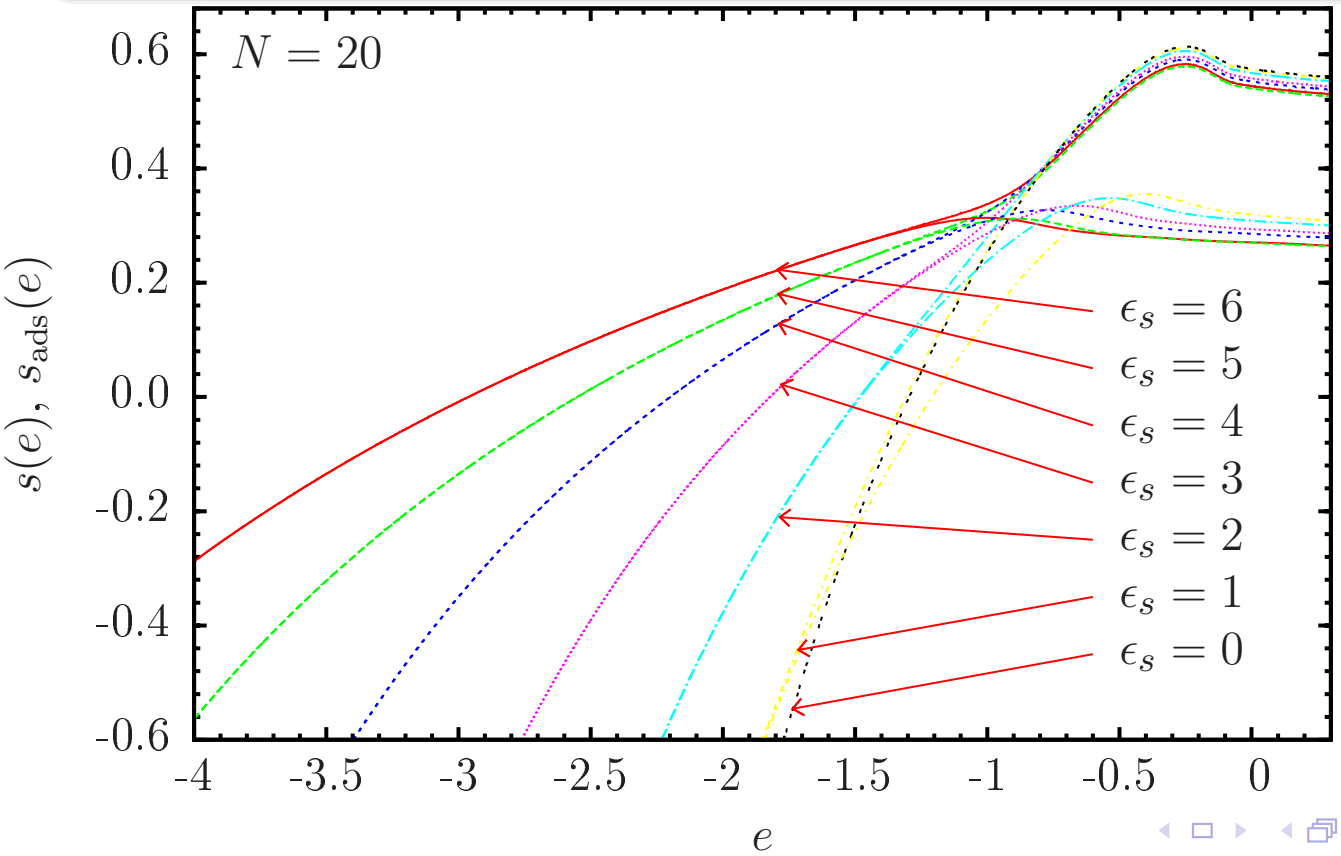


Now add and increase a Substrate Attraction

- for low ϵ_s no convex intruder can be found (continuous adsorption, docking)
- with increasing ϵ_s the amount of low-energy states increases and $s(e)$ gets convex at some ϵ_s
- T_{ads} (inverse slope), Δq and Δs_{surf} increases with ϵ_s



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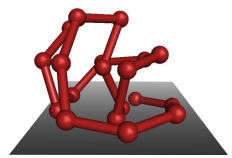

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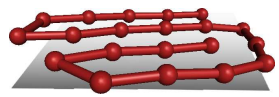

