The Isotropic-Nematic Interface in Anisotropic Colloidal Dispersions

A Monte-Carlo Study

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Overview

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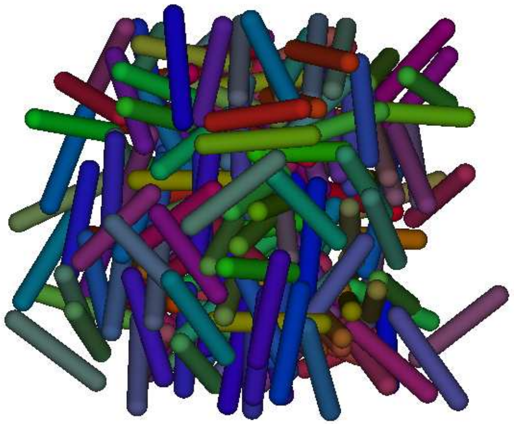
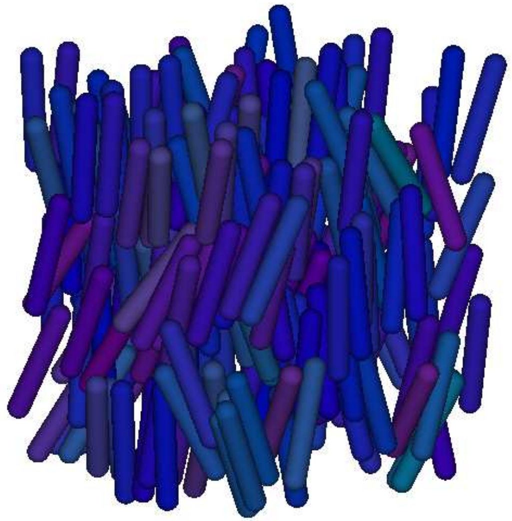
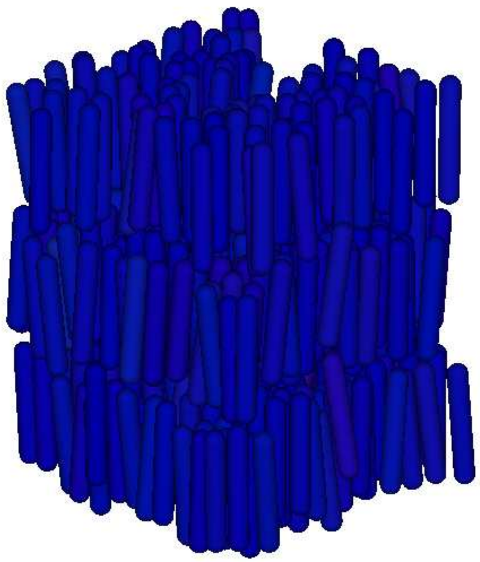
Liquid Crystal Phases



isotropic



nematic



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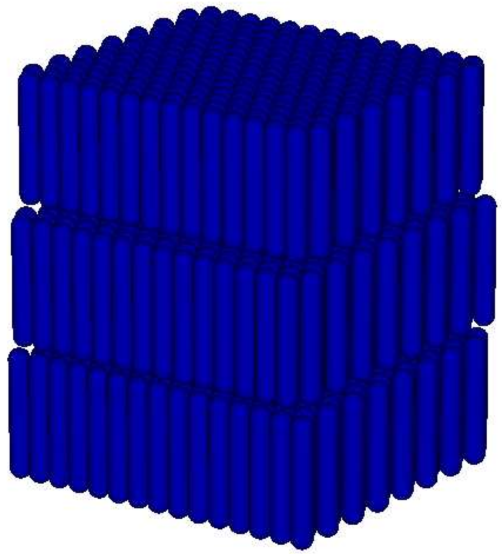
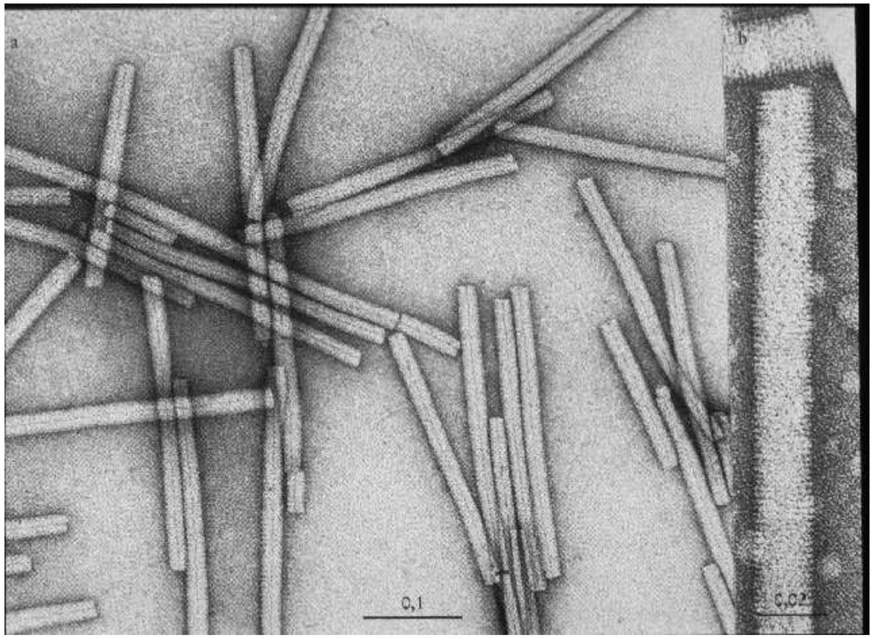


