# *Analytical and numerical investigation of star polymers in confined geometries*

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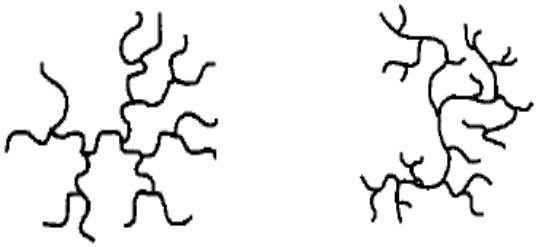
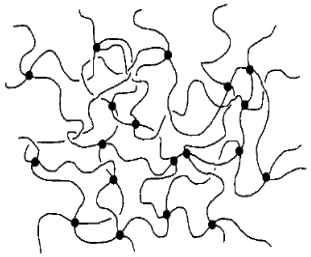
# ❖ *Star polymers*



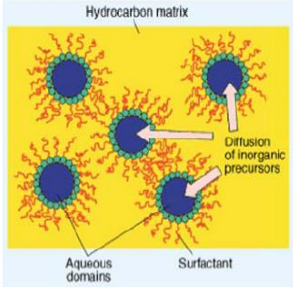
- ***Star polymers are the simplest representatives of a wide class of branched polymers.***

- ***Star polymers are important as building blocks of polymer networks.***



- ***Deeper understanding of the statistical and conformation properties of star polymers is important since it is connected with the investigation of micellar and other polymeric surfactant systems as well as networks.***

**G.S.Grest et al. Adv. Chem. Phys.(1996);**
**C. von Feber, Yu.Holovatch Cond. Matt.Phys. (2002).**
**B. Duplantier, J. Stat.Phys. (1989).**
**L. Schäfer et al. Nucl.Phys. B (1992).**

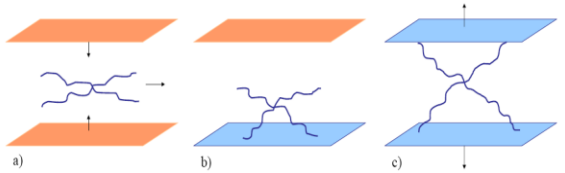



- ***Star polymers have a wide application for the production of new functional materials and can be used in nanotechnology and biological sciences as drug, gene or siRNA/DNA vectors.***

**J.M.Ren et al. Chem. Rev. (2016).**

# ❖ *Investigation of polymer depletion interaction between two parallel walls with different boundary conditions*

- ***Polymer solutions in confined geometries -> a new phenomena.*** *f=3,4,5*
- ***Dilute polymer solution - > single polymer chain.***
- ***The polymer coils tend to collapse at T< Θ (poor solvent).***
- ***RW for ideal polymer chain at Θ solvent.***
- ***SAW for real polymer chain with EVI at T>Θ (good solvent).***
- ***The polymer – magnet analogy:***




$$Z(\mathbf{x},\mathbf{x}',N,\mathrm{v}_0) = I\Im_{\mu_0^2->L_0} < \varphi(\mathbf{x})\varphi(\mathbf{x}') >_{n->0} .$$

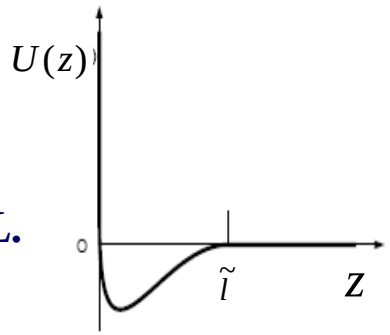
- ***The scaling properties of long-flexible polymers in the limit of an infinite number of steps N -> ∞ may be derived from a formal n->0 limit of the $\varphi^4$ O(n)- vector model at its critical point :***

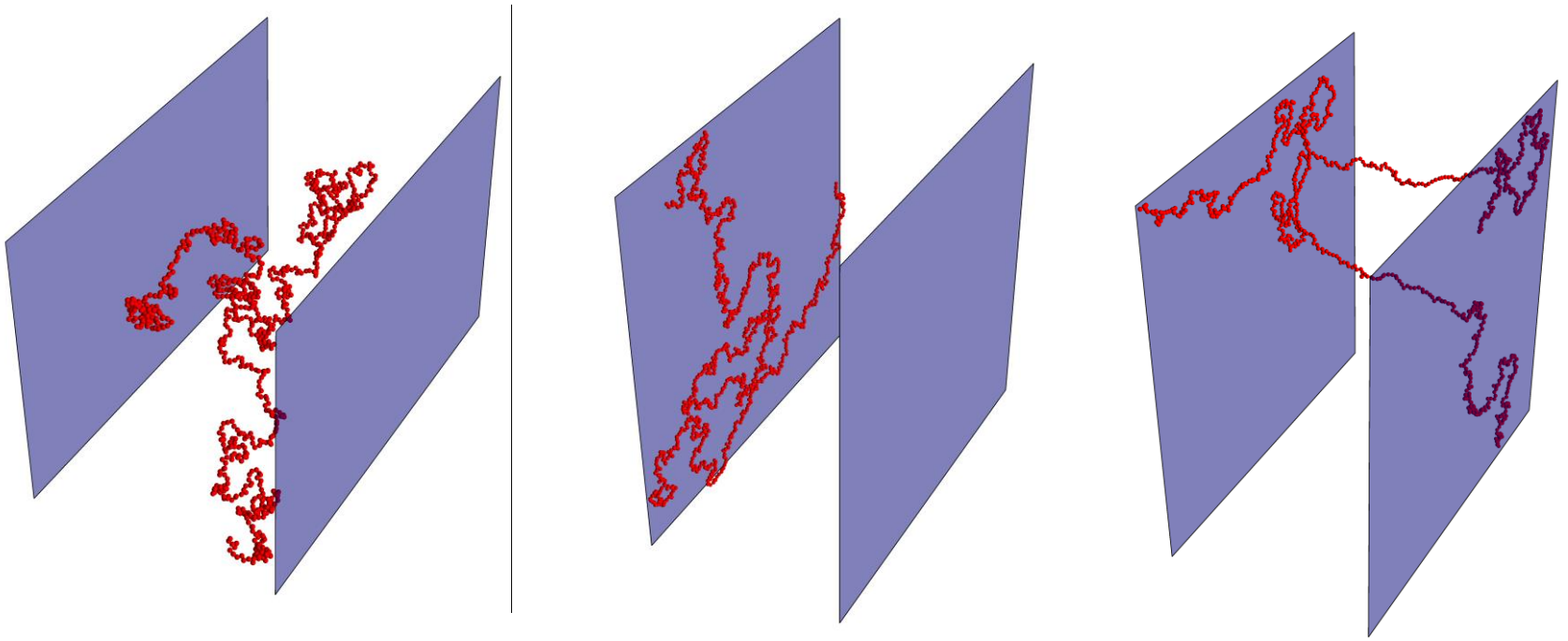
  **P.-G. de Gennes, (1972,1979).**

- ***The analogy between polymer adsorption and surface critical phenomena :***

  **P.-G. de Gennes (1976); Barber et. al (1978).**

- ***The value 1/N plays the role of a critical parameter analogous to the reduced critical temperature in magnetic systems. N – is the total number of monomers of the polymer chain***
- ***The surfaces are impenetrable :*** $U(z) = c\delta(z)$ ***for*** $z \geq 0.$
- 
- $c \sim \dfrac{(T - T_{ads})}{T_{ads}}$ ***- corresponds to the adsorption energy divided by*** $k_B T.$
- ***Relevant lengths :*** $\xi_R = \sqrt{< R_x^2 >} \sim N^{\nu}$ ***and the distance between walls L.***
- ***Properties of the system depend on the ratio*** $L/\xi_R$ .