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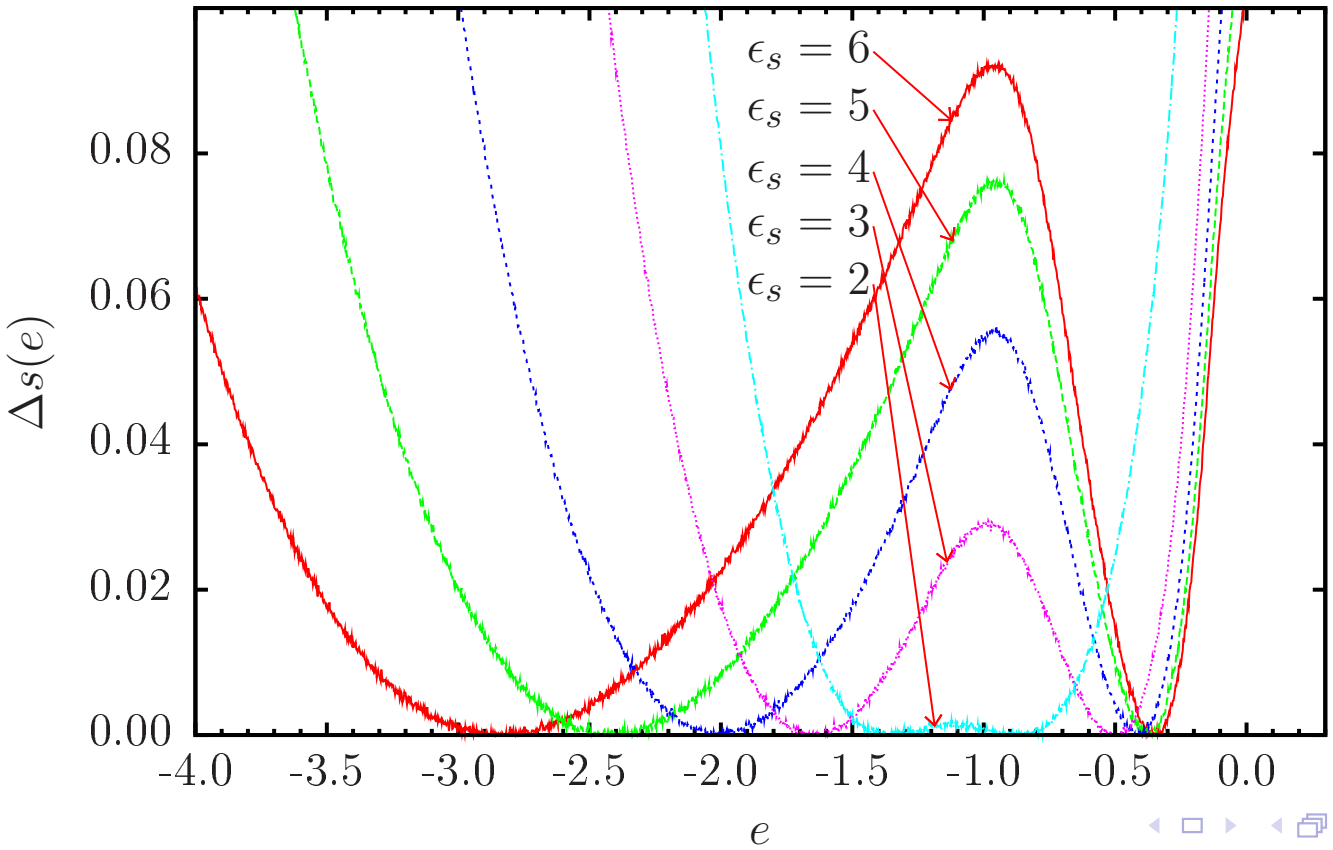

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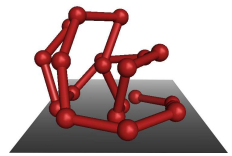

