Curvature Effect of a Confined Polymer

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Abstract

The curvature effect of a confined polymer found by Yaman *et al*. is elucidated in four methods:

(1) Perturbation theory in terms of curved surface coordinates

(2) Scaling theory with the help of the 3D conformal invariance

(3) Intuitive geometric blob theory

(4) Monte Carlo method (Variable range bonding model)

The intuitive theory is developed to explain why the entropy of a polymer confined between parallel surfaces increases when the surfaces are curved. The confinement entropy loss can be attributed to entropy loss at the confining surfaces. The curvature effect is found to exist not only for Gaussian chains, but also for self-avoiding chains.

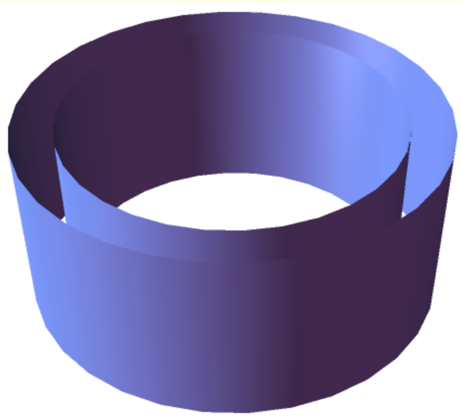
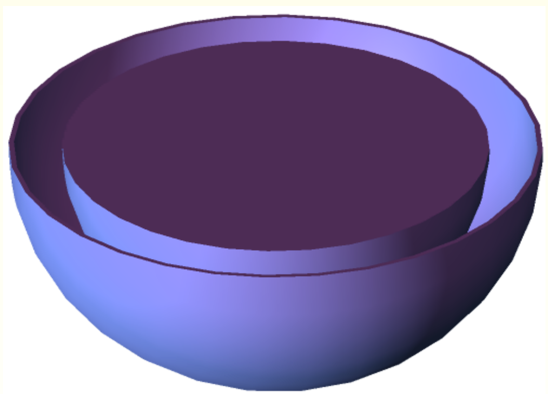
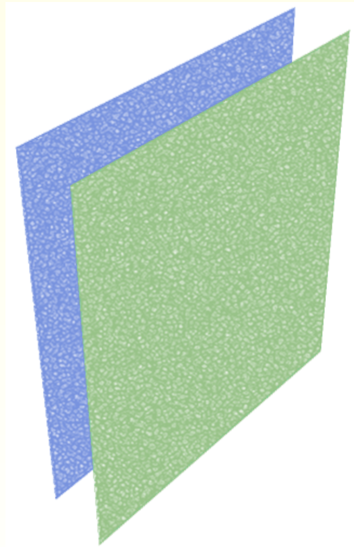
References:

(1) K. Yaman, P. Pincus, F. Solis, and T.A. Witten, Macromolecules 30, 1173 (1997).

(2) T. Dotera and Y.Y. Suzuki, Phys. Rev. E62, 5318 (2000).

What is the curvature effect?

- A confining box consisting of two parallel walls with a constant width increases the entropy of a confined chain when the walls are curved, except for exact spherical walls.
- *Polymers entropically favor curved boxes!*

Basics for the Gaussian chain

The number of paths that connect **r** and **r'** with N steps: $6^N G$

$$\left(\frac{\partial}{\partial N} - \frac{l^2}{6}\nabla_{\mathbf{r}}^2\right) G(\mathbf{r}',\mathbf{r},N) = 0$$

Eigenfunction expansion:

$$\nabla^2 \psi_n(\mathbf{r}) + k_n \psi_n(\mathbf{r}) = 0$$

$$G(\mathbf{r}',\mathbf{r},N) \cong l^3 \sum \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \exp\left(-R_\mathrm{g}^2 k_i / 6\right)$$

Ground-state dominance: The polymer is long enough.

