Numerical simulation for wormlike chains in two-dimensional confinement

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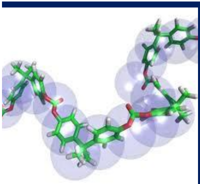
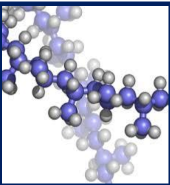
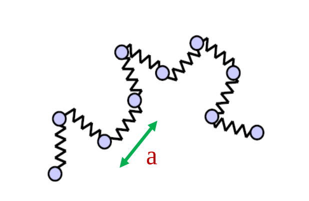
Outline

Motivation

Bead-spring model

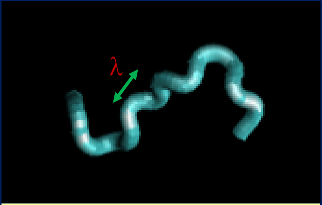


a: Kuhn length; bond length

L=Na: total contour length;

N: number of monomers

Wormlike chain



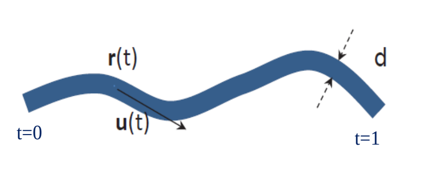
λ: persistence length (a=2λ)

L: total contour length;

N=L/a: number of segments

Motivation

Wormlike-chain model



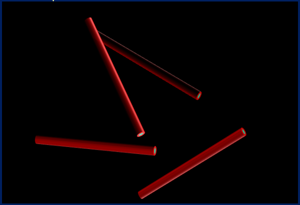
L: total contour length

λ: persistence length

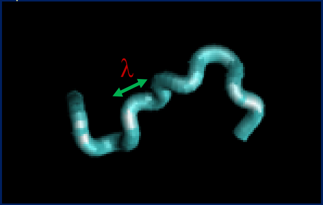
$$\langle \mathbf{u}(t) \cdot \mathbf{u}(t') \rangle = e^{-|t-t'|L/\lambda}$$

$L/\lambda \ll 1$

$L/\lambda \gg 1$



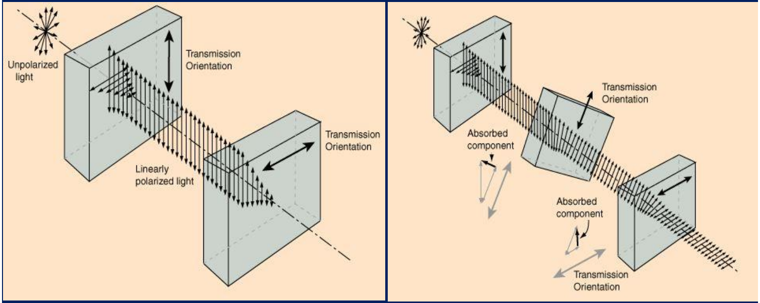
Rodlike limit



Flexible limit

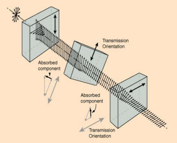
Motivation

Cross-polarization experiment



Motivation

Cross polarization image



Molecular distribution $\rho(\mathbf{r}, \mathbf{u})$

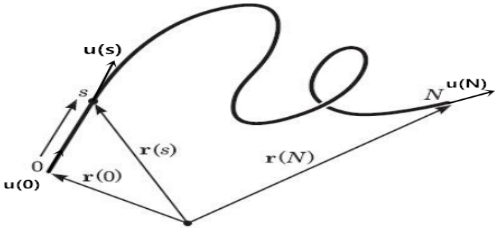
u-dependence: orientational ordering (nematic)

r-dependence: positional ordering (spatial inhomogeneity)

Singularity in the distribution function --- defect

Continuum chain model

Wormlike chain model describes a semiflexible polymer chain by a continuum space curve.

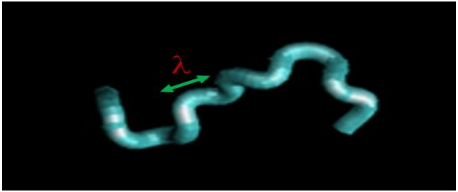


- $\mathbf{r}(s)$: a location parameter;
- $\mathbf{u}(s)$: a direction parameter;
- $\mathbf{u}(s)$ satisfies $\mathbf{u}(s) = \mathrm{d}\mathbf{r}(s)/\mathrm{d}s$ and $|\mathbf{u}(s)| = 1$.

Continuum wormlike chain model

L is the total length and λ is persistence length. The ratio describes the flexibility of the chain and satisfies

$$< \mathbf{u}(s), \mathbf{u}(s') >= \exp(\frac{-|s-s'|L}{\lambda}).$$



- Gaussian chain is flexible with $\lambda << L$;
- Wormlike chain is semi-flexible with $\lambda \sim L$;
- rod is rigid with $\lambda >> L$.

Related works

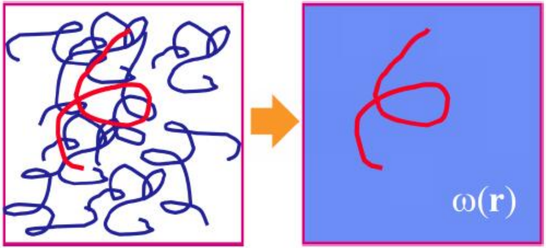
1. Jeff Z.Y.Chen, *Progress in Polymer Science*, 2015.
2. Jeff Z.Y.Chen, *Soft Matter*, 2013.
3. Q. Liang,J.F. Li,P.W. Zhang, Jeff Z.Y.Chen, *J.Chem.Phys.*, 2014.
4. C. Luo, A. Majumdar, R. Erban, *Phys. Rev. E*, 2012.
5. M. Robinson, C. Luo, P.E. Farrellc, R. Erbanc, A. Majumdar, *Liquid Crystals*, 2017.