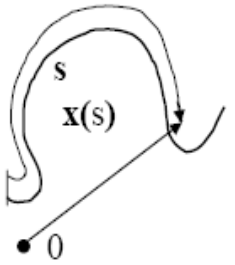
a) b) c)

- ***Star polymer with f=3 arms in a slit with:*** a) D-D b.c.;b) N-D b.c.;c) N-N b.c.

## ❖ *Polymer – magnet analogy*

- ***The Hamiltonian of an Edwards model:***

$$H(\mathbf{x}) = \frac{1}{4}\int_0^{L_0} ds(\dot{\mathbf{x}}(s))^2 + \int_V d^d\mathbf{x}U(\mathbf{x})\rho(\mathbf{x}) + \frac{1}{2}\int_V d^d\mathbf{x}_1\int_V d^d\mathbf{x}_2 U_2(\mathbf{x}_1,\mathbf{x}_2)\rho(\mathbf{x}_1)\rho(\mathbf{x}_2),$$




***where*** $\rho(\mathbf{x}) = \int_0^{L_0} ds\ \delta(\mathbf{x}-\mathbf{x}(s))$ ***- is the monomer density at point x.***

**S.F.Edwards, Proc.Phys.Soc. (1965).**

***The configuration of one polymer is given by a path x(s) and*** $0 \le s \le L_0$ ***in the continuous limit*** $\tilde{l} \to 0$ ***with fixed "Gaussian surface"*** $L_0 = N\tilde{l}^2$ ***, where N – is the total number of monomers of the polymer chain.***

***The one-body interaction potential is:*** $U(\mathbf{x}) \to U(z) - \bar{\mu}(\mathbf{x})$, ***where*** $U(z) = c\delta(z)$ ***for*** $z \ge 0$ **.**

- ***The partition function is:*** $Z_c(\mathbf{x}_2, L_0 \mid \mathbf{x}_1, 0) = \int D[\mathbf{x}(s)]\, e^{-\frac{H(\mathbf{x})}{k_B T}}$ .

- ***The continuous chain model can be mapped onto a corresponding field theory by a Laplace transform in the Gaussian variables*** $L_0$ ***to conjugate chemical potentials*** $\mu_0$ ***:***

$$G(\mathbf{x}_1,\mathbf{x}_2;\mu_0,c) = \int D[\vec{\varphi}(\mathbf{x})]\, e^{-H(\vec{\varphi},\mu_0)}.$$

- ***From another side*** $G(\mathbf{x}_1,\mathbf{x}_2;\mu_0,c)$ ***can be expressed as the n->0 limit of the functional integral over vector fields*** $\vec{\varphi}(x)$ ***with the components*** $\varphi_i(x)$ **,** ***i=1,…,n :***

$$G(\mathbf{x}_1,\mathbf{x}_2;\mu_0,c) = \int_0^\infty dL_0 e^{-\mu_0 L_0} Z_c(\mathbf{x}_2, L_0 \mid \mathbf{x}_1, 0).$$

## ❖ *The model of the system*

- ***The effective LGW Hamiltonian describing the system in semi-infinite*** $(j=1)$ ***or confined geometry of two parallel walls*** $(j=1,2)$ **:**

$$H_{st}[\vec{\varphi}] = \sum_{a=1}^{f} \int_{V} d^{d}x[\tfrac{1}{2}|\nabla\vec{\varphi}_a(\mathbf{x})|^2 + \tfrac{1}{2}\mu_{0,a}^2\vec{\varphi}_a^2(\mathbf{x}) + \tfrac{1}{4!}\mathrm{v}_{0,a}((\vec{\varphi}_a^2(\mathbf{x}))^2)] + \sum_{a=1}^{f}\sum_{j=1}^{2}\frac{c_{j_0,a}}{2}\int_{\partial V} d^{d-1}r\vec{\varphi}_a^2(\mathbf{r}),$$

***where*** $\vec{\varphi}_a(\mathbf{x}), a=1,\ldots,f$ ***is an n-vector field with the components*** $\varphi_a^i(\mathbf{x})$ ***, i=1,…,n and*** $\mathbf{x}=(\mathbf{r},z)$ ***defined on*** $V=L\times A$ ***and bounded by planes*** $z_{1,2}=0,L;$

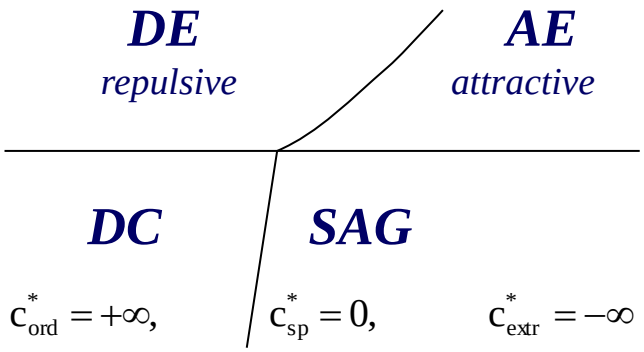
$\mathrm{v}_{0,a}$ ***denotes the bare coupling constant which characterizes the strength of the EVI .***

- ***two repulsive walls*** (D-D b. c.): $\vec{\varphi}_a(\mathbf{r},z_i)=0, \quad z_{1,2}=0,L,$ or $c_1\to\infty, \quad c_2\to\infty.$
- ***repulsive and inert*** (D-N b. c.): $\vec{\varphi}_a(\mathbf{r},z_1=0)=0, \quad \partial_z\vec{\varphi}_a(\mathbf{r},z_2=L)=0,$ or $c_1\to\infty, \quad c_2=0.$
- ***two inert walls*** (N-N b.c.): $\partial_z\varphi_a(\mathbf{r},z_i)=0, \quad z_{1,2}=0,L,$ or $c_1=0, \quad c_2=0.$

**H.W.Diehl and M.Shpot, Phys.Rev.Lett.(1994), Nucl.Phys.B (1998).**

**D.Romeis, Z. Usatenko, Phys.Rev.E,(2009).**
**M.Bachmann,W.Janke, NIC Symposium, (2006).**
**M.Mödel, W.Janke, M.Bachmann, Phys.Chem. Chem.Phys., (2010).**

$$c=\left[\frac{\partial_z\varphi_{E=0}}{\varphi_{E=0}}\right]_{z=\tilde{l}} \propto \frac{(T-T_{ads})}{T_{ads}}.$$



## ❖ *Correlation function*

**H.W.Diehl and M.Shpot, Phys.Rev.Lett.(1994), Nucl.Phys.B (1998)** – ***MFT for semi-infinite systems.***

- ***In the case of a dilute solution of star polymers with f legs in a □ solvent immersed in a confined geometry like a slit of two parallel walls, the respective correlation function has a form:***

$$G_{st}^{f}(\mu_0) = < \sum_{j_1,\ldots,j_f=1}^{n} T_{i_1,\ldots,i_f}\,\varphi^{i_1}(x_0)\ldots\varphi^{i_f}(x_0)\varphi^{j_1}(x_1)\ldots\varphi^{j_f}(x_f) >^{H_{st}[\vec{\varphi}]}_{n\to 0},$$