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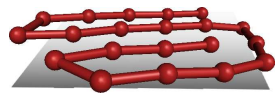
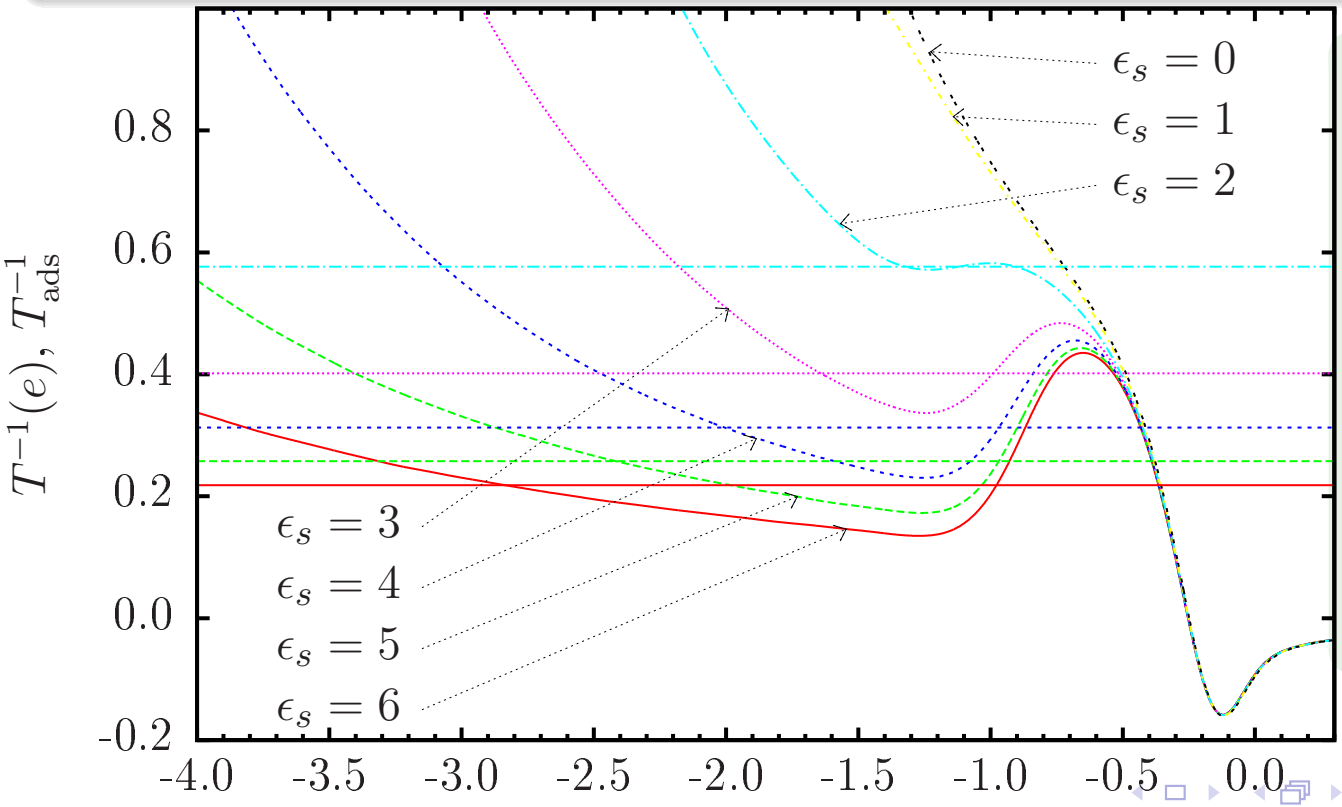


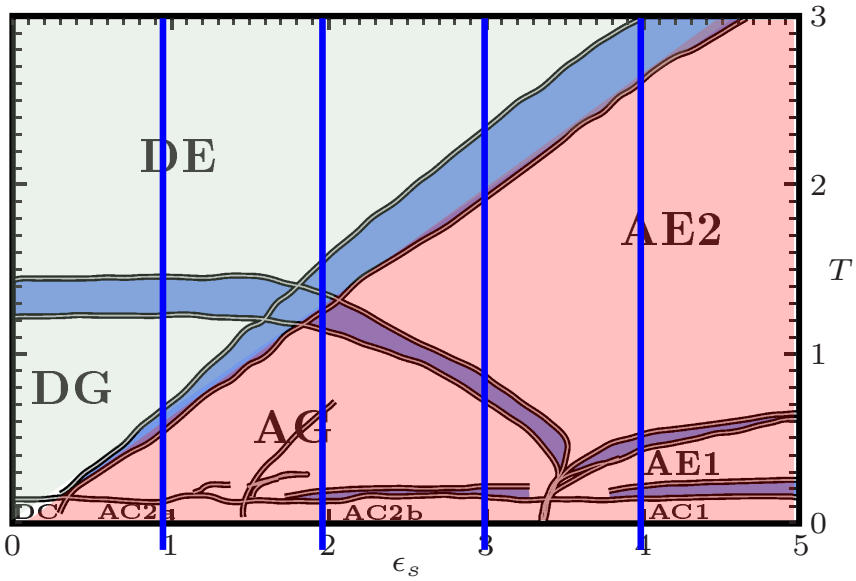
Now add and increase a Substrate Attraction

- for $E < E_{\text{ads}}$, $T(e)$ increases with e and depends on ϵ_s
- for $E > E_{\text{des}}$, $T(e)$ is independent of ϵ_s
  - in the phase coexistence regime there is a region (between max and min of $T^{-1}(E)$), where $T(E)$ decreases with E



- negative specific heat!
- location of e_{sep} seems to be quite independent of ϵ_s
- saddle point: Θ-temperature $=T_{\text{ads}}$

Relation between scaling and conformation



- for $\epsilon_s \gtrapprox 2$ the adsorption transition takes place at higher T than the Θ-transition and scaling converges

  $\rightarrow$ scaling directly linked to conformations?