$$Nl^2(k_i - k_0) = R_\mathrm{g}^2(k_i - k_0) >> 1, \quad (i > 1)$$

$$G(\mathbf{r}',\mathbf{r},N) \cong \psi_0^*(\mathbf{r})\psi_0(\mathbf{r}) \exp\left(-R_\mathrm{g}^2 k_0 / 6\right)$$

k_0 : ground state eigenvalue

R_g : radius of gyration

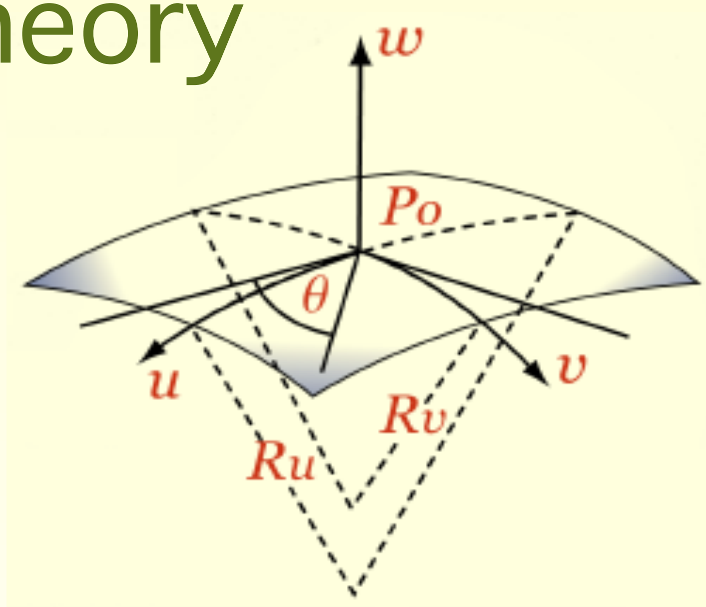
The partition function

$$Z = 1/V \iint d\mathbf{r} d\mathbf{r}' G(\mathbf{r},\mathbf{r}',N)$$

The entropy reduction

$$\Delta S = k_\mathrm{B} \ln Z \approx -k_\mathrm{B} \frac{R_\mathrm{g}^2 k_0}{6}$$

(1) Perturbation theory



Local orthogonal coordinate

$$\mathbf{x} = (u, v, w)$$

Principal curvatures

$$\kappa_u = 1/R_u, \quad \kappa_v = 1/R_v$$

Short distance in space

$$|d\mathrm{x}|^2 = h_u(\mathrm{x})^2 du^2 + h_v(\mathrm{x})^2 dv^2 + dw^2$$

$$h_u(x) = 1 + \kappa_u w \qquad h_v(x) = 1 + \kappa_v w$$

Wave equation

$$\nabla^2 \psi + k\psi = 0$$

$$\frac{1}{h_u h_v}\left[\frac{\partial}{\partial u}\left(\frac{h_v}{h_u}\frac{\partial \psi}{\partial u}\right) + \frac{\partial}{\partial v}\left(\frac{h_u}{h_v}\frac{\partial \psi}{\partial v}\right) + \frac{\partial}{\partial w}\left(h_u h_v \frac{\partial \psi}{\partial w}\right)\right] + k\psi = 0$$

$$\psi = h_u^{-1/2} h_v^{-1/2} \phi$$

dropping out small terms

$$\frac{\partial^2 \phi}{\partial u^2} + \frac{\partial^2 \phi}{\partial v^2} + \frac{\partial^2 \phi}{\partial w^2} \boxed{+ \frac{1}{4}(\kappa_u - \kappa_v)^2 \phi} + k\phi = 0$$

Effective potential

The eigenvalue problem of the curved box is translated into that of a flat box with the effective potential.

$$\Delta S = \frac{k_\mathrm{B} R_\mathrm{g}^2}{24}(\kappa_u - \kappa_v)^2$$

(2) Scaling theory

- Small curvature expansion under usual symmetries (inversion, rotation, translation)