Self-consistent field theory (SCFT)

The mean field W is introduced to summarize the universal interaction between segments. W can be described by density distribution ρ, but ρ is determined by field W conversely.

$$W = W[\rho]$$

$$\rho = \rho[W]$$



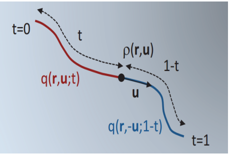
Self-consistent field theory (SCFT)

- $q(\mathbf{r}, \mathbf{u}; s)$: probability distribution function of find segment s locating at position $\mathbf{r}$ and pointing at $\mathbf{u}$.

$$\partial_s q(\mathbf{r}, \mathbf{u}; s) = [-W(\mathbf{r}, \mathbf{u}) - L\mathbf{u} \cdot \nabla_{\mathbf{r}}|_{\mathbf{u}} + \frac{L}{2\lambda}\nabla^2_{\mathbf{u}}] q(\mathbf{r}, \mathbf{u}; s), \quad (1)$$

- The partition function of the wormlike chain

$$Q = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{u} q(\mathbf{r}, \mathbf{u}; s = 1). \quad (2)$$



- $\rho(\mathbf{r}, \mathbf{u})$ is the density distribution, N is the number of chains.
$\rho(\mathbf{r}, \mathbf{u}) = \frac{N}{Q} \int_0^1 \mathrm{d}s q(\mathbf{r}, \mathbf{u}; s) q(\mathbf{r}, -\mathbf{u}; 1 - s)$, $\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{u} \rho(\mathbf{r}, \mathbf{u}) = N$.

Self-consistent field theory (SCFT)

The reduced free energy of the system is

$$\beta F = N \ln(N/Q) - \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{u} W(\mathbf{r},\mathbf{u})\rho(\mathbf{r},\mathbf{u}) + \frac{L^2}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{u}\int \mathrm{d}\mathbf{u}'\rho(\mathbf{r},\mathbf{u})|\mathbf{u}\times\mathbf{u}'|\rho(\mathbf{r},\mathbf{u}'). \tag{3}$$

The minimization of the energy with respect to $\rho(\mathbf{r},\mathbf{u})$ gives

$$\frac{\partial(\beta F)}{\partial\rho} = 0 \Rightarrow W(\mathbf{r},\mathbf{u}) = L^2\int \mathrm{d}\mathbf{u}'|\mathbf{u}\times\mathbf{u}'|\rho(\mathbf{r},\mathbf{u}).$$

The procedure of SCFT

1. give an initial guess for $W(\mathbf{r}, \mathbf{u})$;
2. calculate $q(\mathbf{r}, \mathbf{u}; s)$ from solving MDE

$$\frac{\partial}{\partial s} q(\mathbf{r}, \mathbf{u}; s) = [-W(\mathbf{r}, \mathbf{u}) - L\mathbf{u} \cdot \nabla_{\mathbf{r}}|_{\mathbf{u}} + \frac{L}{2\lambda} \nabla^2_{\mathbf{u}}] q(\mathbf{r}, \mathbf{u}; s);$$

3. obtain Q and $\rho(\mathbf{r}, \mathbf{u})$

$$Q = \int \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{u} q(\mathbf{r}, \mathbf{u}, 1),$$

$$\rho(\mathbf{r}, \mathbf{u}) = \frac{N}{Q} \int_0^1 \mathrm{d}s q(\mathbf{r}, \mathbf{u}; s) q(\mathbf{r}, -\mathbf{u}; 1 - s);$$

4. update field $W(\mathbf{r}, \mathbf{u})$ with

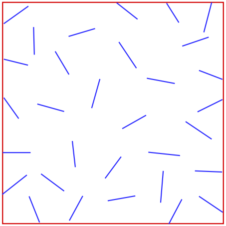
$$W(\mathbf{r}, \mathbf{u}) = L^2 \int \mathrm{d}\mathbf{u}' |\mathbf{u} \times \mathbf{u}'| \rho(\mathbf{r}, \mathbf{u});$$

5. come to step 2 until $W(\mathbf{r}, \mathbf{u})$ convergers.

Outline

Rods situation with $L/\lambda = 0$

N rods confined in a rectangle with side lengths a and b. Set $\mathbf{r}$ to be $(x, y) \in [0, a] \times [0, b]$ and $\mathbf{u}$ to be $(\cos\theta, \sin\theta)$ with $\theta \in [0, 2\pi]$.



Due to the above steps of the *SCFT*, finding the solutions of the *MDE* turns to be an important step. $W(\mathbf{r}, \mathbf{u}) \neq 0$

$$\frac{\partial}{\partial s} q(\mathbf{r}, \mathbf{u}; s) = [-W(\mathbf{r}, \mathbf{u}) - L\mathbf{u} \cdot \nabla_{\mathbf{r}}|_{\mathbf{u}} + \frac{L}{2\lambda} \nabla^2_{\mathbf{u}}] q(\mathbf{r}, \mathbf{u}; s);$$

Rods situation with $L/\lambda = 0$

That is $\frac{L}{2\lambda}\nabla_{\mathbf{u}}^2 q(\mathbf{r},\mathbf{u};s) = 0$ and $\mathbf{u}(s) = \mathrm{d}\mathbf{r}(s)/\mathrm{d}s$

$$\partial_s q(x,y,\theta;s) = [-L\cos\theta\partial_x - L\sin\theta\partial_y - W(x,y,\theta)]q(x,y,\theta;s),$$

B.C.

$$q(0,y,\theta;s) = 0, \quad q(a,y,\theta;s) = 0, \;\; s \neq 0,$$
$$q(x,0,\theta;s) = 0, \quad q(x,b,\theta;s) = 0, \;\; s \neq 0,$$
$$q(x,y,0;s) = q(x,y,2\pi;s),$$

I.C.

$$q(x,y,\theta;0) = 1.$$

Upwind scheme is used to solve the problem.