solid

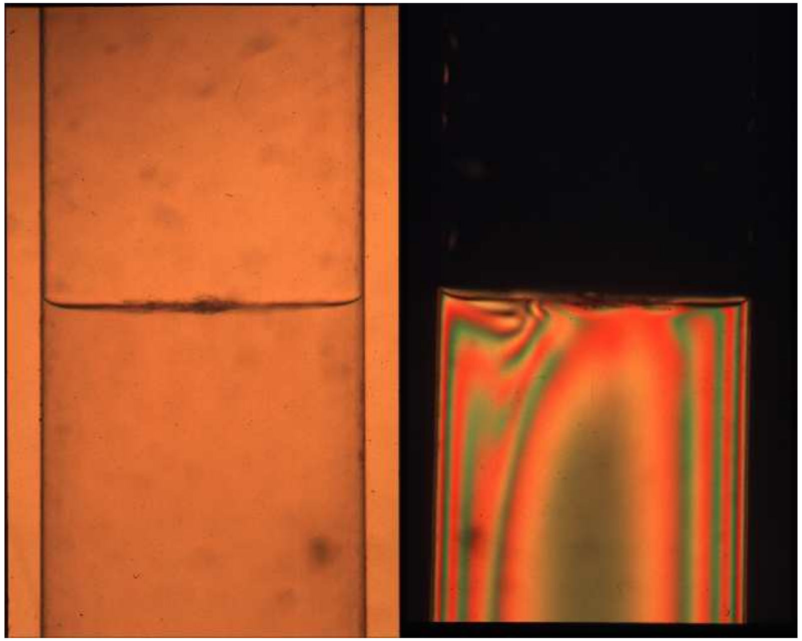
Introduction

Tobacco Mosaic Virus

$$L \approx 300nm, D \approx 20nm$$



a

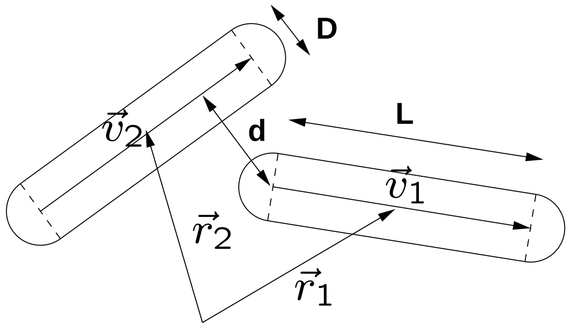


b

a [Carl Wetter, Biologie in unserer Zeit 3, 81-89 (1985)]

b [http://www.elsie.brandeis.edu]

Hard Spherocylinders - a Modell for Anisotropic Colloids



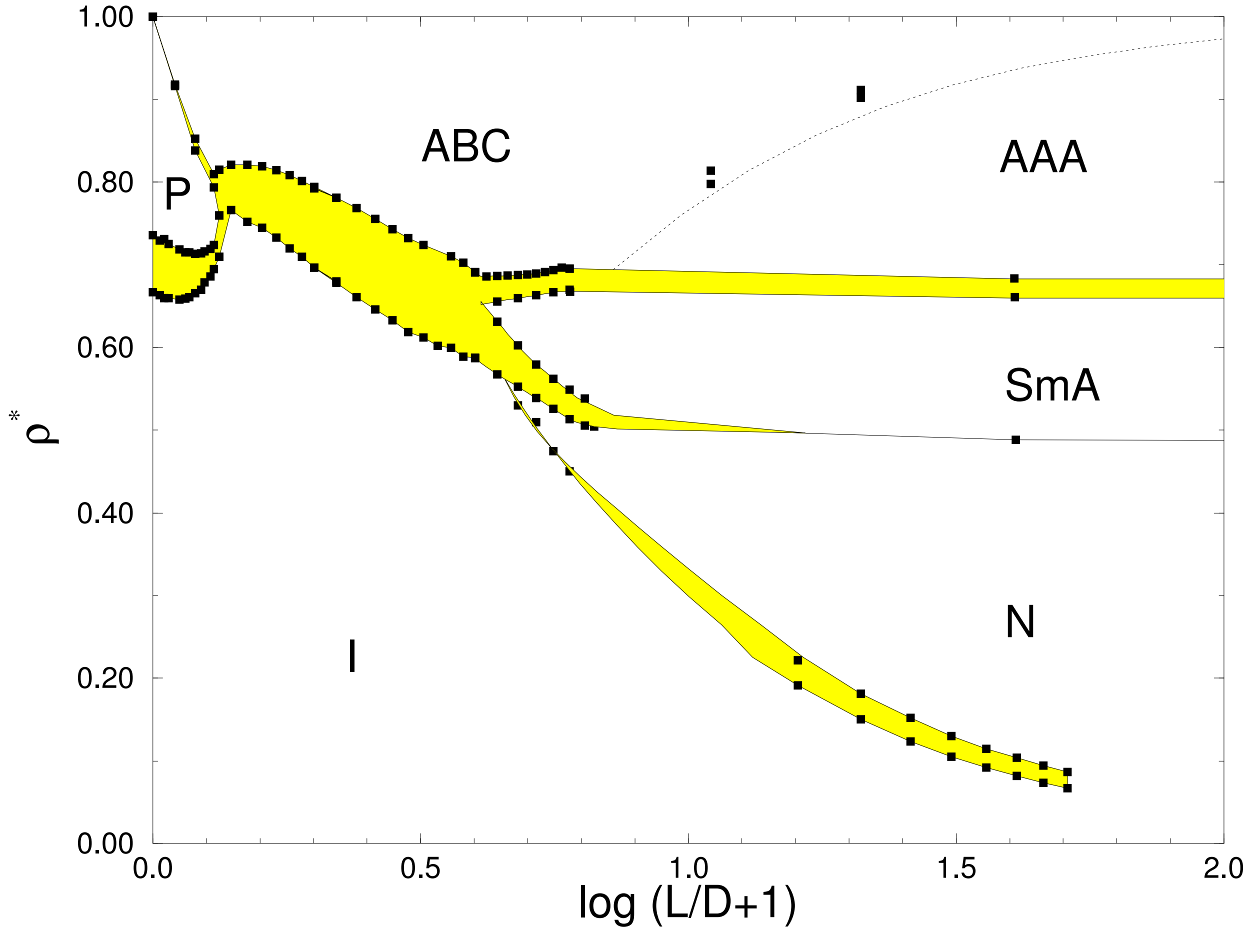
- Description of rod like particles as hard spherocylinders

- Pair potential:

$$V(\vec{r}_1, \vec{v}_1, \vec{r}_2, \vec{v}_2) = \begin{cases} \infty & \text{particles overlap} \\ 0 & \text{else} \end{cases}$$