$$\Delta S = \alpha H^2 + \beta K + \ldots$$

$$H = (\kappa_u + \kappa_v)/2 \qquad K = \kappa_u \kappa_v$$

- Entropy is extensive $\Delta S \propto N \sim R_g^{1/\nu}$

- Entropy is dimensionless $\Delta S \sim [\mathrm{L}]^0$

ν : Flory exponent

d : slit width

$$\Delta S(R_g, d, H, K) = R_g^{1/\nu} d^{2-1/\nu} \left(?\,H^2 + ?\,K \right)$$

Nowhere to go

3-dim Conformal Symmetry

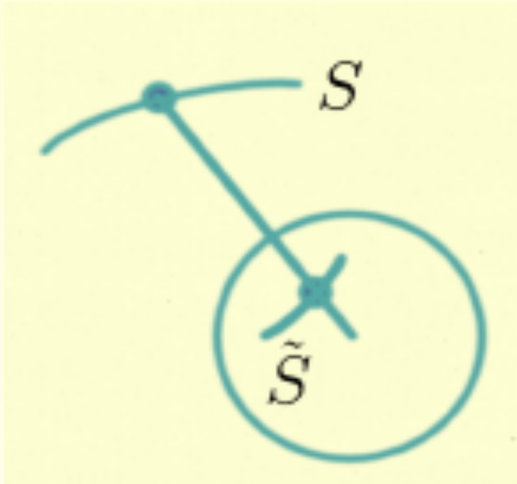
- Map: Surface in 3d → Surface in 3d
- Translations + Rotations + Scaling + Special conformal transformations (Cardy)

(Inversion → Translation → Inversion)

The only combination of principal curvatures
to the quadratic order that is conformally invariant is

$$\Delta S = \alpha\left(H^2 - K\right) + \ldots$$

Inversion mapping



$$\boxed{\mathbf{r} \to \tilde{\mathbf{r}} = \frac{\mathbf{r}}{r^2}}$$

$$\mathrm{d}\tilde{\mathbf{r}} = \frac{\mathrm{d}\mathbf{r}}{r^2} - \frac{2\mathrm{d}r\mathbf{r}}{r^3}$$

$$\mathrm{d}\tilde{\mathbf{r}} \cdot \mathrm{d}\tilde{\mathbf{r}} = \mathrm{d}\mathbf{r} \cdot \mathrm{d}\mathbf{r} / r^4 \qquad \mathrm{d}\tilde{S} = \mathrm{d}S / r^4$$

$$\boxed{\tilde{\kappa}_i = -r^2\kappa_i - 2\mathbf{r} \cdot \mathbf{n}}$$

$$\frac{1}{4}(\tilde{\kappa}_u + \tilde{\kappa}_v)^2 - \tilde{\kappa}_u\tilde{\kappa}_v = r^4\left\{\frac{1}{4}(\kappa_u + \kappa_v)^2 - \kappa_u\kappa_v\right\} \left(= \frac{r^4}{4}(\kappa_u - \kappa_v)^2\right)$$

$$\boxed{\left(\tilde{H}^2 - \tilde{K}\right)\mathrm{d}\tilde{S} = \left(H^2 - K\right)\mathrm{d}S}$$

G. Thomsen (1923)

(3) Intuitive geometric blob theory

Blobs reflect.

The number of the nearest positions: z

Assumption: A walk with N steps reflects off walls every N' steps.

Let M_+ and M_- be numbers of reflections on the outer wall and inner wall.

$$M_+ + M_- \sim N/N'$$

Total number of walks:

$$W \sim z^{N-N/N'}\left(\frac{z}{2} - zf_+\right)^{M_+}\left(\frac{z}{2} + zf_-\right)^{M_-} = z^N\left(\frac{1}{2}\right)^{N/N'}(1-2f_+)^{M_+}(1+2f_-)^{M_-}$$

Curvature effect = deviation from *z*/2

f_+ The fraction of solid angle deficit by the outer wall

f_- The fraction of solid angle surplus by the inner wall

$$S/k_B = \ln W \sim \sigma_0 + \sigma_1 + \Delta\sigma$$

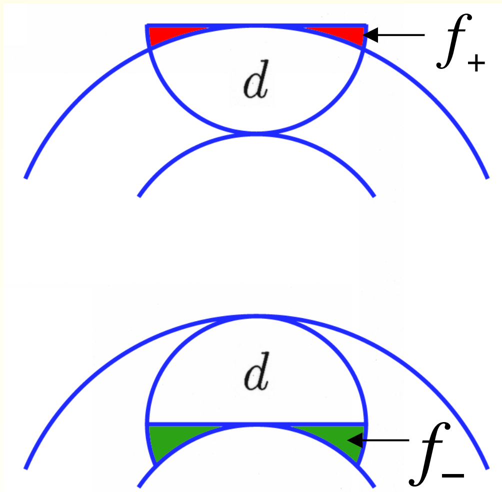
Free space + confinement between || walls +curvature effect

$$\sigma_0 = N \ln z$$

$$\sigma_1 = -(N/N')\ln 2 \sim -(N/N')(\pi^2/6) \quad \text{(exact)}$$

$\Delta\sigma$ = Number of reflections × entropy change / reflection

$$\boxed{\Delta\sigma = -2M_+ f_+ + 2M_- f_-}$$



Available solid angles for blobs

$$M_+ \sim \frac{N}{2N'}(1-2f_+)\frac{S(d/2)}{S(0)} \qquad S(w) \equiv (R_u + w)(R_v + w)$$