pseudophase	typical configuration
DE	
DG	
DC	
AE1	
AE2	
AC1	
AG	
AC2a	
AC2b	

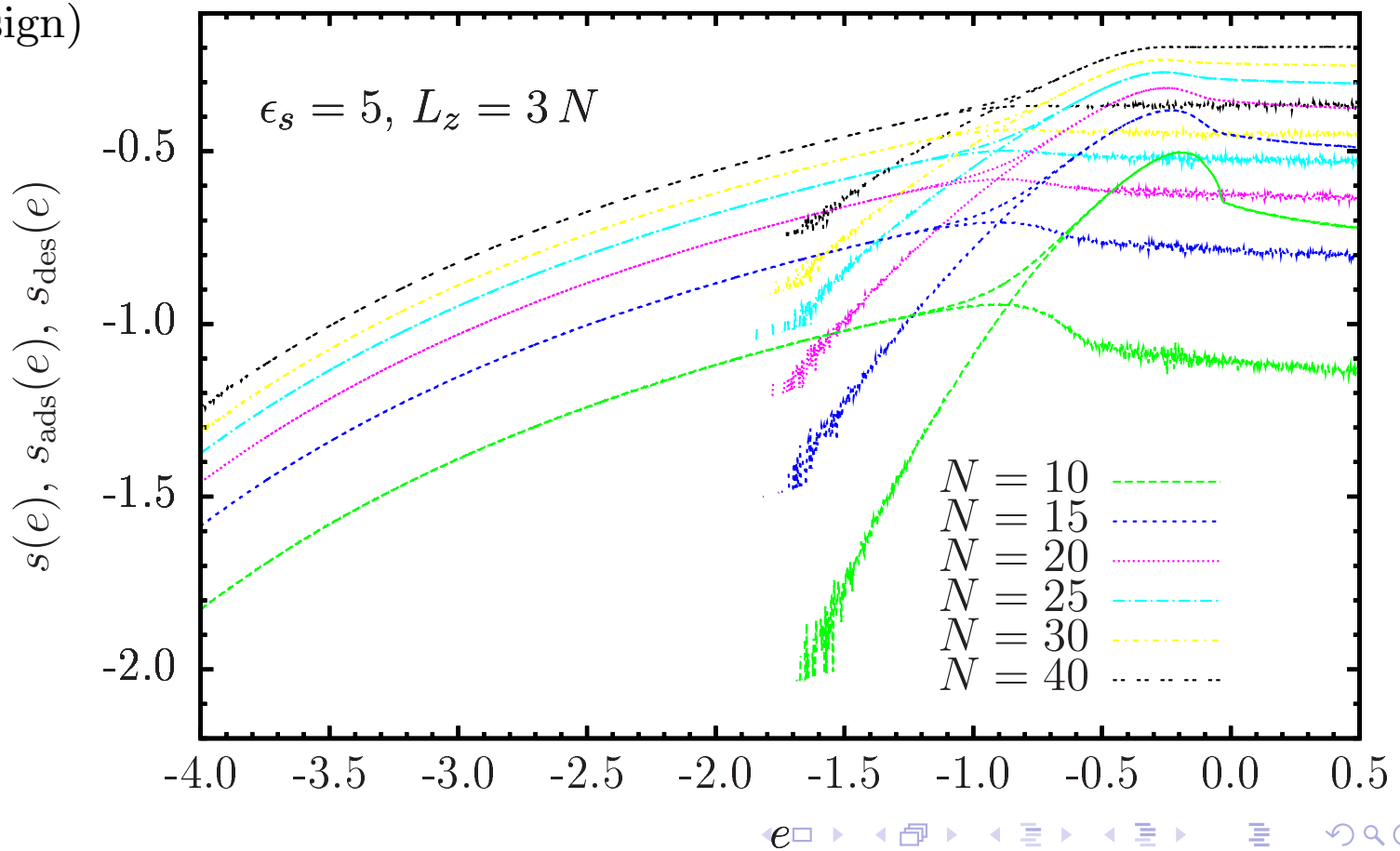
desorbed

adsorbed

M. Möddel, M. Bachmann, and W. Janke, J. Phys. Chem. B **113**, 3314 (2009).

And what happens for longer Polymers?

- the maximum in $s(e)$ disappears for long chains
- Δs_{surf} as well as Δq decrease with N, while T_{ads} seems to saturate
- slope for high e increases with N (microcanonical temperature changes sign)