- Purely entropic interaction

The Phase Diagram of Hard Spherocylinders



*[Peter Bolhuis, PHD-thesis, chapter 5 (1996)]

The Orientational Order-Parameter and Biaxiality

- $Q_{\alpha\beta} = \left\langle v^i_\alpha v^i_\beta - \frac{1}{3}\delta_{\alpha\beta} \right\rangle$
- Properties: traceless and symmetric
- Diagonalisation leads to

$$\underline{Q} = \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}S + \eta & 0 \\ 0 & 0 & -\frac{1}{3}S - \eta \end{pmatrix}$$

- Scalar order-parameter: $S_2 = \frac{3}{2}S$ (maximum eigenvalue)
- Biaxiality order-parameter: η
- Eigenvector to the maximum eigenvalue is called **director**

Methods to Obtain the IN-Interfacial Tension

Theory

- Onsager theory
- Beyond Onsager theory (Somoza-Tarazona)

Experimental Methods

- Experiments are complicated due to complex interactions, e.g. polydispersity and long range interactions

Computer Simulation Methods

- Pressure tensor methods $\gamma = \int (P_N - P_T) dz$ [*]
  $\longrightarrow$ prone to large statistical errors
  $\longrightarrow$ complicated when interactions are hard sphere like
- Capillary wave spectrum methods $\langle h(\vec{q}) \rangle \sim \frac{1}{\gamma}$ [†]
  $\longrightarrow$ requires large system sizes
  $\longrightarrow$ it is an approximation only
- **Grand canoncial Monte Carlo method**
  $\longrightarrow$ coexistence properties and interfacial properties can be probed.
  $\longrightarrow$ finite size scaling algorithms are available

[*] [Michael Allen, Chem.Phys.Lett. **331** (2000) 513-518]

[†] [Nobuhiko Akino, Friederike Schmid and Michael Allen, Phys.Rev. E **63**:041706, 2001]

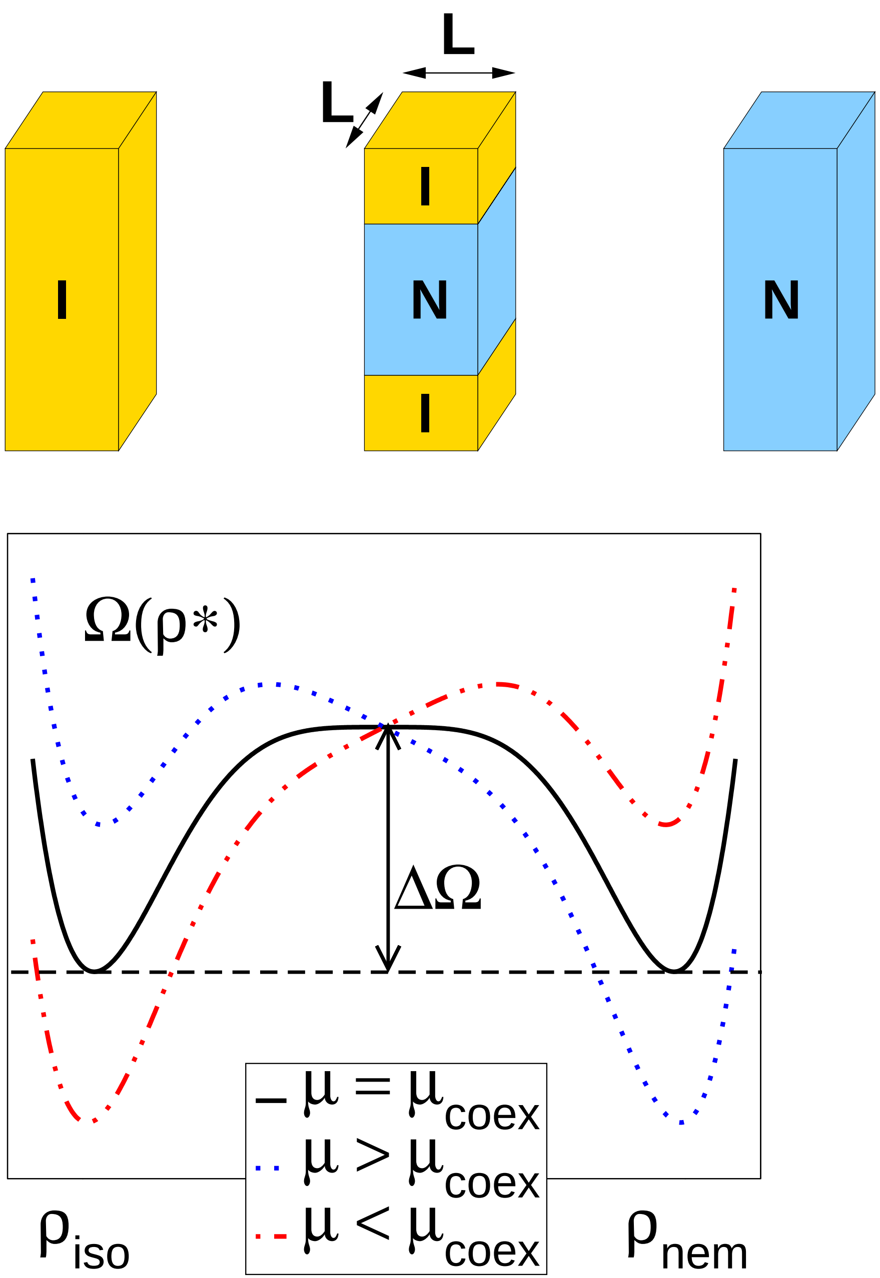
The Grand Canonical Monte Carlo Method

- Monte Carlo simulation with fixed μ, V, T
  $\rightarrow$ the number of particles N fluctuates
  $\rightarrow$ crucial quantity $P(\rho)$