$$M_- \sim \frac{N}{2N'}(1+2f_-)\frac{S(-d/2)}{S(0)}$$

Available solid angles

Area changes

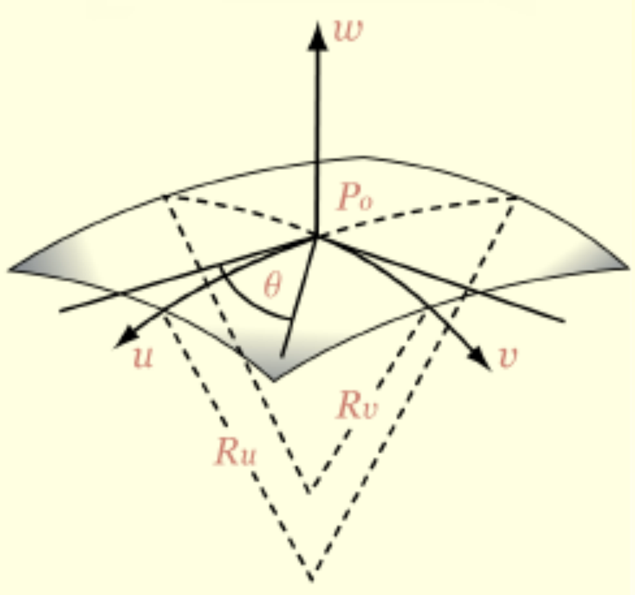
cf. $\psi = h_u^{-1/2} h_v^{-1/2} \phi$ $\qquad S(w)/S(0) = h_u h_v$

$$f_+ = \frac{d}{4}H(d/2) \qquad f_- = \frac{d}{4}H(-d/2)$$

Cancellation is very subtle, but the result is not bad.

$$\boxed{\Delta\sigma = \frac{R_g^{1/\nu} d^{2-1/\nu}}{16}(\kappa_u - \kappa_v)^2}$$

$16 \sim 24$



To clculate deficit or surplus

$$\kappa(\theta) = \frac{\cos^2\theta}{R_u} + \frac{\sin^2\theta}{R_u}$$

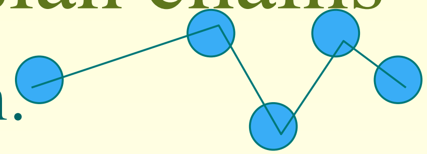
$$\frac{1}{4\pi}\int_0^{2\pi}\frac{d}{2}\kappa(\theta)d\theta = \frac{d}{4}\cdot\frac{1}{2}\left(\frac{1}{R_u} + \frac{1}{R_v}\right)$$

$$H(w) \equiv \frac{1}{2}\left(\frac{1}{R_u + w} + \frac{1}{R_v + w}\right)$$

Typical examples

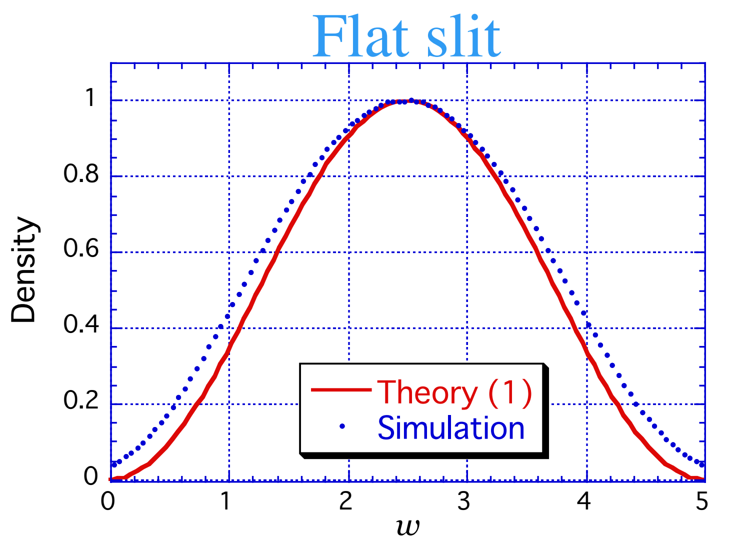
- *Minimal surfaces* (R_u=-R_v=R): Entropy gain from both walls.
- Cylinders ($R_u = R$, $R_v = \infty$): *solid angle* $\propto 1/R$, *Density* $\propto 1/R$, *area* $\propto R$; The effect remains.
- Spheres ($R_u = R_v = R$): solid angle $\propto 1/R$, *Density* $\propto 1/R$, *area* $\propto R^2$; No effect.