***D – D b.c.***

- ***The star vertex is related to the local composite operator***

$$(\varphi)^{f}_{st}(x) = T_{i_1\ldots i_f}\,\varphi^{i_1}(x)\ldots\varphi^{i_f}(x),$$

***where*** $T_{i_1,\ldots,i_f}$ ***is a traceless symmetric SO(n) tensor fulfilling the condition:***

$$\sum_{i=1}^{n} T_{i,i,i_3,\ldots i_f} = 0$$

***D – N b.c.***

***introduced by*** **D.J.Wallace and R.K.P. Zia, J.Phys. C (1975).**

## ❖ *Normalization conditions*

***The UV singularities of the correlation function in the bulk can be absorbed through a mass shift:*** $\mu_{0,a}^2 = \mu_a{}^2 + \delta\mu_a{}^2.$

***The UV singularities of the correlation function on the surfaces can be absorbed through a surface enhancement shift:*** $c_{0,a} = c_a + \delta c_a.$

- ***The bulk fields*** $\varphi_a(\mathbf{x}_i)$ *and* ***the surface fields*** $\varphi_{s_i,a}(\mathbf{r}_{j_i})$, $i=1,2$ *and* ***surface and bulk operators*** *should be reparametrized by different UV-finite renormalization factors:*

$$\varphi = Z_\varphi^{1/2}\varphi_R, \qquad \varphi_{s1} = Z_\varphi^{1/2} Z_1^{1/2}\varphi_{s1,R}, \qquad \varphi_{s2} = Z_\varphi^{1/2} Z_2^{1/2}\varphi_{s2,R},$$

$$\varphi^2 = \left[Z_{\varphi^2}\right]^{-1}\varphi_R^2, \qquad \varphi_{s1}^2 = \left[Z_{\varphi_{s1}^2}\right]^{-1}\varphi_{s1,R}^2, \qquad \varphi_{s2}^2 = \left[Z_{\varphi_{s2}^2}\right]^{-1}\varphi_{s2,R}^2.$$

- ***Coupling constant*** $v_{0,a}$ ***normalized via standard normalization conditions of infinite systems.***

- ***Wide slit limit :*** $\mu L >> 1$ ***or*** $\dfrac{L}{R_x} >> 1.$

- ***Narrow slit limit:*** $\dfrac{L}{R_x} << 1.$

## ❖ *The radius of gyration for star polymers*

- ***The mean – squared radius of gyration*** $< R_g^2 >$ ***for star polymer chains is:***

$$< R_g^2 >= \frac{Nl^2}{6f}\left(3 - \frac{2}{f}\right),$$

***where*** $l$ ***– is the monomer size.***

- ***The mean – squared radius of gyration for star polymer with f = 3 legs:***

$$< R_g^2 >= \frac{7}{18} < R_x^2 > .$$

- ***The mean – squared radius of gyration for star polymer with f = 4 legs:***

$$< R_g^2 >= \frac{5}{16} < R_x^2 > .$$

- ***The mean – squared radius of gyration for star polymer with f = 5 legs:***

$$< R_g^2 >= \frac{13}{50} < R_x^2 > .$$

## ❖ *Grand canonical ensemble*

- ***We consider the dilute solution of phantom ring polymers in a slit geometry of two parallel walls and permit the exchange of polymer coils between the slit and the reservoir.***
- ***The free energy of interaction (depletion energy):***

$$\delta F = \Omega(L) - \Omega(L \to \infty) = -k_B T \tilde{N} \ln\left(\frac{Z_{f,II}(L)}{Z_{f,II}(L \to \infty)}\right),$$

***where*** $Z_{f,II}(L)$ ***is the partiion function of one star polymer located in the volume V containing two walls at the distance L.***

**F.Schlesener, A.Hanke, R.Klimpel, S. Dietrich, Phys.Rev.E, (2001).**

**D.Romeis, Z. Usatenko, Phys.Rev.E, (2009).**

- ***The reduced free energy of interaction between the walls*** (A=1) ***:***

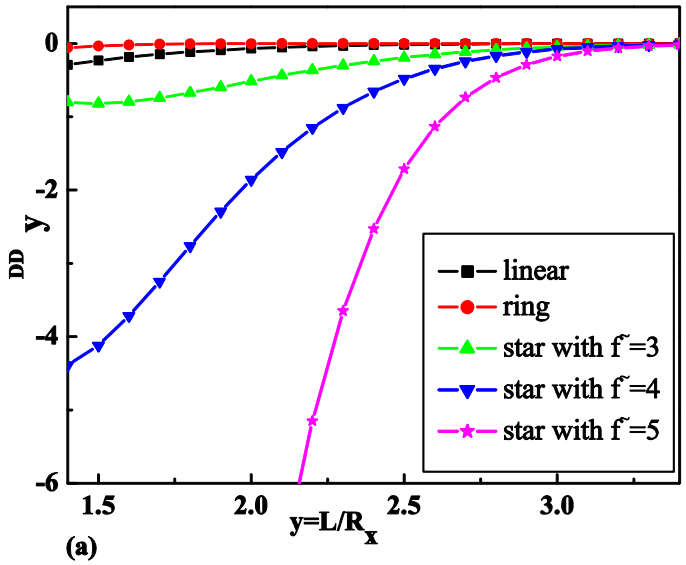
$$\delta \tilde{f}_f = \frac{\delta F_f}{n_B k_B T} = -(L f_b + f_{s_1,f} + f_{s_1,f} + L\omega_f).$$

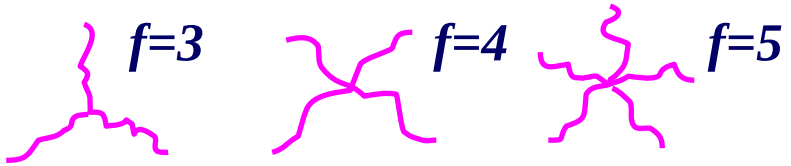
***The reduces bulk free energy per unit volume :*** $f_b = -1.$

***The reduces surface free energy :*** $f_{s_1,f} = \int_{V_{HS}} dz(1 - \frac{Z_{HS_i,f}(z)}{Z_b}).$

- ***The total grand canonical free energy of polymer solution within the slit :*** $\Omega_f = -n_B k_B T A L \omega_f$ ***where*** $\omega_f(L) = \frac{1}{L}\int_{v_I} dz \frac{Z_{i,f}(z)}{Z_b}.$
- ***The depletion interaction potential :*** $\Theta_f(y) = \frac{\delta \tilde{f}_f}{R_x}$, ***where*** $y = \frac{L}{R_x}.$
- ***The depletion force:*** $\Gamma_f(y) = -\frac{d(\delta \tilde{f}_f)}{dL} = -\frac{d\Theta_f(y)}{dy}.$
- ***The force which polymer exerts on the walls:*** $K_f(L) = \frac{d(\delta \tilde{f}_f)}{dL}.$

❖*Depletion interaction potential between two repulsive walls, one repulsive and one inert wall for star polymers with f =3,4,5 legs.*