- Relevant Monte-Carlo moves are particle insertion and removal

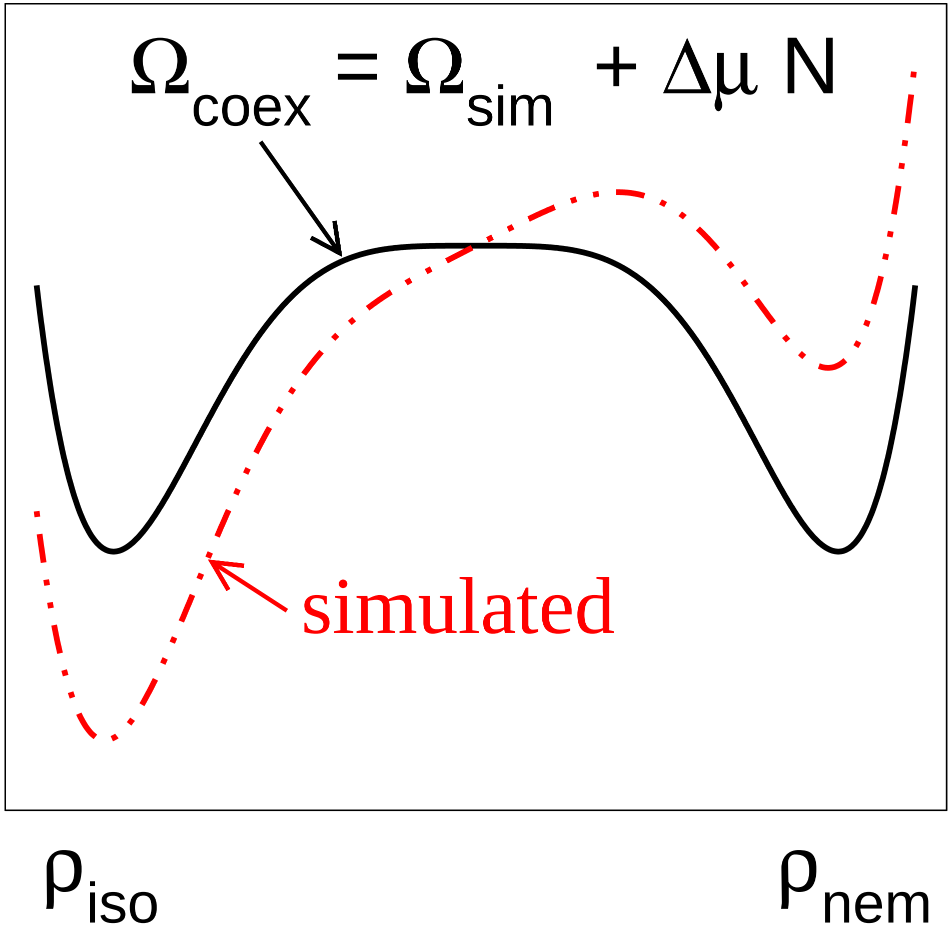
- Each step is accepted with a Metropolis criterion, depending on
  - Energy change ΔU (particle overlap)
  - Chemical potential μ
  - Volume V
  - Temperature T (in our case a trivial factor)

Simulation Methods



- At coexistence Ω exhibts a double-peak structure
- Peak locations give coexistence densities
- Flat region corresponds to interfacial state
- ΔΩ is the free energy cost of the interface
- IN-interfacial-tension $\gamma = \frac{\Delta\Omega}{(2L^2)}$