Numerical schemes

Operator splitting:

$$q_{i,j,k}^{n+1} = q_{i,j,k}^{n} + \widehat{H}_x q_{i,j,k}^{n+1} + \widehat{H}_y q_{i,j,k}^{n+1} + H_W q_{i,j,k}^{n+1}. \qquad (4)$$

Here $H_W = -\Delta s W_{i,j,k}$ and the operators $\widehat{H}_x$ and $\widehat{H}_y$ yield

$$\widehat{H}_x q_{i,j,k}^{n+1} = \begin{cases} -L\cos\theta_k \frac{\Delta s}{\Delta x}(q_{i,j,k}^{n+1} - q_{i-1,j,k}^{n+1}), (\textit{left wind}) & \cos\theta_k \geq 0, \\ -L\cos\theta_k \frac{\Delta s}{\Delta x}(q_{i+1,j,k}^{n+1} - q_{i,j,k}^{n+1}), (\textit{right wind}) & \cos\theta_k < 0. \end{cases}$$

$$\widehat{H}_y q_{i,j,k}^{n+1} = \begin{cases} -L\sin\theta_k \frac{\Delta s}{\Delta y}(q_{i,j,k}^{n+1} - q_{i,j-1,k}^{n+1}), (\textit{left wind}) & \sin\theta_k \geq 0, \\ -L\sin\theta_k \frac{\Delta s}{\Delta y}(q_{i,j+1,k}^{n+1} - q_{i,j,k}^{n+1}), (\textit{right wind}) & \sin\theta_k < 0 \end{cases}$$

Mass distribution

$$\phi(x,y) = \int_0^{2\pi} f(x,y,\theta)\mathrm{d}\theta,$$

$$f(\mathbf{r},\mathbf{u}) = \frac{n}{\rho Q}\int_0^1 \mathrm{d}s q(\mathbf{r},\mathbf{u};s)q(\mathbf{r},-\mathbf{u};1-s).$$

Order parameters

$$S(x,y) = \int_0^{2\pi} \mathrm{d}\theta \cos(2\theta) f(x,y,\theta)/\phi(x,y),$$

$$T(x,y) = \int_0^{2\pi} \mathrm{d}\theta \sin(2\theta) f(x,y,\theta)/\phi(x,y),$$

$$\Lambda(x,y) = \sqrt{S^2(x,y) + T^2(x,y)}.$$

Light intensity for α-crossed-polarizer

$$I_\alpha(x,y) = \frac{1}{4}\int_0^{2\pi} \mathrm{d}\theta[\sin(2\theta - 2\alpha)]^2 f(x,y,\theta)$$

- Location where $\Lambda(x,y) = 0$ is taken as defect points.

Three most relevant, dimensionless parameters that control the type of resulting nematic patterns in these systems.

- b/a: the aspect ratio of a confining rectangle, where a and b are the short- and long-side lengths.
- a/L: the box-rod size ratio, where L is the length of a rodlike particle, define the confinement geometry.
- $L^2\rho \equiv L^2 n/ab$: determines the degree of orientational ordering in a system consisting of n sterically repelling particles.

Figure1: $a = b$

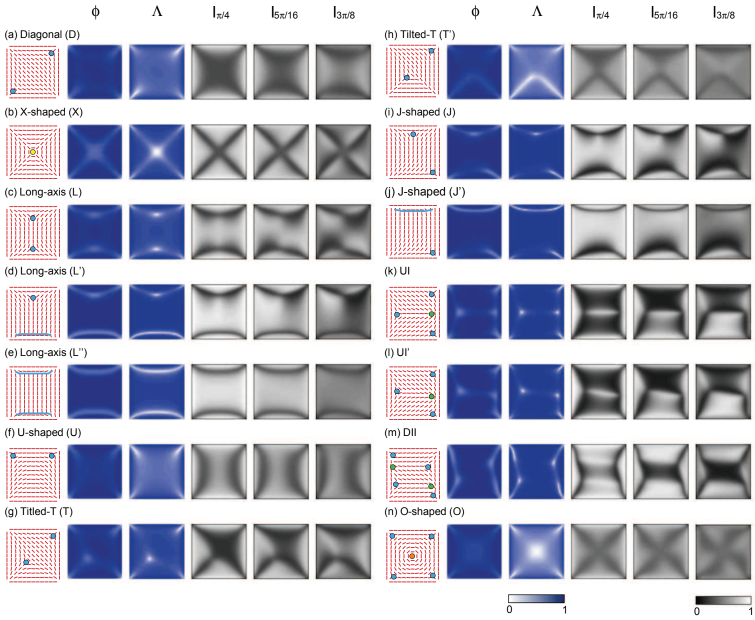
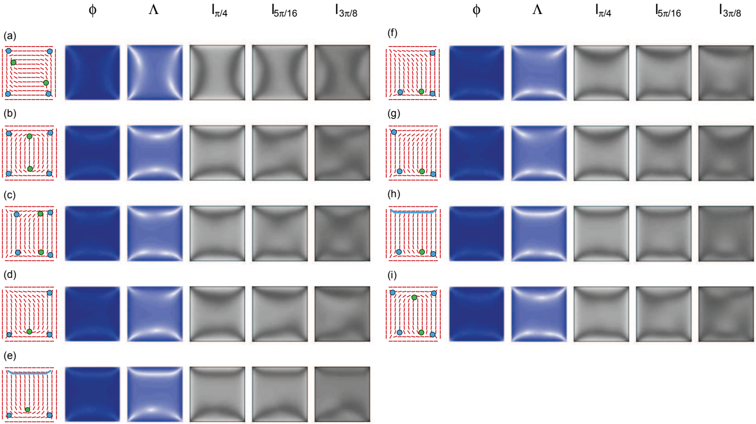