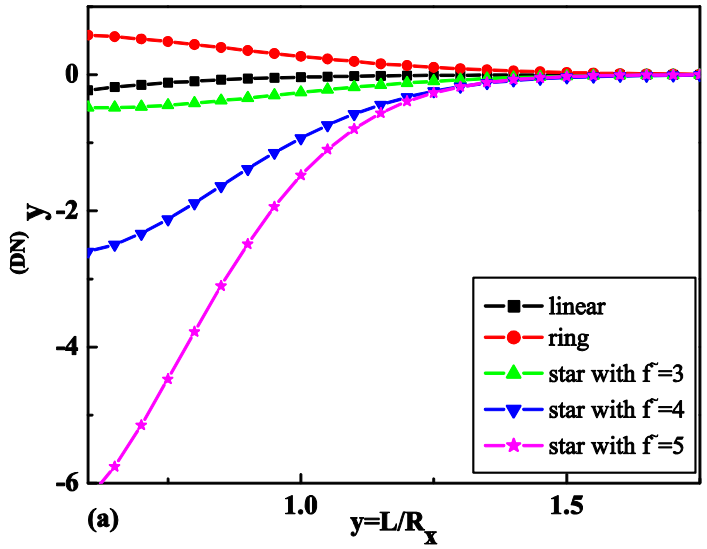



*Two repulsive walls.*

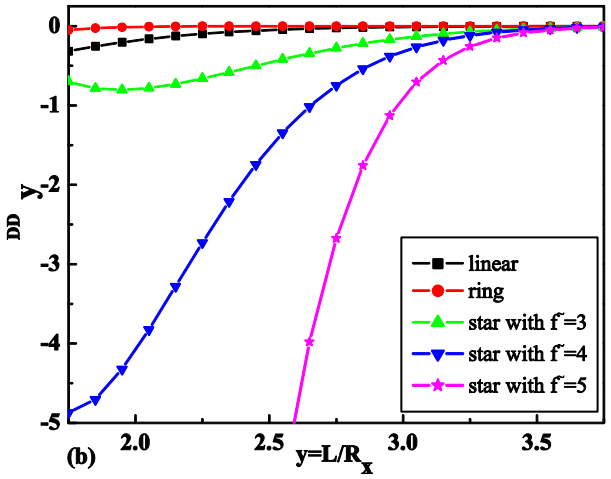
$$\Theta_f(y) = \frac{\delta \tilde{f}_f}{R_x}.$$

- *One repulsive and other one inert wall.*

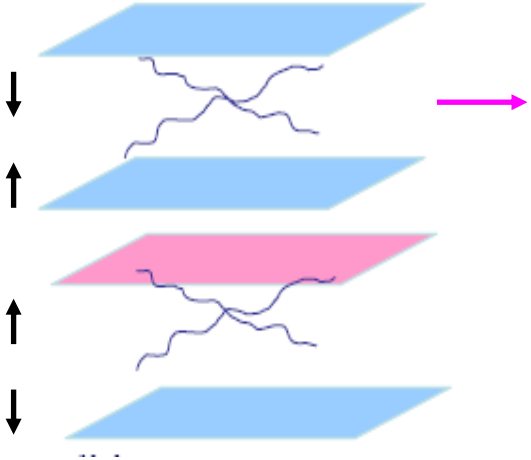


## ❖ *Depletion force between two repulsive walls, one repulsive and one inert wall for star polymers with f =3,4,5 legs.*

***Two repulsive walls;***

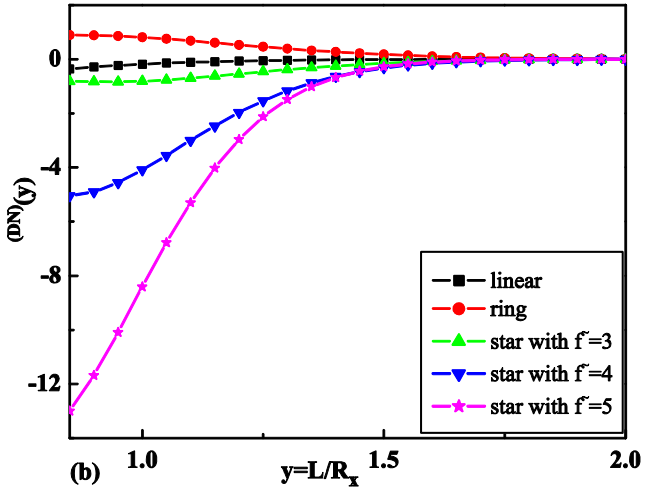



$$\Gamma_f(y) = -\frac{d(\delta\tilde{f}_f)}{dL} = -\frac{d\Theta_f(y)}{dy}.$$



$$\frac{L}{R_x} >> 1.$$

- ***One repulsive and other one inert wall.***



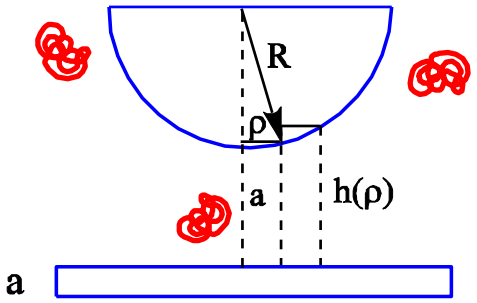

- ***Application – small scale devices:***

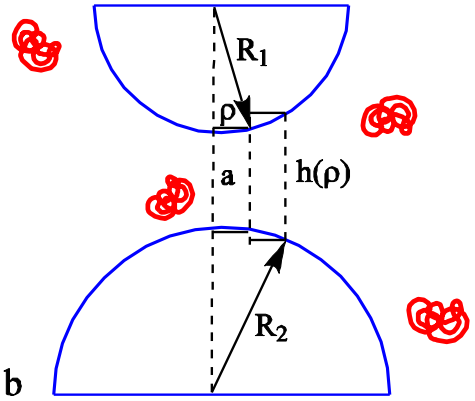
***new Nano - and Micro – Elektro-Mechanical Systems with low static friction.***

## ❖*Derjaguin approximation:*

a) ***spherical particle and a wall*** (***SW***);

b) ***two spherical particles*** (***SS***).




- ***Depletion interaction potential:***

$$\frac{\phi_{depl,f}(\tilde{a})}{n_B k_B T} = 2\pi \tilde{R} R_x^2 \int_{\frac{\tilde{a}}{R_x}}^{\infty} dy \Theta_f(y),$$

$$\tilde{R} = \begin{cases} R, & particle + wall, \\ \dfrac{R_1 R_2}{R_1 + R_2}, & particle + particle. \end{cases}$$

- ***Depletion force:***

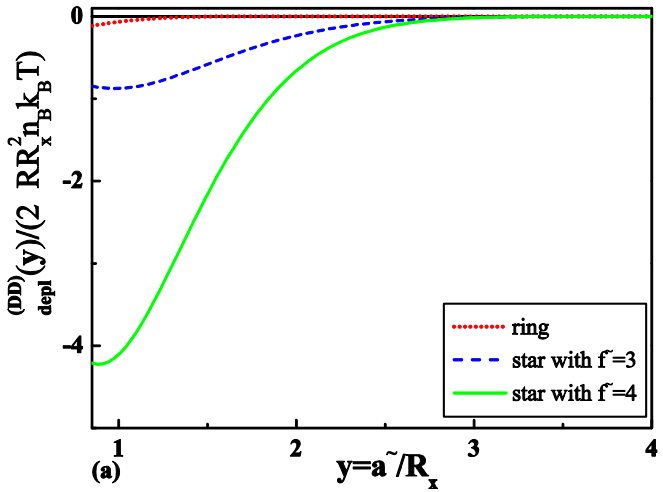
$$\Delta\tilde{f}_f = -\frac{d\phi_{depl,f}(\tilde{a})}{d\tilde{a}}.$$