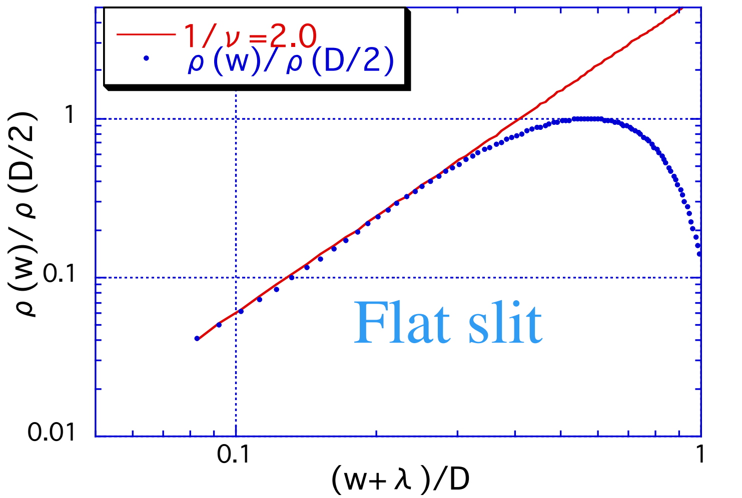
(4) Monte Carlo method for Gaussian chains

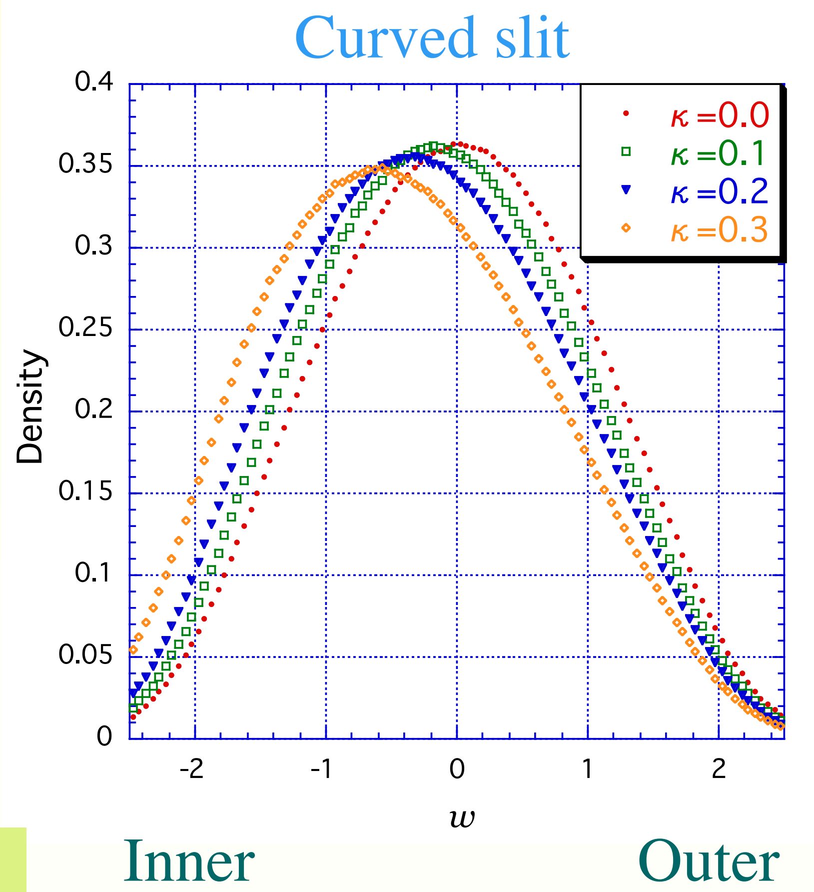


- **Variable range bonding model** in the *d*-dim.
- Distances between neighboring monomers are less than 1.
- Select a monomer randomly and move it according to the Gaussian distribution with the deviation 0.3; Check the distance between monomers.
- The mean squared length is given by $\langle \mathbf{r}^2 \rangle^{1/2} = \sqrt{d/d+2} = \sqrt{3/5}$ (Gaussian chain).
- Check geometry if the monomer is in the confining box.
- Here, the confining boxes are cylinders, the distance between parallel walls is 5.
- The number of monomers in a chain is 200.