ϕ
Λ
$I_{\pi/4}$
$I_{5\pi/16}$
$I_{3\pi/8}$
(a) Diagonal (D)
(b) X-shaped (X)
(c) Long-axis (L)
(d) Long-axis (L')
(e) Long-axis (L'')
(f) U-shaped (U)
(g) Titled-T (T)
(h) Tilted-T (T')
(i) J-shaped (J)
(j) J-shaped (J')
(k) UI
(l) UI'
(m) DII
(n) O-shaped (O)
0
1
0
1

Figure2: $a = b$



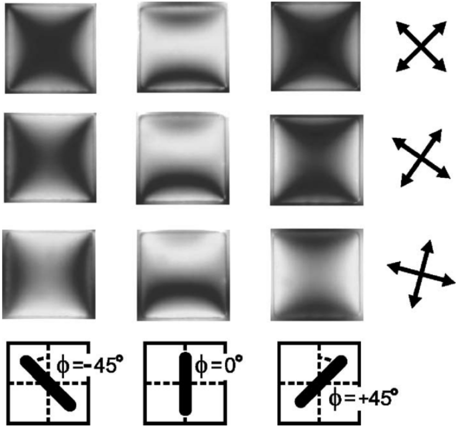
- blue point $\mapsto$ -1/2 defect
  yellow point $\mapsto$ -1 defect
  green point $\mapsto$ 1/2 defect
  orange point $\mapsto$ 1 defect
  The total values of defects add up to -1 for each structure.

- The system displays both density and orientational field defects by contrasting $\phi(x, y)$ and $\Lambda(x, y)$.

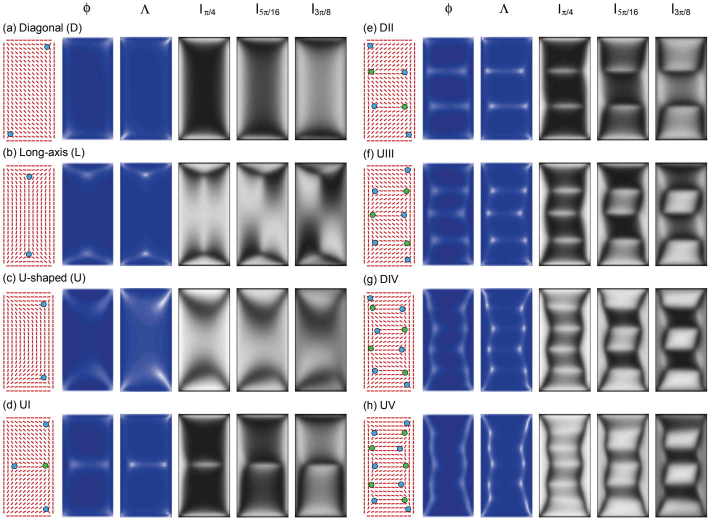
- When a/L becomes small,
  the two defects in (D) and (L) will draw closer to each other;
  the middle two defects in (UI) will vanish then the structure turns into (U).

Discovery

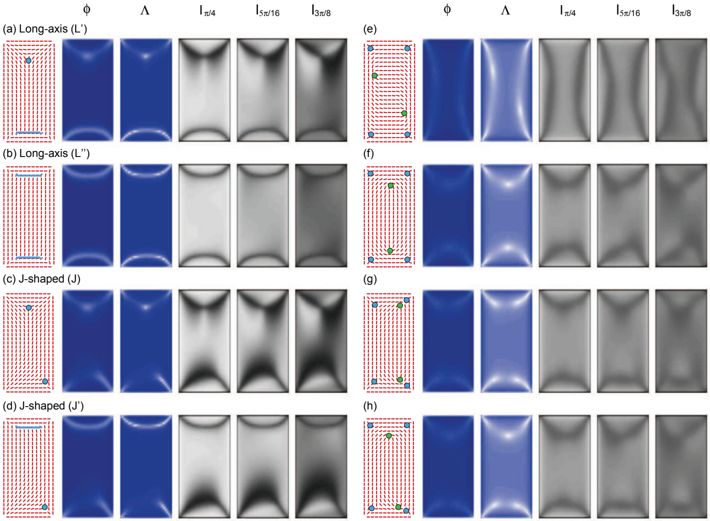
- Tsakonas *et al* [APL,2007] reported light intensity images observed by crossed polarizers, which is nearly identical to $I_{\pi/4}, I_{5\pi/16}, I_{3\pi/8}$ of (D) and (U).