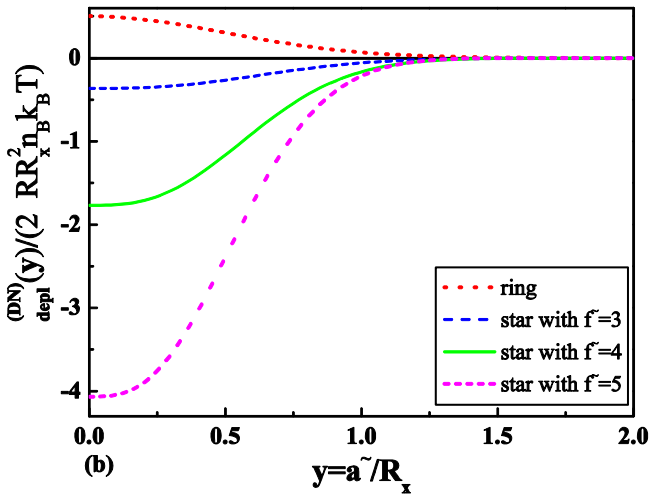
## ❖*Depletion interaction potential and depletion force for star polymers with f=3,4,5 legs in a solution of mesoscopic colloidal particles of big size*

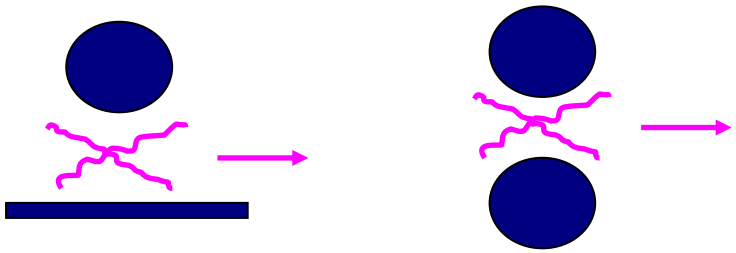
- ***Depletion interaction potential:***

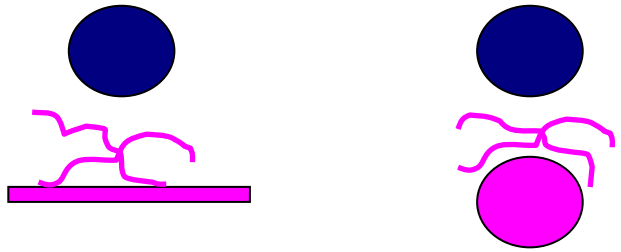
$$\frac{\phi_{depl,f}(\tilde{a})}{n_B k_B T} = 2\pi \tilde{R} R_x^2 \int_{\frac{\tilde{a}}{R_x}}^{\infty} dy \Theta_f(y), \qquad \tilde{R} = \begin{cases} R, & particle + wall, \\ \dfrac{R_1 R_2}{R_1 + R_2}, & particle + particle. \end{cases}$$

- ***D – D b.c.*** ***D – N b.c.***





- ***Depletion force:*** $\Delta\tilde{f}_f = -\dfrac{d\phi_{depl,f}(\tilde{a})}{d\tilde{a}}.$

## ❖ *The monomer density profiles for star polymer chains with f = 3,4,5 legs in confined geometries*

**Joanny, Leibler & de Gennes (1979):**

- ***the monomer density profiles of dilute polymer solution bounded by repulsive wall has a depletion region of mesoscopic width of order of the coil size*** $R_x \approx N$ ***(where N is the number of monomers per chain) and for*** $l << z << R_x$ ***the profile increases as:***

$$\rho(z) \sim z^{1/\nu}$$

- ***with Flory exponent*** $\nu$ ***:  ideal chain*** $\nu = 1/2$***;  real chain*** $\nu \approx 0.588.$
- ***The monomer density close to the wall is proportional to the force per unit area.***
- ***The monomer density is:***

$$\rho_{\lambda.f}(\mathbf{x})d\mathbf{x} = \frac{(2R_{g,f})^{1/\nu}}{N} dN_{\lambda,f}(\mathbf{x}).$$

**E.Eisenriegler, Phys.Rev.E, (1997).**

***The scaling dimension of*** $\rho$ ***is*** $\tilde{l}^{1/\nu - d}$ ***the same as*** $\Psi_a(\mathbf{x}) = \frac{(2R_{g,f})^{1/\nu}}{L_0} \frac{\vec{\varphi}_a^2(\mathbf{x})}{2}.$

- ***Taking into account the polymer-magnet analogy developed by de Gennes, the monomer density is:***

$$< \rho_f(\mathbf{x}) >= \frac{I\Im_{\mu_0^2 \to L_0} \sum_{a=1}^{f} < \Psi_a(\mathbf{x}) \cdot \vec{\varphi}_a(\mathbf{x}_1)\vec{\varphi}_a(\mathbf{x}_2) >_{ww}}{I\Im_{\mu_0^2 \to L_0} \sum_{a=1}^{f} < \vec{\varphi}_a(\mathbf{x}_1)\vec{\varphi}_a(\mathbf{x}_2) >_{ww}},$$

***where*** $L_0 = Nl^2.$

## ❖ *The universal density-force relation for star polymers*

- ***Taking into account the normalization condition:*** $\int d^d\mathbf{x} < \rho_f(\mathbf{x}) >= (2R_{g,f})^{1/\nu}$

  ***the property*** $\int d^d\mathbf{x}\, I\Im < \Psi_a(\mathbf{x}) \cdot \vec{\varphi}_a(\mathbf{x}_1)\vec{\varphi}_a(\mathbf{x}_2) >_{ww} = (2R_{g,f})^{1/\nu}\, I\Im < \vec{\varphi}_a(\mathbf{x}_1)\vec{\varphi}_a(\mathbf{x}_2) >_{ww}$ ***takes place.***

- ***The short-distance expansion is :*** $\Psi_a(\mathbf{x}) \to B\, z^{1/\nu} \dfrac{(\vec{\varphi}_{a,\perp}(\mathbf{r}))^2}{2}$ ***with*** $\vec{\varphi}_{a,\perp} = \dfrac{\partial \vec{\varphi}_a(\mathbf{r}, z)}{\partial z}|_{z=0}$

  ***for the distances*** $l << z << R_x$.

- ***The shift identity for the case of slit geometry is:***

$$\int d^{d-1}\mathbf{r} < \frac{[\vec{\varphi}_{a,\perp}(\mathbf{r})]^2}{2} \vec{\varphi}_a(\mathbf{x}_1)\vec{\varphi}_a(\mathbf{x}_2) >_{ww} = \left( \frac{\partial}{\partial L} + \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right) < \vec{\varphi}_a(\mathbf{x}_1)\vec{\varphi}_a(\mathbf{x}_2) >_{ww} .$$

***For the layer monomer density*** $\rho_{\lambda,f}(z) = \int d^{d-1}\mathbf{r}\rho_f(\mathbf{r}, z)$

- ***the universal density-force relation :*** $< \rho_{\lambda,f}(z) >_w = B\, z^{1/\nu} \dfrac{\tilde{f}_f}{k_B T}$