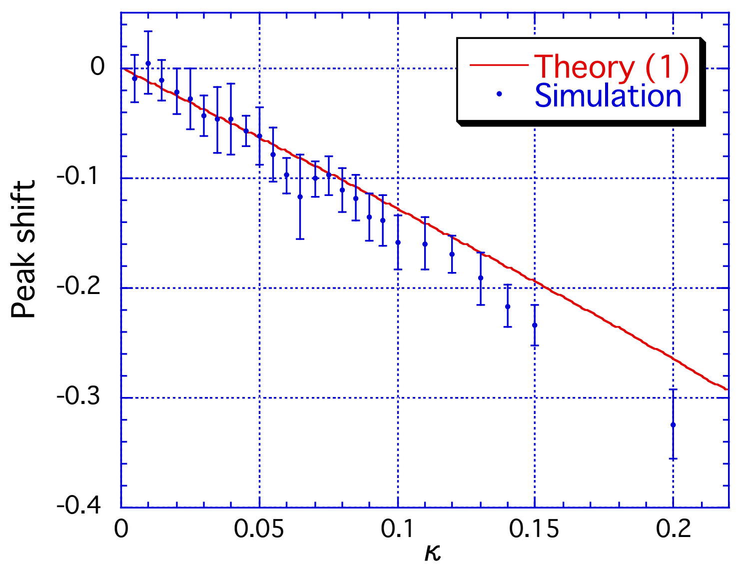
Density profile of a single chain (D=5.0, N=200, $\varkappa=1/R$)