Numerical results: $a \neq b$

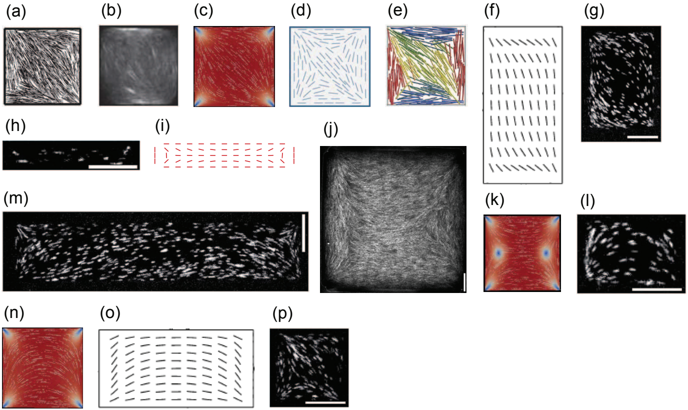


Numerical results: $a \neq b$



Discovery

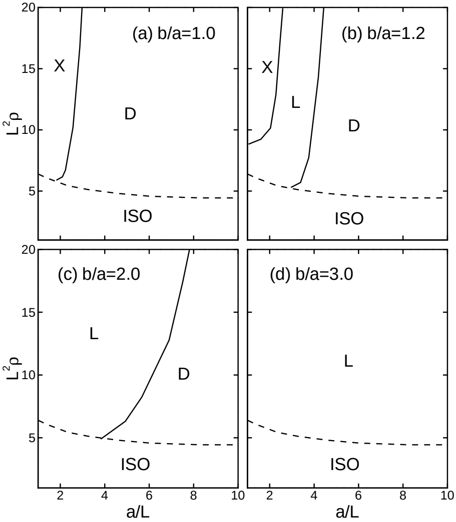
- Some of the above structures have been seen from experiments (black figures).



Some figures are from following authors' works: Louis Cortes, Bela Mulder, Wolfgang Losert, Apala Majumdar, et al.

Phase diagram

Phase diagram in terms of a/L and $L^2\rho$ for $b/a = 1, 1.2, 2, 3$.

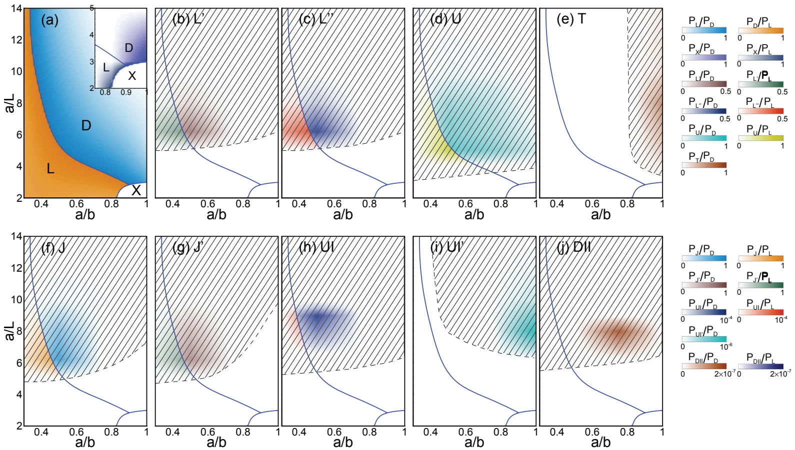


Stable and metastable

- Structures in figure1 [except T' and O] are always stable or metastable in most parameters region($L^2\rho \gtrsim 5, a/L \gtrsim 5$);
- T', O, and structures in figure2 can only exist when $L^2\rho$ is low($\lesssim 6$) and a/L is high($\gtrsim 8$);

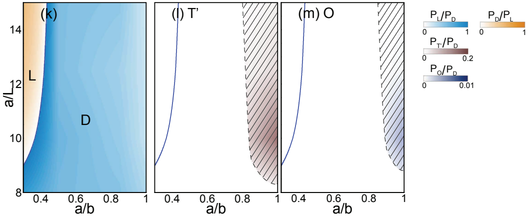
Stable and metastable for figure1

- Phase diagram for $L^2\rho = 10$ fixed and the probabilities for appearance of metastable states.



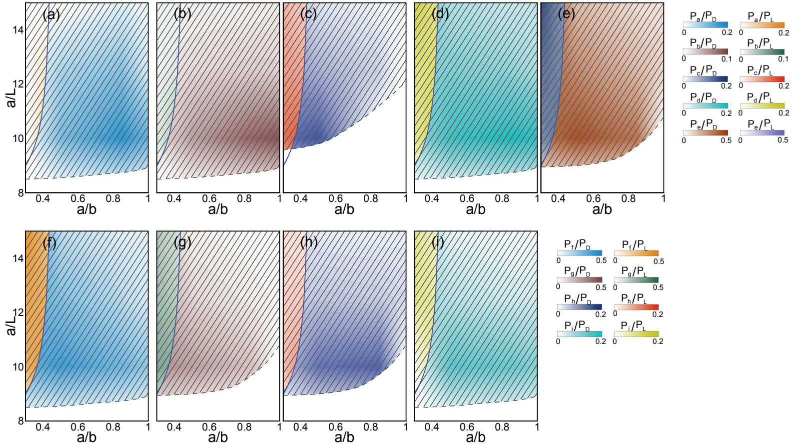
Stable and metastable for figure1

- Phase diagram for $L^2\rho = 6$ fixed and the probabilities for appearance of metastable states.



Stable and metastable for figure2

- Phase diagram for $L^2\rho = 6.0$ fixed and the probabilities for appearance of metastable states.