  ***takes place for*** $l << z << 2R_g$, ***where***

$$\frac{\tilde{f}_f}{k_B T} = \frac{\partial}{\partial L} \ln[ I\Im \int d^d\mathbf{x} \int d^d\mathbf{x}' \sum_{a=1}^{f} < \vec{\varphi}_a(\mathbf{x})\vec{\varphi}_a(\mathbf{x}') >_{ww} ]$$

***- is the fluctuation-induced force per area*** (A=1).

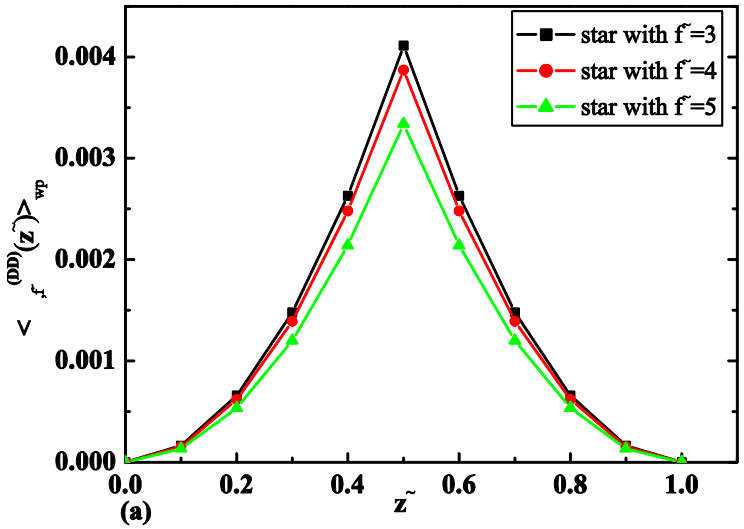
## ❖ *The layer monomer density profiles for star polymers in confined geometries*

- ***The layer monomer density of a dilute polymer solution of star polymers in a semi-infinite geometry containing a spherical particle of a big radius:***

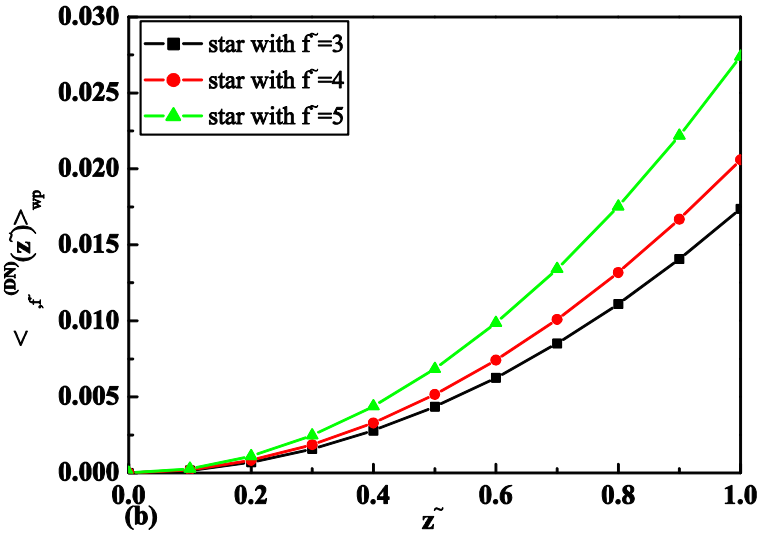
$$< \rho_{\lambda,f}(\tilde{z}) >= B\tilde{z}^{1/\nu}\left(\frac{\Delta\tilde{f}_f}{k_B T} + n_B\right), \qquad < \rho_{\lambda,f}(\tilde{z}) >= B\frac{\tilde{z}^{1/\nu}}{L}\left(1 + 2\pi R R_x \Theta_f\left(\frac{\tilde{a}}{R_x}\right)\right),$$

***where*** $n_B = \tilde{N}/V$ ***is the polymer density in the bulk far from the wall.***

***D – D b.c.***



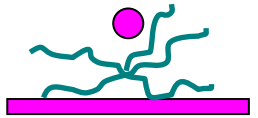

***D – N b.c.***



## ❖ *Polymer chains in a solution of small colloidal or nano-particles*

- ***The Boltzmann weight for small R*** ( $R << z_s, R_x, L$ ):

$$W_S[\mathbf{x}_j] -> 1 - \tilde{A} R^{d-1/\nu} < \rho(\mathbf{x}_s) >$$ ***- the small sphere expansion,***



***where*** $z_s = L + R/2$ ***is the distance of the center of the sphere from the boundary wall.***

- ***Immersing a small spherical particle in a polymer solution in a half space changes the polymer free energy by:***

$$\frac{F}{k_B T} = -\{W - 1\}_{(hs)} = \tilde{A} R^{d-1/\nu} R_x^{1/\nu} n_p M(z_s / R_x),$$

***where*** $M(z/R_x) =< \rho(\mathbf{x}) >_{(fc,h)} / n_p R_x^{1/\nu}$ ***- is the bulk normalized monomer density in the half space without the sphere,*** $n_p$ ***- is the polymer density in the bulk.***

- ***For ideal chain at d=3:*** $\tilde{A} = 2\pi.$
- ***The free energy of interaction between sphere and wall:***

$$\delta F = F - \lim_{z_s -> \infty} F = -k_B T n_p \tilde{A} R^{d-1/\nu} R_x^{1/\nu} (1 - M(z_s / R_x)).$$

- ***The depletion force in a dilute polymer solution between a small spherical particle and the wall is:***

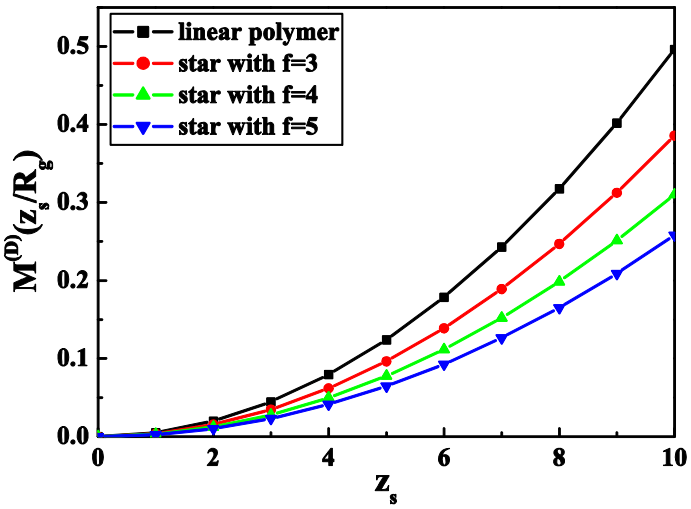
$$\frac{\delta f}{n_B k_B T} = -\tilde{A} R^{d-1/\nu} R_x^{1/\nu} \partial_{z_s} M(z_s / R_x),$$