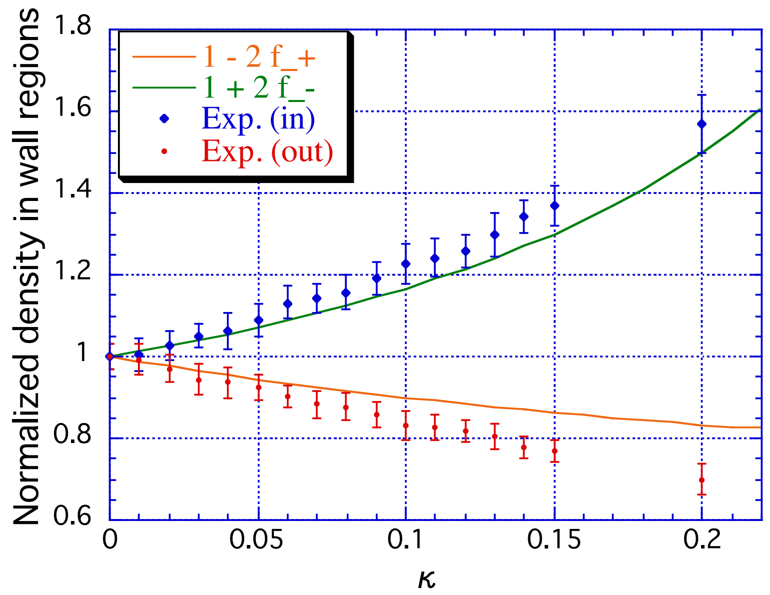




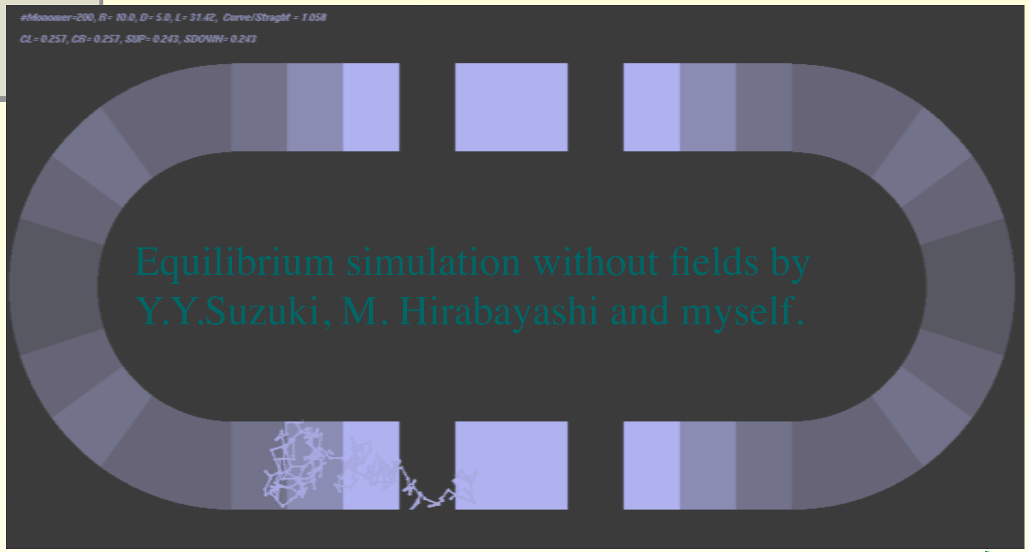


•λ: Extrapolation length found by Milchev and Binder, Eur. Phys. J. B3, 477 (1998). Here we take the half of the mean bond length as λ.



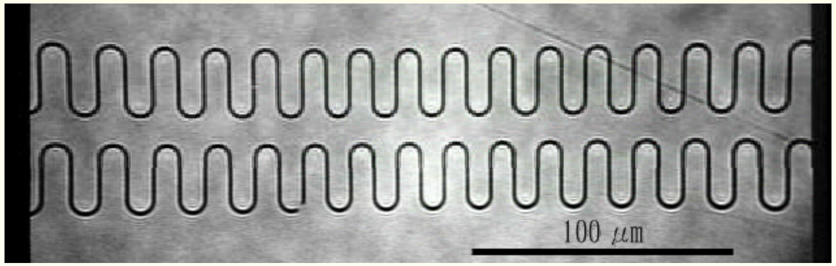


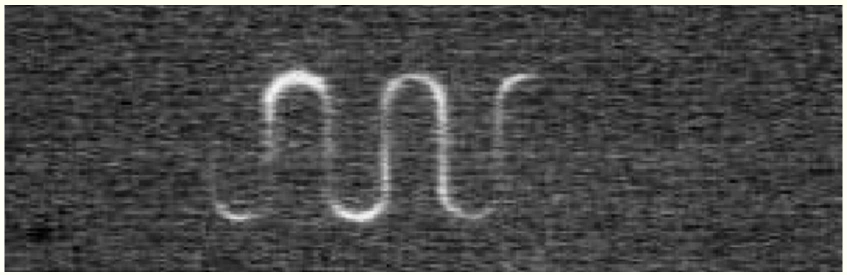
- An inward peak shift as a function of the curvature is observed, and is explained by the analytical theory (1).
- In wall regions (within the mean bond length), the density increase (in) or decrease (out) as a function of the curvature is explained by the solid angle deficit or surplus (theory (3)).

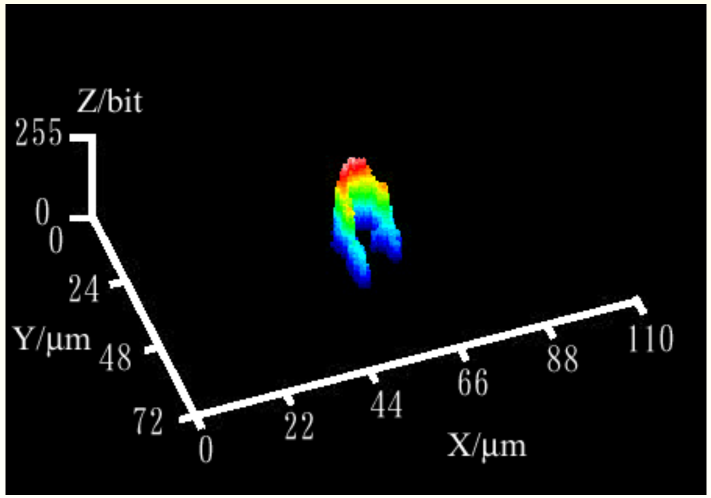


Equilibrium simulation without fields by Y.Y.Suzuki, M. Hirabayashi and myself.