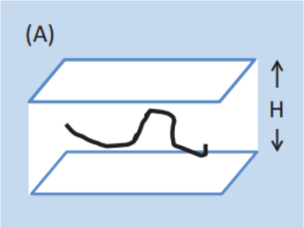


Outline

Problem description for a single chain

To analyze the behavior of one wormlike polymer sterically confined between two parallel, structureless walls, separated by a distance H when changing H, L, λ .

As it is a singe chain, no field W. Solve the MDE in confined region.

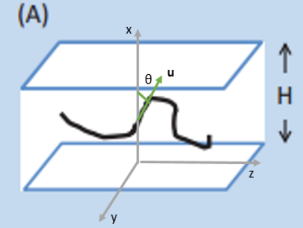


Two special cases: strong confinement($H << \lambda$) and weak confinement($H >> \lambda$).

Numerical schemes

Consider MDE equation: $W(\mathbf{r}, \mathbf{u}) = 0$

$$\frac{\partial}{\partial s} q(\mathbf{r}, \mathbf{u}; s) = \left(-L\mathbf{u} \cdot \nabla_{\mathbf{r}} + L[(\mathbf{u} \cdot \nabla_{\mathbf{r}})\mathbf{u}] \cdot \nabla_{\mathbf{u}} + \frac{L}{2\lambda} \nabla_{\mathbf{u}}^2\right) q(\mathbf{r}, \mathbf{u}; s). \quad (5)$$



Set $\mathbf{u} = \cos\theta \ x + \sin\theta \cos\varphi \ y + \sin\theta \sin\varphi \ z$, where $x = x/H$.

- $\theta \in [0, \pi], \varphi \in [0, 2\pi]$,
- y, z: translation invariance; x: rotational invariance.

Numerical schemes

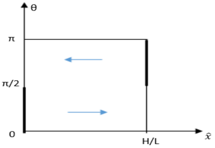
$$\frac{\partial}{\partial s}q(x,\theta;s) = \left(-\frac{L}{H}\cos\theta\frac{\partial}{\partial x} + \frac{L}{2\lambda}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta})\right)q(x,\theta;s). \tag{6}$$

I.C.

$$q(x,\theta;0) = 1.$$

B.C.

$$\begin{aligned} q(0,\theta;s) &= 0, \quad \textit{if } \theta \in [0,\pi/2) \textit{ and } s \neq 0, \\ q(1,\theta;s) &= 0, \quad \textit{if } \theta \in (\pi/2,\pi] \textit{ and } s \neq 0, \\ \frac{\partial}{\partial\theta}q(x,0;s) &= 0, \quad \frac{\partial}{\partial\theta}q(x,\pi;s) = 0. \end{aligned}$$



Numerical schemes

Operator splitting:

$$O_1 q(x,\theta;s) = -\frac{L}{H}\cos\theta\frac{\partial}{\partial x}q(x,\theta;s), \tag{7}$$

$$O_2 q(x,\theta;s) = \frac{L}{2\lambda}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}q(x,\theta;s)\right), \tag{8}$$

then

$$q(x,\theta;s+h) = e^{\frac{h}{2}O_1}e^{hO_2}e^{\frac{h}{2}O_1}q(x,\theta;s). \tag{9}$$

- Upwind scheme of O_1:

$$\frac{q_{j,k}^{n+1}-q_{j,k}^{n}}{\Delta s} = -\frac{L}{H}\cos\theta_k\frac{q_{j,k}^{n+1}-q_{j-1,k}^{n+1}}{\Delta x}, (\textit{left wind})\ \theta_k\in[0,\pi/2];$$

$$\frac{q_{j,k}^{n+1}-q_{j,k}^{n}}{\Delta s} = -\frac{L}{H}\cos\theta_k\frac{q_{j+1,k}^{n+1}-q_{j,k}^{n+1}}{\Delta x}, (\textit{right wind})\ \theta_k\in[\pi/2,\pi].$$

Numerical schemes

- Operator O_2: central difference scheme.

$$O_2 q(x,\theta;s) = \frac{L}{2\lambda}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}q(x,\theta;s)\right),$$

when $\theta \to 0$, $\frac{\cos\theta}{\sin\theta}\frac{\mathrm{d}q}{\mathrm{d}\theta} < \infty$, $\lim_{\theta\to 0}\frac{\cos\theta}{\sin\theta}\frac{\mathrm{d}q}{\mathrm{d}\theta} = \lim_{\theta\to 0}\frac{\frac{\mathrm{d}q}{\mathrm{d}\theta}}{\theta} = \lim_{\theta\to 0}\frac{\mathrm{d}^2 q}{\mathrm{d}\theta^2}$,

$$\lim_{\theta\to 0}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}q)\right) = \lim_{\theta\to 0}\left(\frac{\cos\theta}{\sin\theta}\frac{\mathrm{d}q}{\mathrm{d}\theta} + \frac{\mathrm{d}^2 q}{\mathrm{d}\theta^2}\right) = \lim_{\theta\to 0}\left(2\frac{\mathrm{d}^2 q}{\mathrm{d}\theta^2}\right).$$

We get

$$O_2 q(x,\theta;s) = \frac{L}{\lambda}\frac{\mathrm{d}^2}{\mathrm{d}\theta^2}q(x,\theta;s) \quad (\theta \to 0),$$
$$O_2 q(x,\theta;s) = \frac{L}{\lambda}\frac{\mathrm{d}^2}{\mathrm{d}\theta^2}q(x,\theta;s) \quad (\theta \to \pi).$$

Numerical schemes

The central difference scheme of O_2 :