The Equal Area Rule

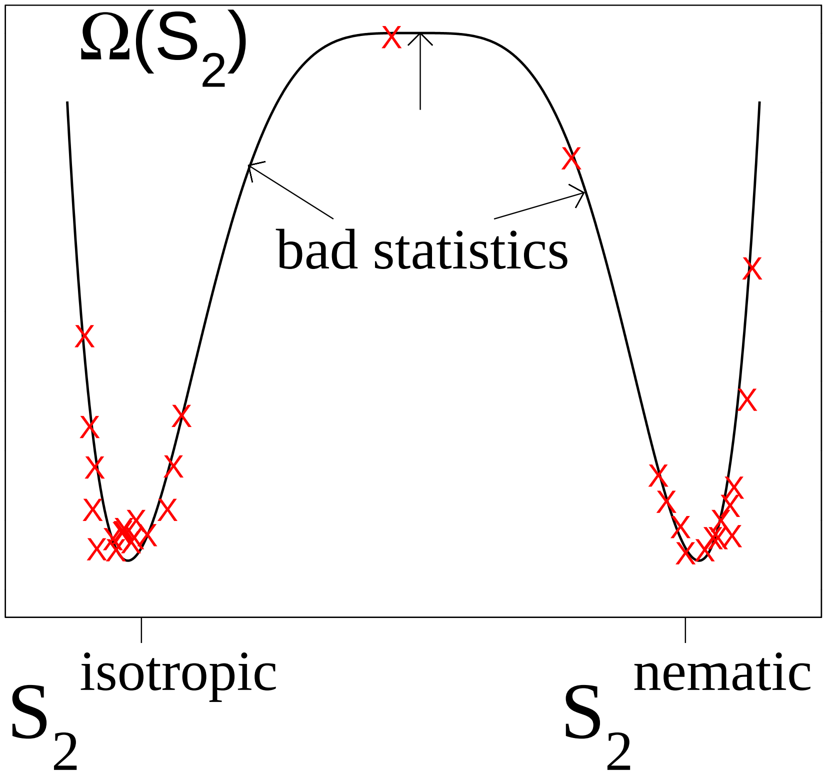


- γ and $\mu_{coex} = \mu_{sim} + \Delta\mu$ can be probed

Naive Grand Canonical Sampling

Configurations are accepted with probabiltiy

$$\propto \; e^{-\beta\,[U\,+\,\mu N\,]}$$



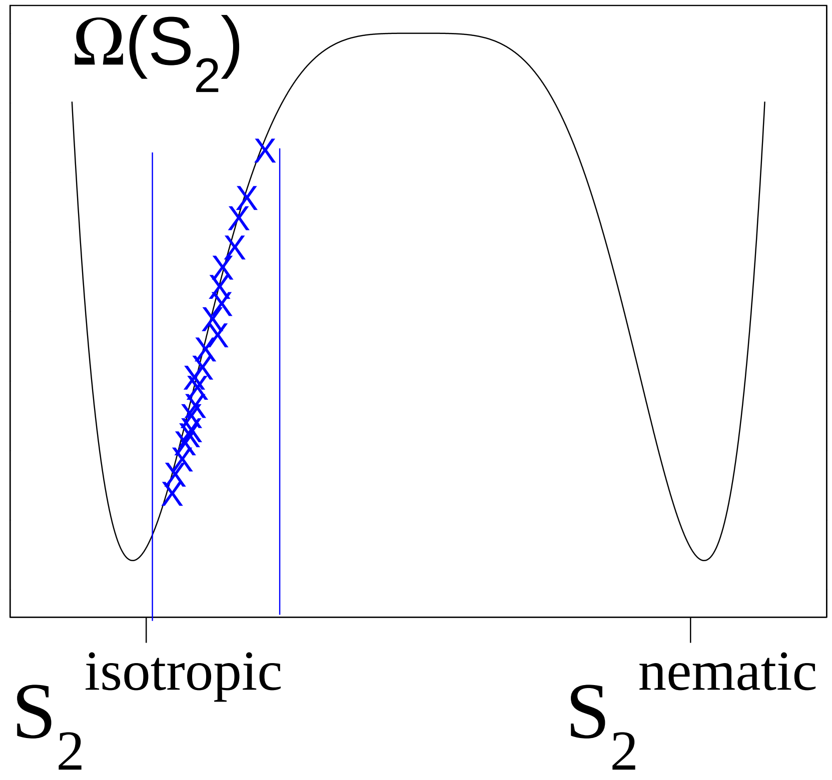
Umbrella Sampling Technique

- Introduce weight function

$$W\left(S_2\right) = e^{-\beta\left[k\left(S_2 - S_{20}\right)^2\right]}$$

- Sample with probability

$$\propto e^{-\beta\,[U\,+\,\mu N\,]} \times W\left(S_2\right)$$



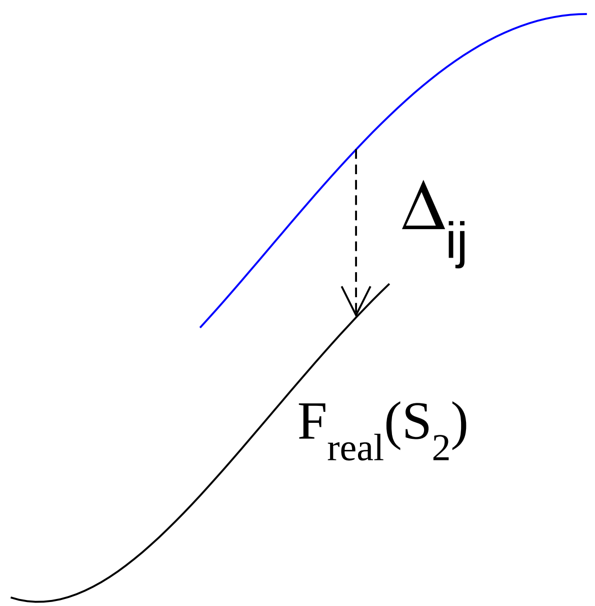
Histogram Reweighting

- Reweight the obtained distribution

$$P_{real}(S_2) = P_{biased}(S_2)/W(S_2)$$

$$\Omega_{real}(S_2) = \Omega_{biased}(S_2) - \beta\left[k(S_2 - S_{20})^2\right]$$

- Slopes match up to a constant



Simulation Details and Results

Input Needed for this Method:

- An estimate for the coexistance chemical potential μ_{coex}
  $\longrightarrow$ We measured the transition curves $\rho(\mu)$

- An estimate of the interfacial width
  $\longrightarrow$ We measured the density- and order-parameter profiles in an elongated system in coexistence