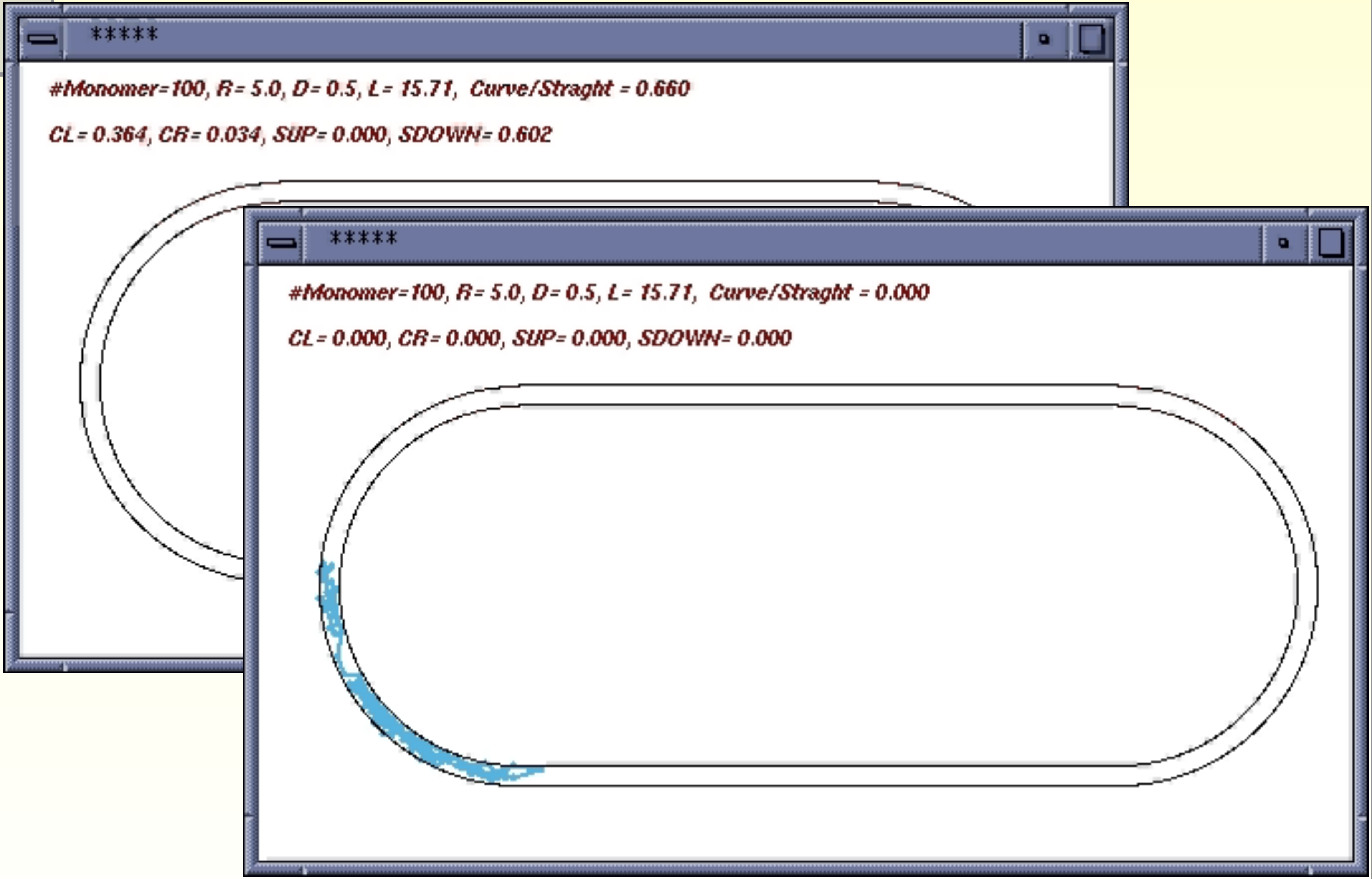
•Ueda *et al*. have shown a different curvature effect of DNA, which is different from entropic mechanism: The electric field is not homogenius in the curved region, and the DNA strecthes and sticks to the inner walls. Electrophoresis (2002), 23, 2635.







Microfluidic dynamic experiment under an electric field


*****
#Monomer=100, R= 5.0, D= 0.5, L= 15.71, Curve/Straght = 0.660
CL= 0.364, CR= 0.034, SUP= 0.000, SDOWN= 0.602
*****
#Monomer=100, R= 5.0, D= 0.5, L= 15.71, Curve/Straght = 0.000
CL= 0.000, CR= 0.000, SUP= 0.000, SDOWN= 0.000