$\theta \in (0, \pi)$:

$$\frac{q_{j,k}^{n+1} - q_{j,k}^{n}}{\Delta s} = \frac{L}{2\lambda}\frac{1}{\sin\theta_k}\frac{1}{\Delta\theta}\left(\sin\theta_{k+\frac{1}{2}}\frac{q_{j,k+1}^{n+1} - q_{j,k}^{n+1}}{\Delta\theta} - \sin\theta_{k-\frac{1}{2}}\frac{q_{j,k}^{n+1} - q_{j,k-1}^{n+1}}{\Delta\theta}\right),$$

$\theta = 0,\ \pi$:

$$\frac{q_{j,k}^{n+1} - q_{j,k}^{n}}{\Delta s} = \frac{L}{\lambda}\frac{q_{j,k+1}^{n+1} - 2q_{j,k}^{n+1} + q_{j,k-1}^{n+1}}{\Delta\theta^2}.$$

Numerical Results

Mass distribution $\rho(x) = \frac{\int \rho(x,\theta) d\theta}{\int \rho(x,\theta) dx d\theta}$,

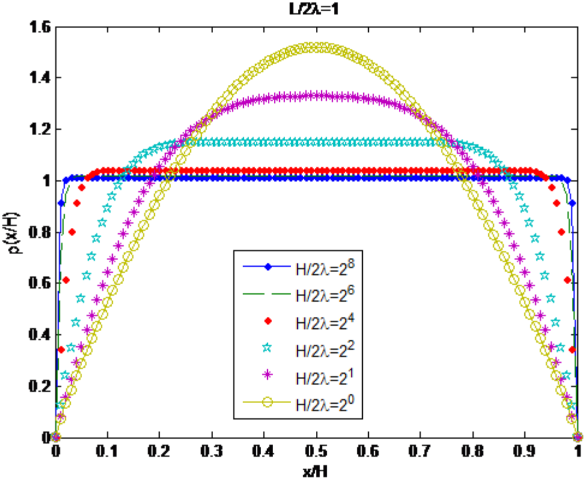
Direction distribution $\rho(\theta) = \frac{\int \rho(x,\theta) dx}{\int \rho(x,\theta) dx d\theta}$.

Then consider

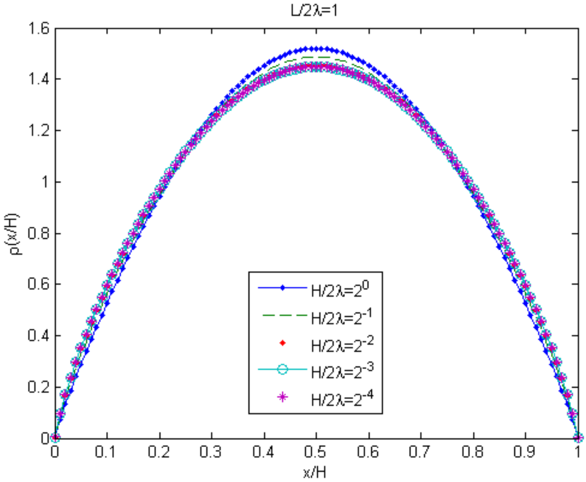
- Fix L,λ and decrease H.
- Fix λ,H and increase L.
- Fix H,L and increase λ.

Fix L,λ and decrease H

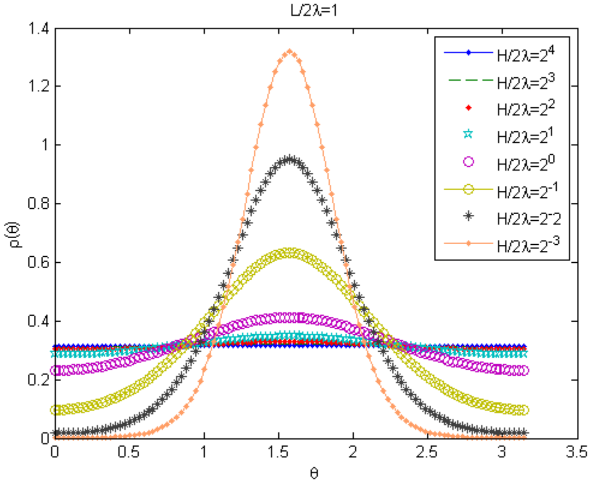
Picture of $\rho(x)$:



Picture of $\rho(x)$:

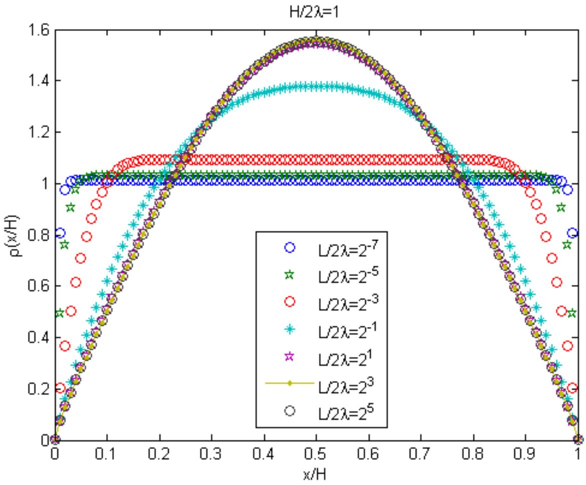


Picture of $\rho(\theta)$:

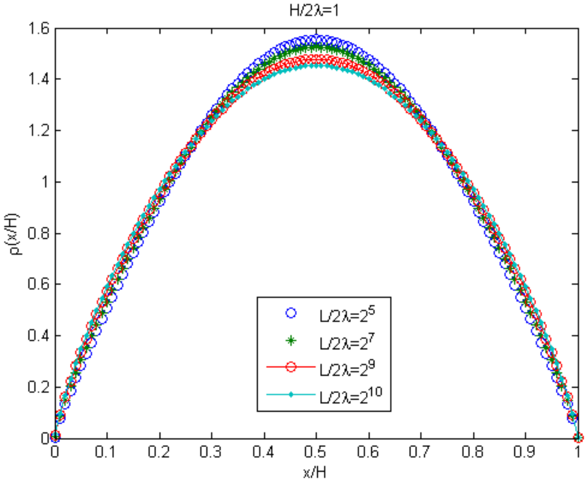


Fix λ,H and increase L.