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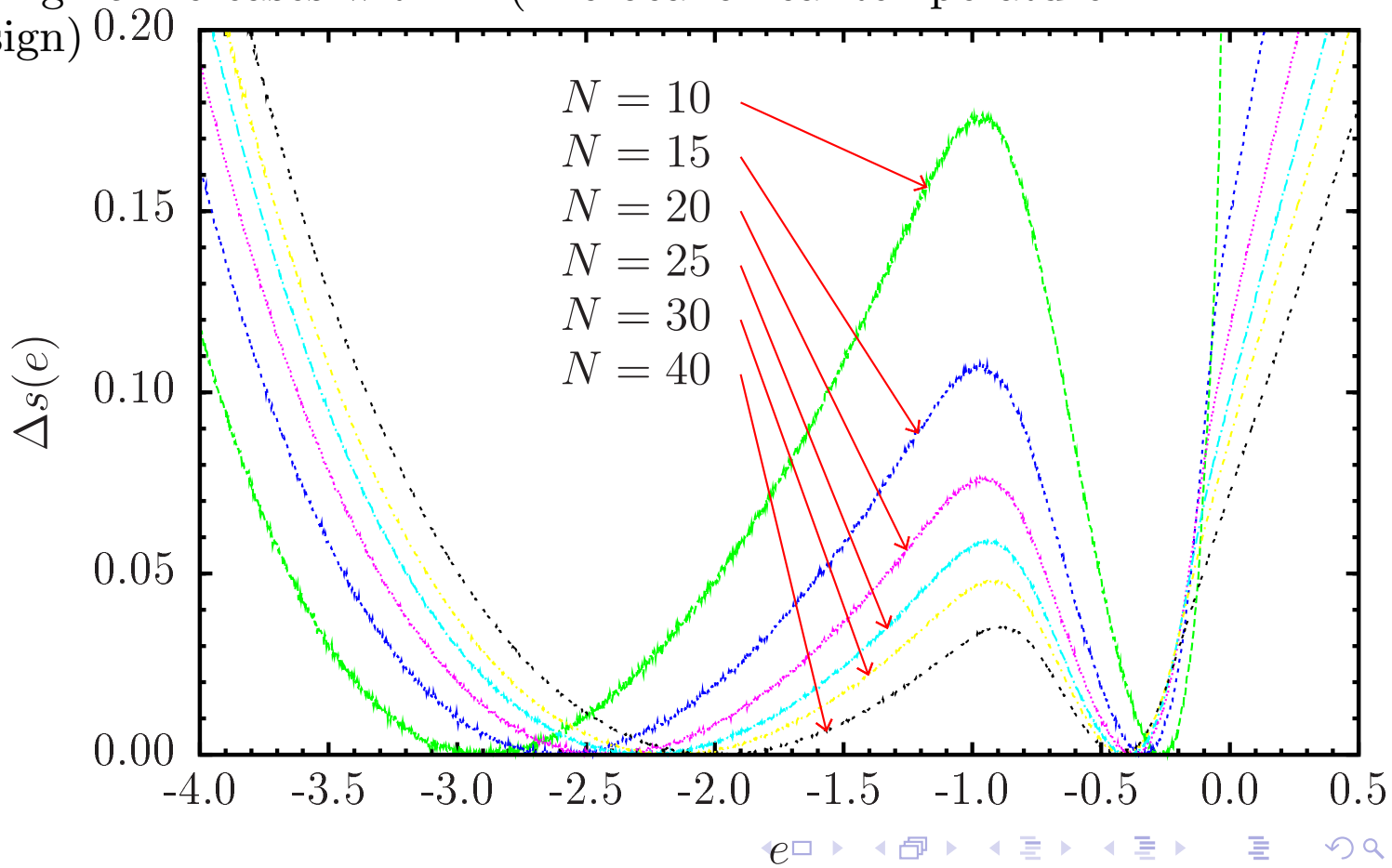