The Transition Curves $\rho(\mu)$ and $S_2(\mu)$

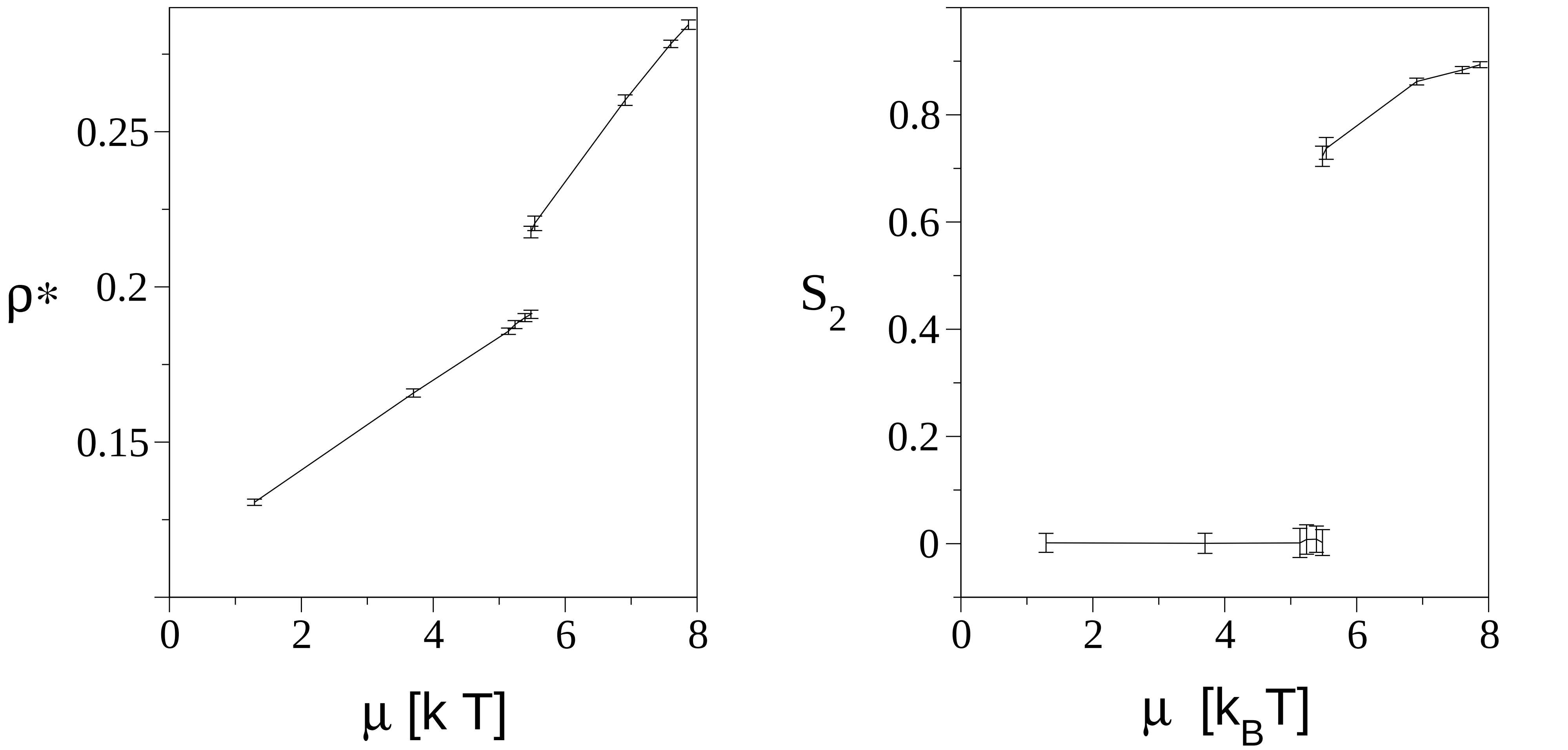
Simulation Setup

- Aspect ratios
  $L/D = 15, 20, 25, 30$

- Cubic boxes with sides $\sim 3.3L/D$

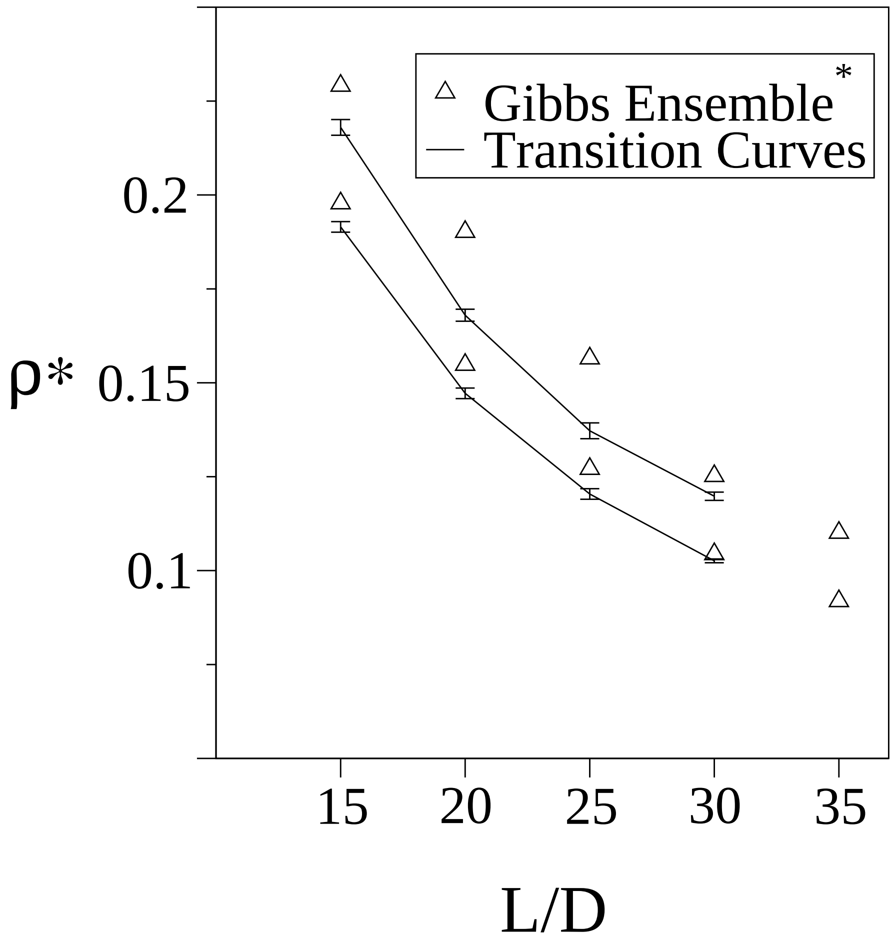
- Acceptance rate is only $\sim$ 0.006%!
  $\rightarrow$ we need a large number ($\sim 10^7$ per particle) of Monte Carlo steps
  $\rightarrow$ short rods (< 15) are **very expensiv** to compute