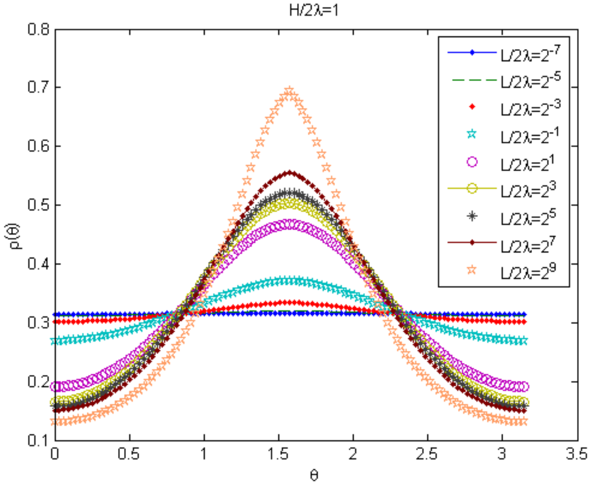
Picture of $\rho(x)$:



Picture of $\rho(x)$:

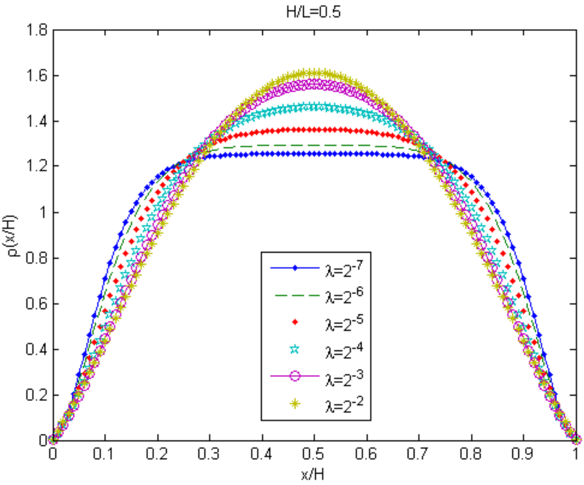


Picture of $\rho(\theta)$:

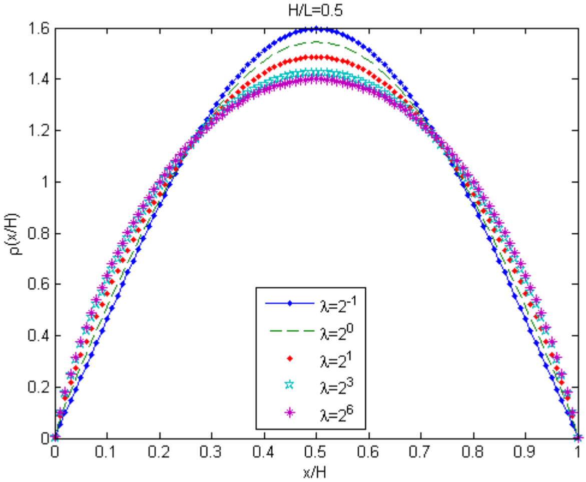


Fix H,L and increase λ

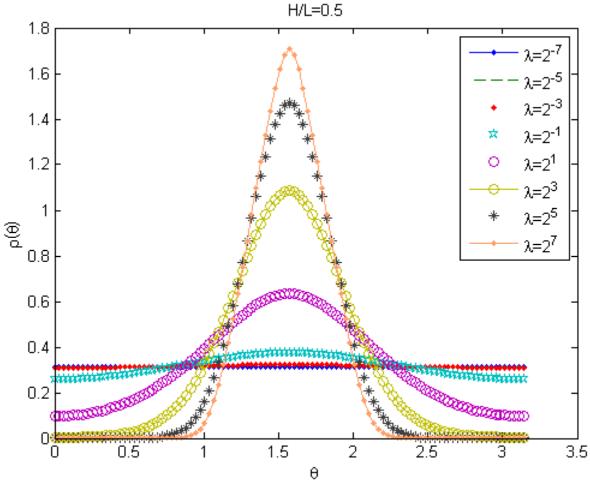
Picture of $\rho(x)$:



Picture of $\rho(x)$:



Picture of $\rho(\theta)$:



Numerical results

When decreasing H only,or increasing L only,or increasing λ only,

- the density of the chain in the middle of the walls increases first and then decreases.
- the orientation of the chain is more likely parallelling to the walls.

Numerical results

Reasons:

- The increase of the density: the chain is compressed and getting to the middle as H decreases.
- The decrease of the density: when $H \sim \sqrt{2L\lambda}$, the chain is mainly behaved as the Gauss chain and the size is minimum. Going on decreasing H(or increasing L,or increasing λ), the chain is mainly behaved as the wormlike chain. The excluded volume interaction lead to the increase of the size.
- The orientation is not only parallelling, but also at a small angle to the walls: for the inflexibility of the chain.

Outline

Conclusion

- Rods confined in a rectangle: 23 different structures
- A single chain confined between hard walls
- Further problems: mathematical analysis

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Thank you!