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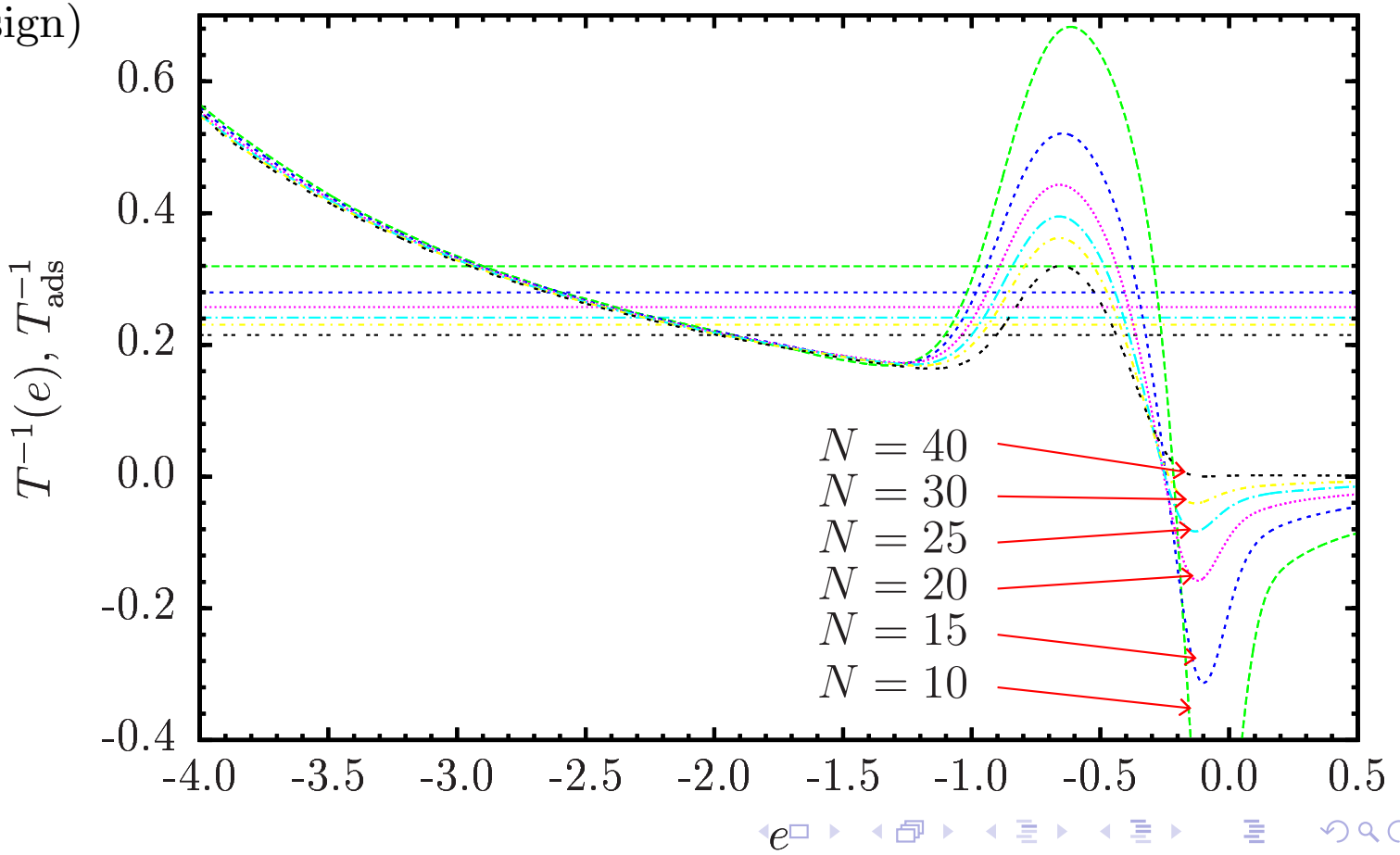