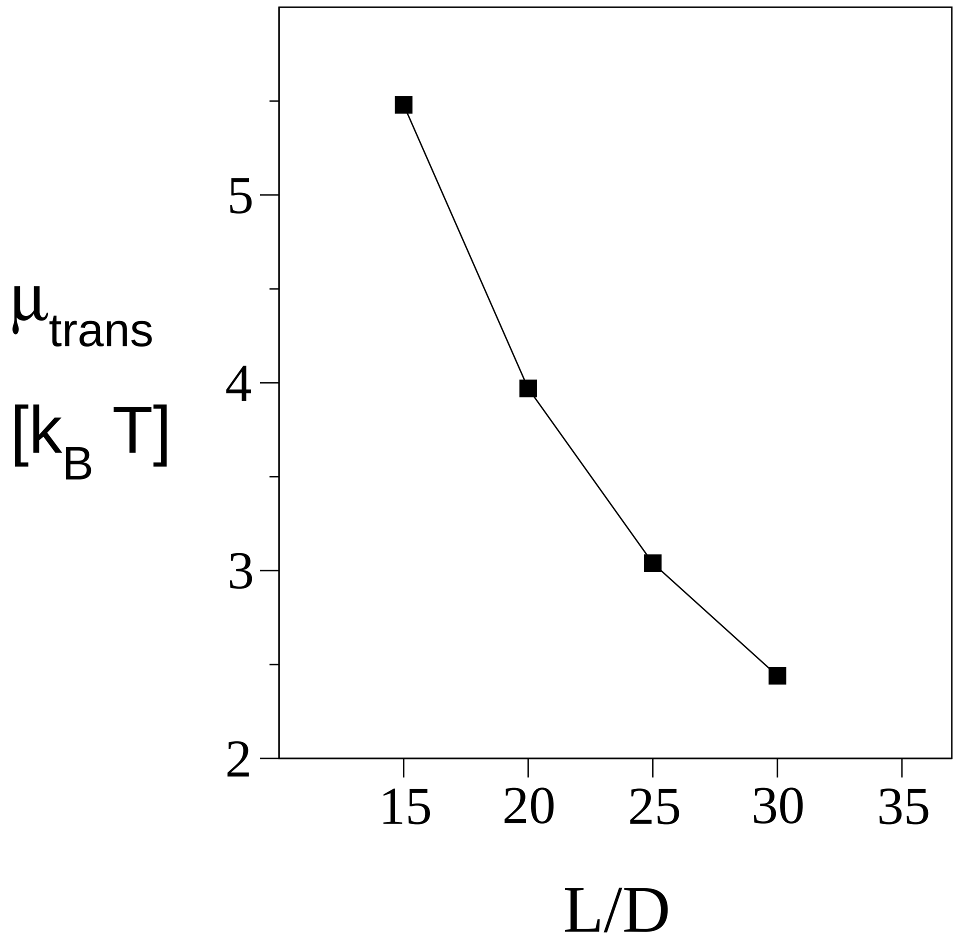
Result for $L/D = 15$



Simulation Details and Results

$\rho*_{trans}$ and μ_{trans} for Different Aspect Ratios

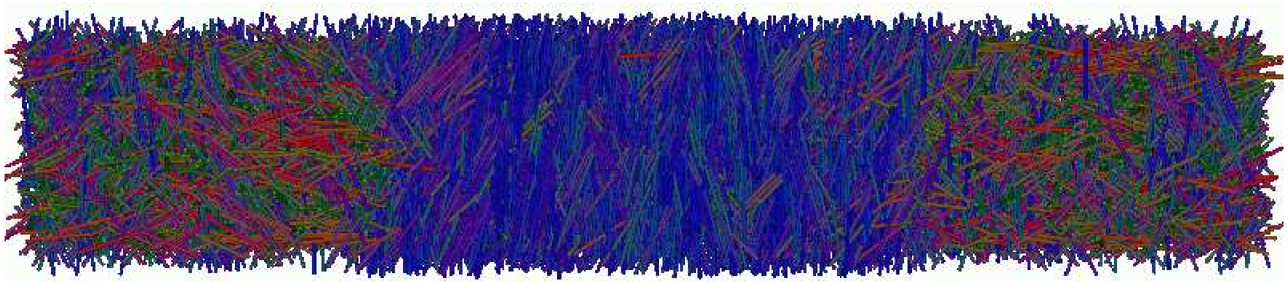




*[Peter Bolhuis, PHD-Thesis, Chapter 5 (1996)]

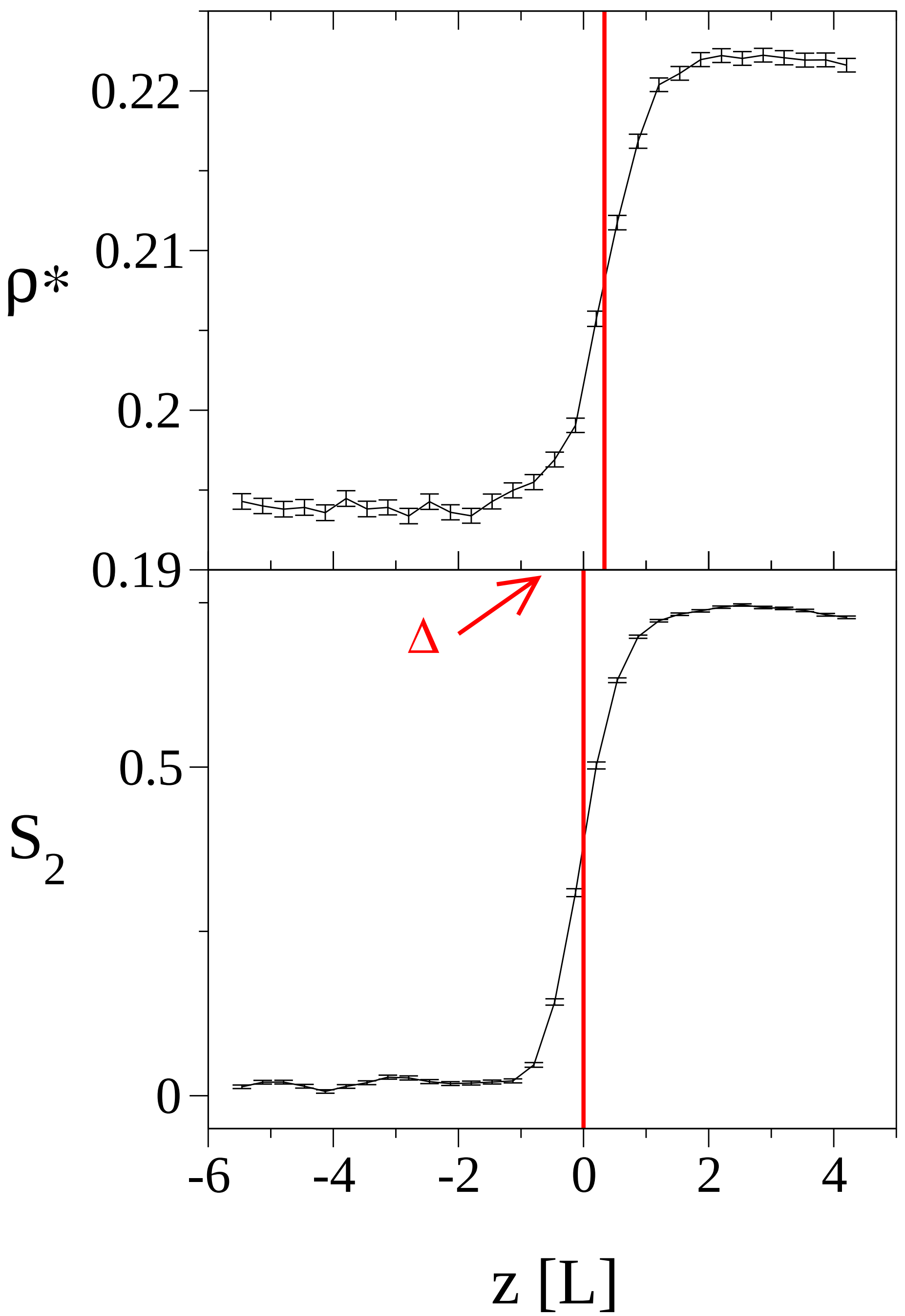
Simulation Details and Results

Density- and Order-Parameter Profiles



- Preparation of systems with 2 isotropic-nematic interfaces
  - Particles alined parallel to the plane of the interface
  - Box dimensions: $\sim 3.3L \times 3.3L \times 20L$
  - $\rho = \frac{1}{2}(\rho_i + \rho_n)$
  - Monte Carlo simulation in NVT-ensemble
    $\rightarrow$ Fixed number of particles
    $\rightarrow$ Positions and orientations are varied