***where*** $M(z_s / R_x) = B\left(\frac{z_s}{2R_g}\right)^{1/\nu}.$

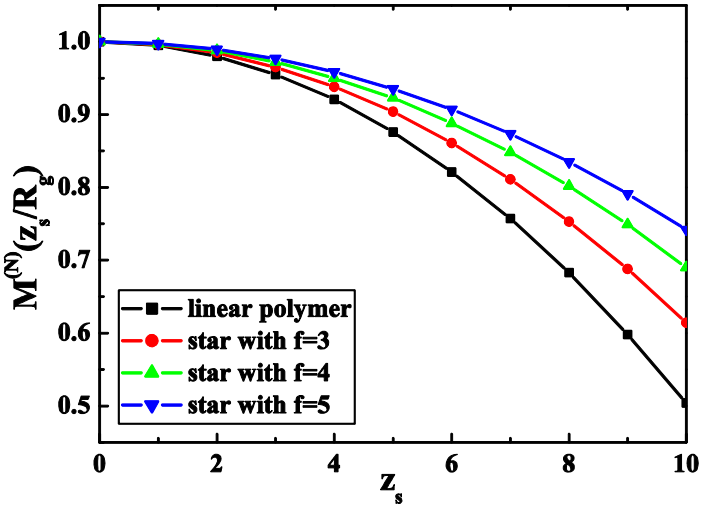
**E.Eisenriegler, Phys.Rev.E (1997).**

❖ *The dimensionless value of the normalized monomer density $M(z_s/R_g)$*

- *The case of Dirichlet b.c.*




*The case of Neumann b.c.*




**J. Halun, Z. Danel, Entropy (2021).**

## ❖ *Molecular dynamic simulations. Comparison with numerical data.*

- ***N=300 monomers, bead-spring model.***
- ***For star polymers:*** N=901 (3x300+1), N=1201 (4 x 300+1), N=1501(5x300+1) ***monomers.***
- ***The interaction between monomers by shifted LJ potential 12-6 with:***

$$U_{LJ}(r)=\begin{cases}4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}+\frac{1}{4}\right], & r\le 2^{1/6}\sigma,\\ 0, & r>2^{1/6}\sigma\end{cases}$$

- ***The interaction between monomers and surface by shifted LJ potential 9-3 with:***

$$U_{LJ}(r)=\frac{3\sqrt{3}}{2}\varepsilon\left[\left(\frac{\sigma}{r}\right)^{9}-\left(\frac{\sigma}{r}\right)^{3}\right], \qquad r_{cut}=3^{1/6}\sigma \quad and \quad \varepsilon=1.0, \quad \sigma=1.$$

$r_{cut}^{attr}=10\sigma,$ - ***for the attractive wall;***

$r_{cut}^{rep}=3^{1/6}\sigma$ - ***for the repulsive wall.***

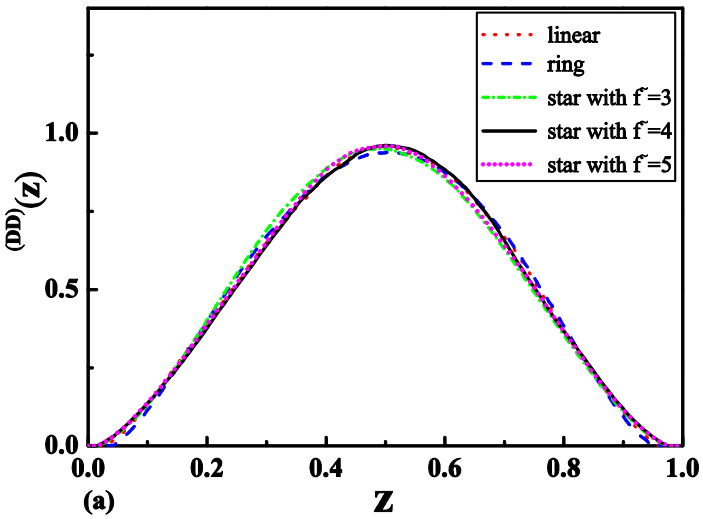
- ***The interaction of the neighoring monomers was modeled by the finite extensible nonlinear elastic*** (FENE) (***attractive part***) ***and the Weeks-Chandler-Andersen*** (**WCA**) (***repulsive part***) ***potentials:***

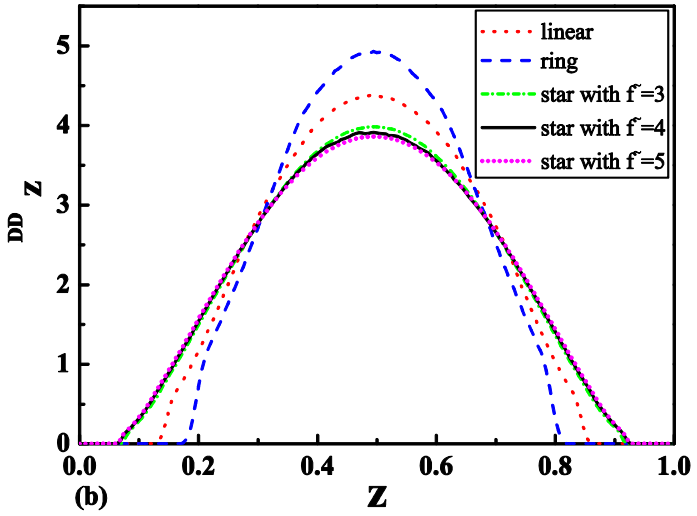
$$U_{FENE}(r)=\begin{cases}-\varepsilon, & if \quad r<2^{1/6}\sigma,\\ 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], & if \quad r\ge 2^{1/6}\sigma.\end{cases} \qquad U_{WCA}(r)=\begin{cases}-\frac{1}{2}kR_0^2\ln\left[1-\left(\frac{r}{R_0}\right)^2\right], & if \quad r<R_0,\\ +\infty, & if \quad r\ge R_0.\end{cases} \qquad k=30.0, \quad R_0=3/2.$$

**P. Karbowniczek, Z. Danel,Entropy (2021).**

- ***Radius of gyration $R_g$:***
  ***for linear polymers:*** $R_g = 14.65(47);$
  ***for ring polymers:*** $R_g^R = 10.91(15);$
  ***for star polymers:*** $R_{g,f=3} = 26.99(92);\quad R_{g,f=4} = 29.43(68);\quad R_{g,f=5} = 29.8(10).$

- ***The monomer density profiles*** $\rho(z)$ ***of linear, ring and star-shaped polymers between two repulsive walls:***