Scaling of the Convex Intruder for different ϵ_s

Δs_{surf} and Δq

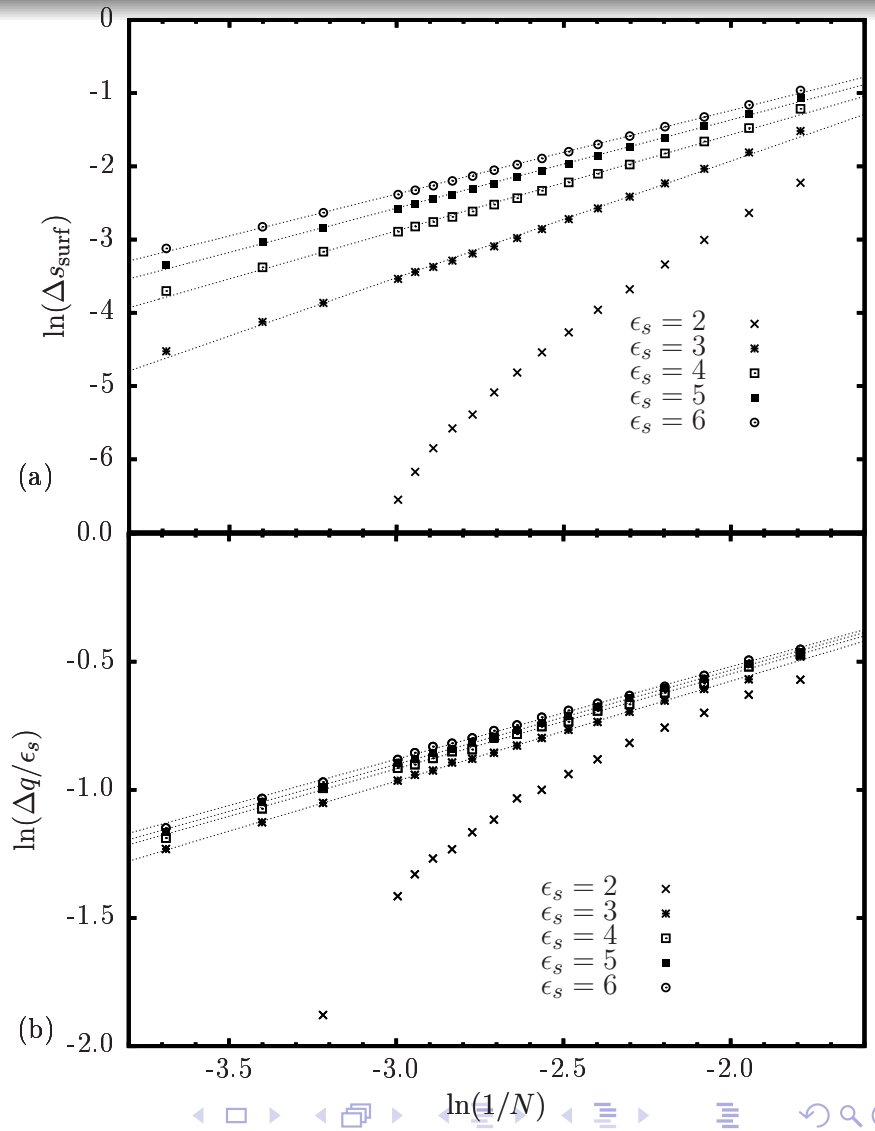
the data clearly suggest

- $\Delta s_{\text{surf}} \propto N^{-\kappa_s}$
- $\Delta q \propto N^{-\kappa_q}$

for $\epsilon_s \gtrapprox 2$

ϵ_s	κ_s	κ_q
3	1.647 ± 0.014	0.390 ± 0.004
4	1.360 ± 0.013	0.368 ± 0.004
5	1.237 ± 0.008	0.367 ± 0.003
6	1.166 ± 0.005	0.358 ± 0.004

- for $\epsilon_s \gtrapprox 4$ single layer conformations get likely at low T and $\Delta q \propto \epsilon_s$



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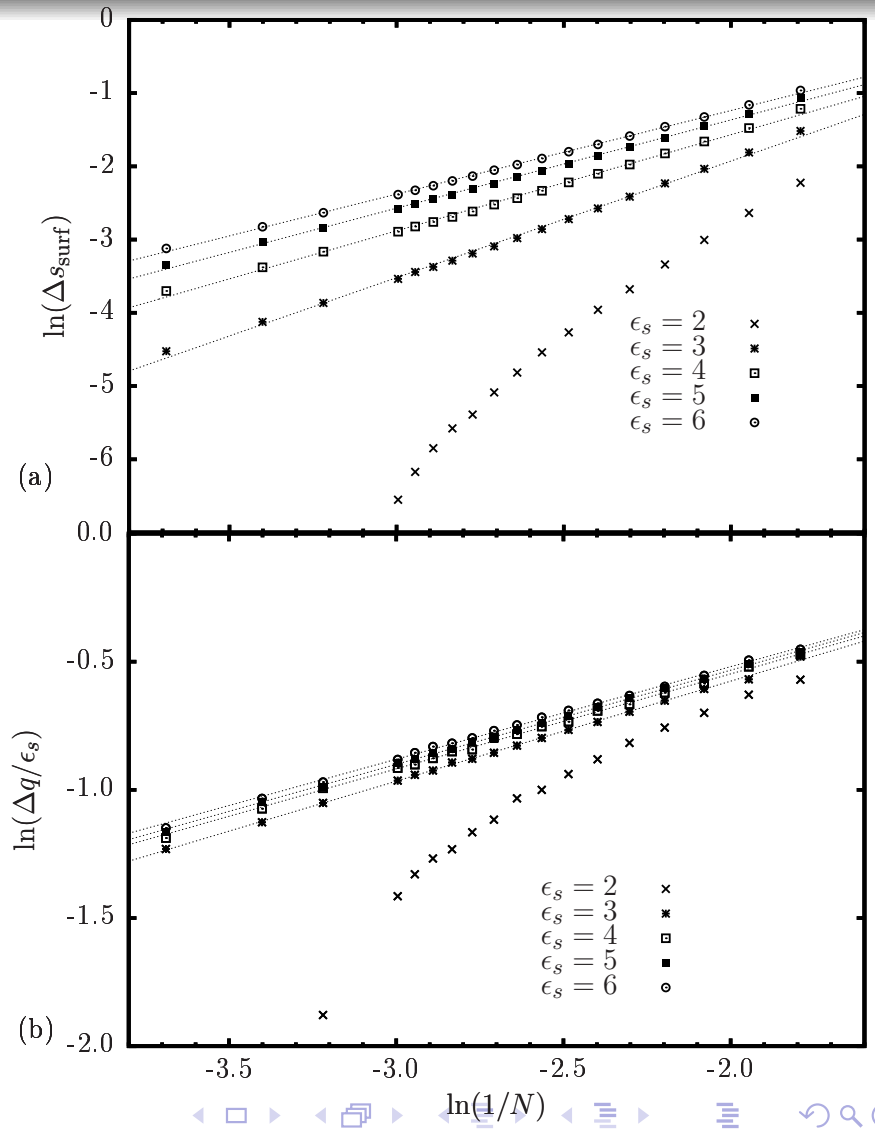
for comparison:

First order: $\Delta s_{\text{surf}} \sim N^{-1}$

$\Delta q - \Delta q_{\epsilon_s \to \infty} \sim N^{-1}$, $\Delta q_{\epsilon_s \to \infty} \neq 0$