Simulation Details and Results



- Profile $\frac{L}{D} = 15$, in plane
- Centers are shifted by $\Delta = 0.334L$
- In agreement with other simulation and theoretical investigations [a] [b]

[a][K.Shundyak, PhD Thesis (2004)]

[b][Muatz S. Al-Barwani, Michael Allen, Phys. Rev.E **62**, 6706 (2000)]

The IN-Interfacial Tension

Simulation Setup

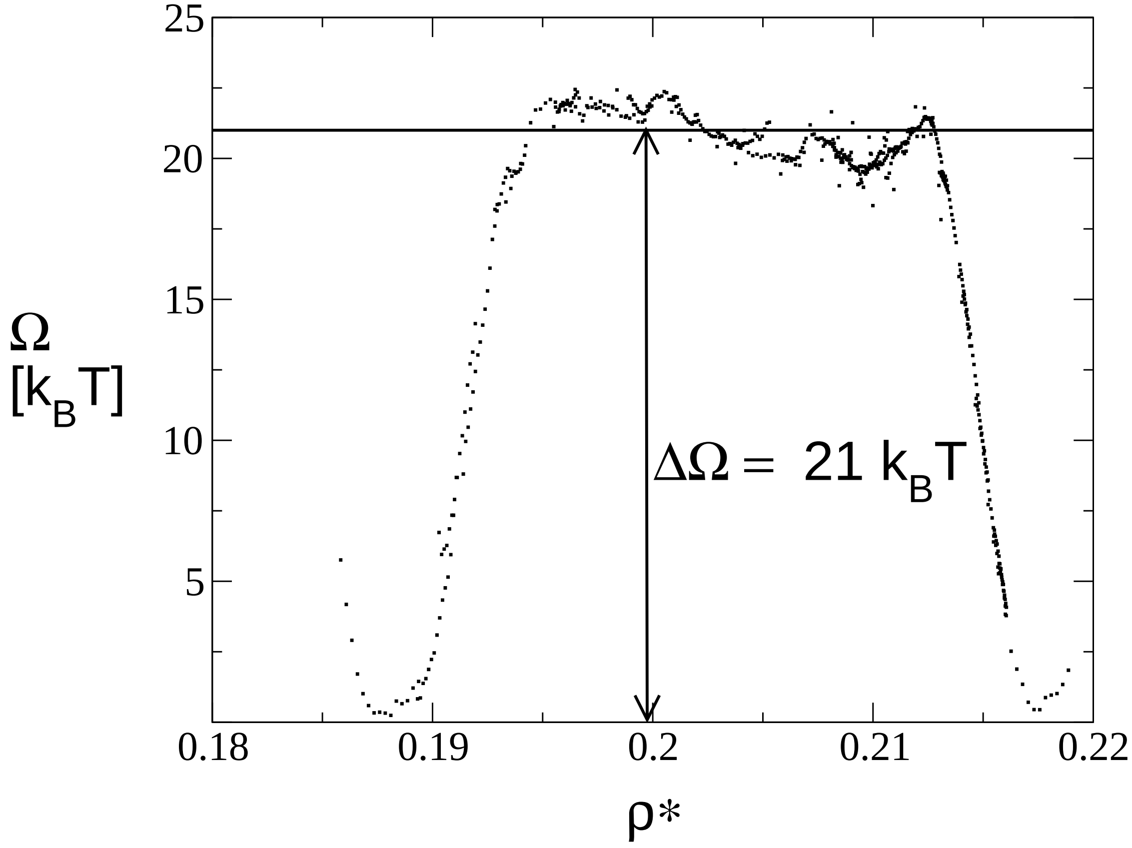
- Grand canonical Monte Carlo simulation with umbrella sampling
- Chemical potential near the coexistence value
- Aspect ratio $L/D = 15$
- Elongated boxes with dimensions $\sim 3.3L \times 3.3L \times 10L$

Results

- An estimate for the interfacial tension and μ_{coex}

$$\mu_{coex} \approx 5.4 k_B T$$

$$\gamma_{IN} \approx (0.063 \pm 0.009) \frac{k_B T}{LD}$$



IN-Interfacial Tension of Soft-Spherocylinders

- A modified model of soft spherocylinders [‡]
- Pair potential:

$$V(\vec{r}_1, \vec{v}_1, \vec{r}_2, \vec{v}_2) = \begin{cases} \epsilon & \text{particles overlap} \\ 0 & \text{else} \end{cases}$$

- Advantage: acceptance rate $\sim 6\%$
- same phase diagram, shifted densities
- $$\gamma_{soft} = 0.089 \frac{k_B T}{LD}$$

[‡] [Richard Vink, Tanja Schilling accepted by Phys.Rev.E, 2005]

Conclusion and Outlook

- We measured the transition curves $\rho\,(\mu)$ and $S_2\,(\mu)$ near μ_{coex} and profiles
- Profiles of the IN-Interface show agreements with theoretical predictions: We found a shift of $\frac{1}{3}L$ between the profiles
- The IN-Tension could be estimated by grand canonical monte-carlo. It is lower than theoretical estimates
- How does the IN-Tension depend on the tilt angle between director and interfacial plane?
- How one can adapt finite size scaling algorithms for isotropic systems to anisotropic systems ?

References and Acknowledgment

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