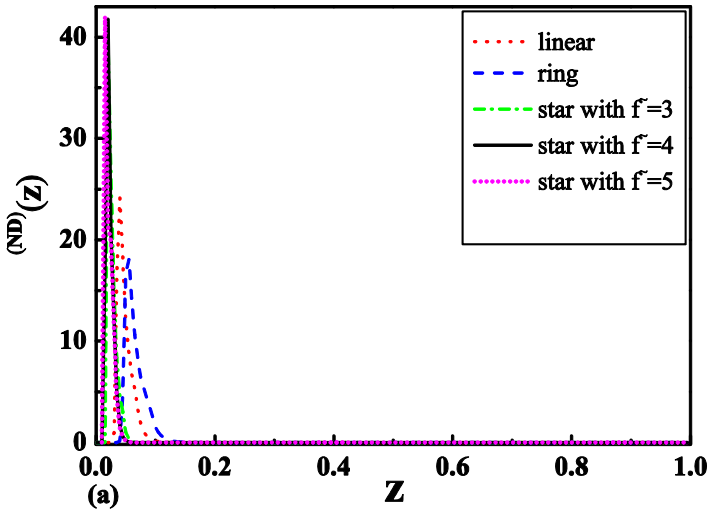

***wide slit*** $L=2R_g$. ***narrow slit*** $L=0.5R_g$.

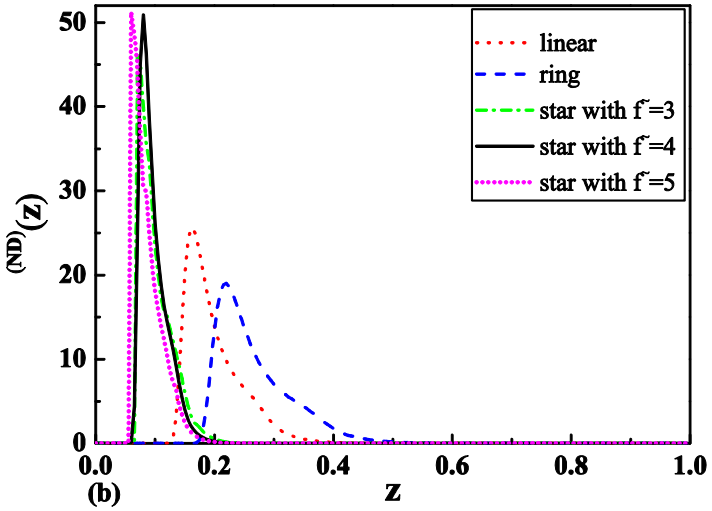
**P.Karbowniczek, Z. Danel, Entropy (2021).**

- ***We performed the calculation of the ratio*** $R_{g\perp}/R_{gII}$ ***of the perpendicular to the surfaces and the parallel to the surfaces contribution to the radius of gyration for a dilute solution of star polymer with f=3,4,5 arms for the case of narrow slit with*** $L = 0.5R_{g,f}$ ***and for the case of wide slit with*** $L = 2R_{g,f}$.

| $L$ | $b.c.$ | $\tilde{f}=3$ | $\tilde{f}=4$ | $\tilde{f}=5$ |
|---|---|---|---|---|
| $0.5R_g,$ | N-N | 0.135 | 0.135 | 0.135 |
| $0.5R_g,$ | N-D | 0.007 | 0.008 | 0.007 |
| $0.5R_g,$ | D-D | 0.082 | 0.092 | 0.076 |
| $2.0R_g,$ | N-N | 0.634 | 0.661 | 0.646 |
| $2.0R_g,$ | N-D | 0.008 | 0.008 | 0.010 |
| $2.0R_g,$ | D-D | 0.328 | 0.364 | 0.356 |

- ***The monomer density profiles*** $\rho(z)$ ***of linear, ring and star-shaped polymers between attractive and repulsive wall.***

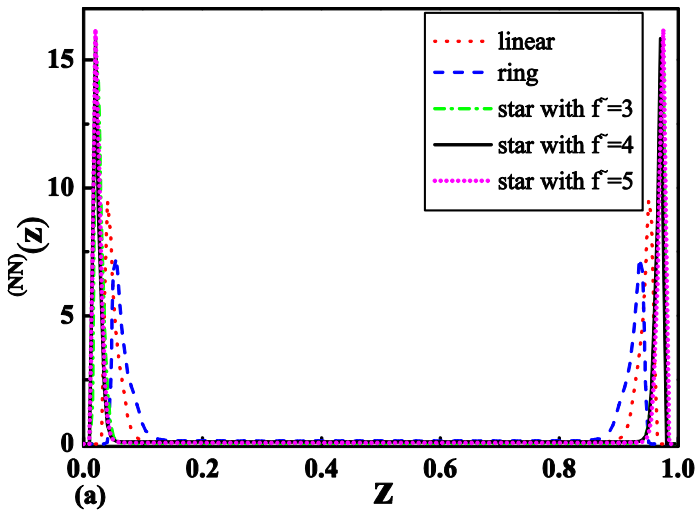


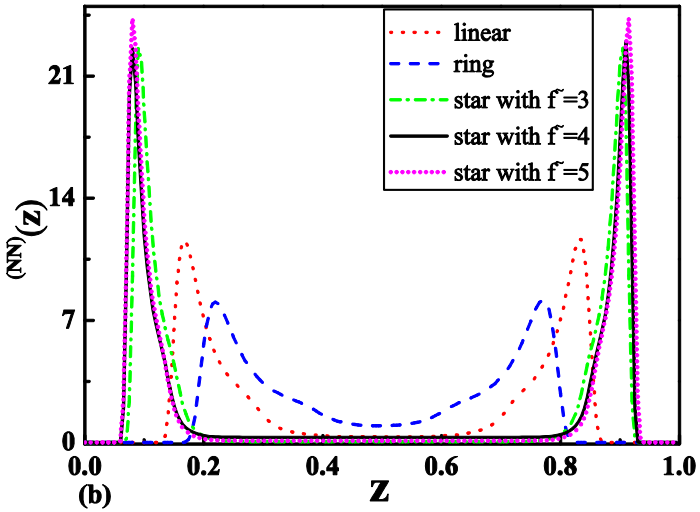




***wide slit*** $L=2R_g$. ***narrow slit*** $L=0.5R_g$.

**P.Karbowniczek, Z. Danel, Entropy (2021).**

- ***The monomer density profiles*** $\rho(z)$ ***of linear, ring and star-shaped polymers between two attractive walls.***




***wide slit*** $L=2R_g$. ***narrow slit*** $L=0.5R_g$.

## ❖ Conclusion

- ***The investigation of a dilute solution of star polymers with f = 3,4,5 legs in a Θ - solvent immersed in confined geometries like slit of two parallel walls and in a solution of big and small spherical colloidal particles with different adsorbing and repelling properties in respect to polymer were performed.***

- ***The layer monomer density profiles of a dilute solution of ideal star polymers with f = 3,4,5 legs immersed in a slit geometry of two parallel walls with repulsive surfaces, as well as in the case of one repulsive and the other one inert surface were obtained.***

- ***The smaller radius of gyration corresponds to more complicated topological structure. It leads to decreasing of the layer monomer density with increasing the complexity of the topological structure in the region between two repulsive surfaces, as well as in the region near the surface where the adsorption threshold takes place in the case of mixed surfaces.***

- ***In the case of a dilute solution of star polymers at Θ - temperature immersed in a solution of small colloidal particles and wall with surface at Neumann b.c. we observed that polymer adsorb on the wall. The results in the case of a dilute solution of ring or linear polymers at Dirichlet b. c. show that polymers prefer to escape from the space between wall and small particle or nano-particle.***

- ***The obtained results for the case of a dilute solution of star polymers with f =3,4,5 legs immersed in a slit geometry of two parallel walls with repulsive surfaces and with one repulsive and the other one inert surface indicate that the depletion force in both cases for a dilute solution of star polymers is attractive, but bigger than the respective forces for linear and ring polymer chains in the case of two repulsive surfaces.***

- ***The depletion force in the case of a dilute solution of star polymers with f = 3,4,5 legs immersed in a slit geometry of one repulsive and the other one inert surface is smaller than in the case of two repulsive surfaces and demonstrates opposite behaviour than in the case of a dilute solution of ring polymer chains in confined geometries of two parallel walls with mixed surfaces.***

- ***Dilute solution of ring and star polymers can be used for production of new functional materials, because behaviour of these solutions depends from topology of polymers as well as from nature and geometry of confined surfaces. These properties can find wide application in nanotechnology as well as in a biotechnology for drug and gene transmission.***