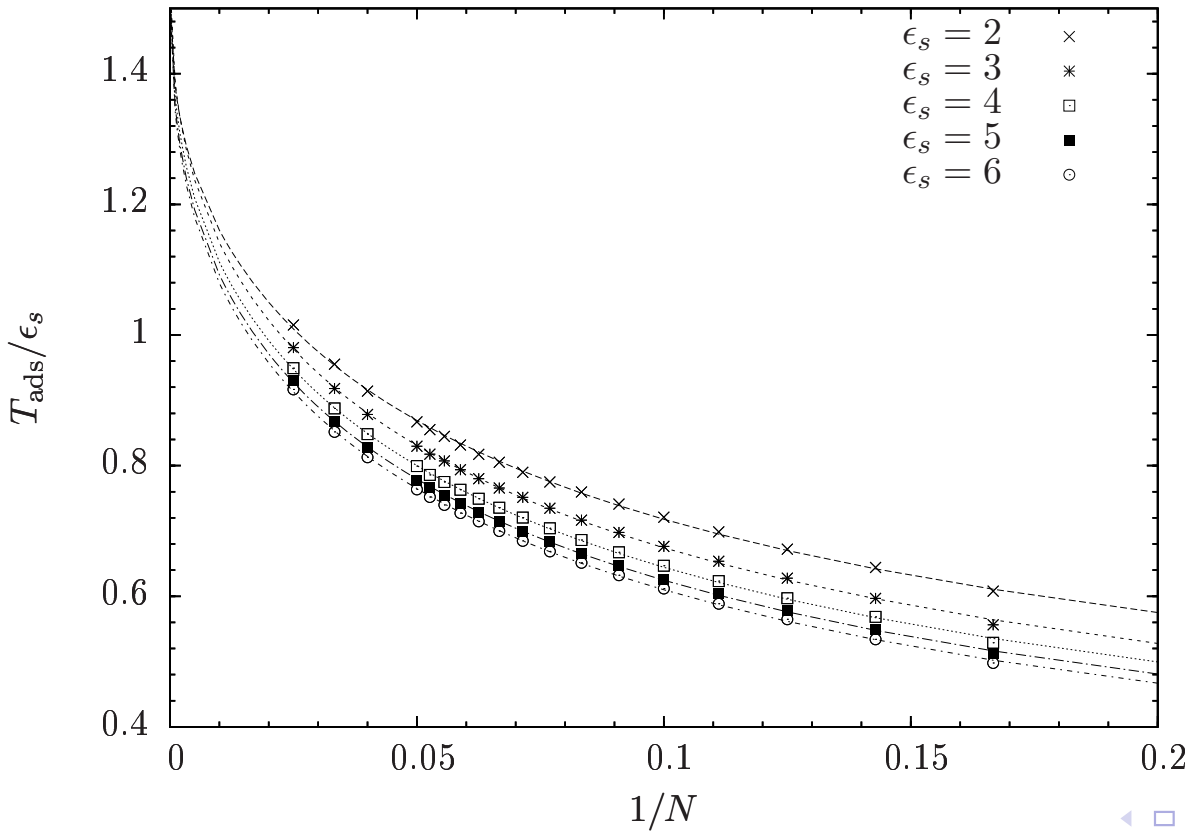
here: $\Delta q_{\epsilon_s \to \infty} = 0$

different scaling $\rightarrow$ continuous transition



Saturation of the Adsorption Temperature with Chain Length

- T_{ads} monotonically increasing with N
- likely not diverging, but reaching a fixed (probably universal) value for $N \to \infty$



- fit was performed on function derived from simple mean-field argument
- suggests a finite T_{ads}^{∞}

Conclusions

- Adsorption transition exhibits clear signals of a first-order-like conformational transition in the important case of finitely long polymers
  - expressed by coexistence of adsorbed and desorbed conformations at the adsorption temperature
- A better understanding can be obtained by separating $s(e)$ in adsorbed and desorbed part or deriving it for very short chains
- The transition crosses over into a second-order phase transition in the thermodynamic limit, as expected
- Scaling of Δs_{surf} and Δq was found for not too small ϵ_s
- Approach also feasible for a study of simulation box/density-dependence

Conclusions

- Adsorption transition exhibits clear signals of a first-order-like conformational transition in the important case of finitely long polymers
  - expressed by coexistence of adsorbed and desorbed conformations at the adsorption temperature
- A better understanding can be obtained by separating $s(e)$ in adsorbed and desorbed part or deriving it for very short chains
- The transition crosses over into a second-order phase transition in the thermodynamic limit, as expected
- Scaling of Δs_{surf} and Δq was found for not too small ϵ_s
- Approach also feasible for a study of simulation box/density-dependence

Thank you for your attention.

Bonus Material