ENTROPY-INDUCED SEPARATION OF STAR POLYMERS IN POROUS MEDIA

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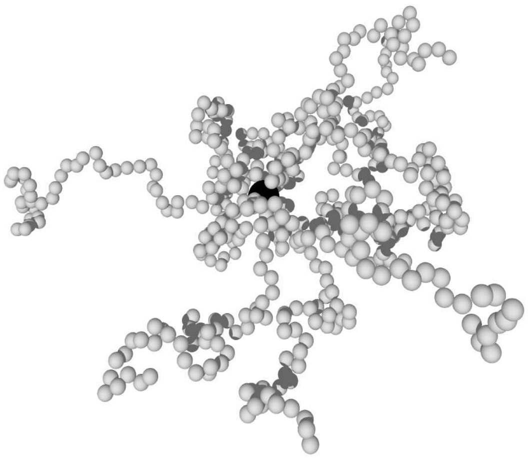
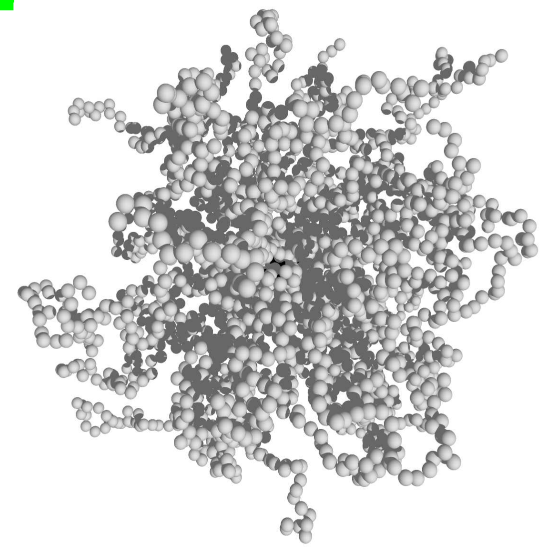
Star polymers



$f = 10, N = 50$



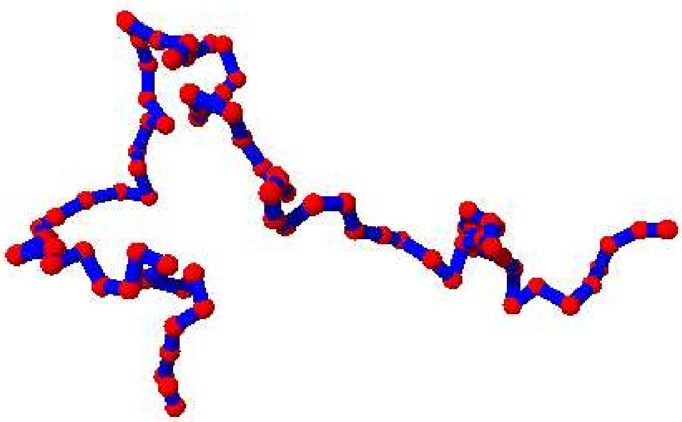
$f = 50, N = 50$

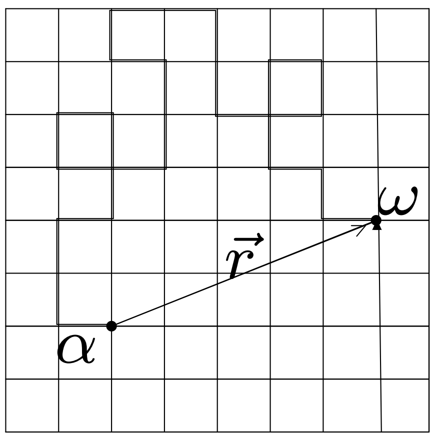
industry:
- viscosity modifiers
- coating materials
- pharm., med.

experiment:
monodisperse
polyisoprene $f = 8, 18$
polybutadiene $f = 128$
(SANS, SAXS)

theory:
polymer physics
$\Leftrightarrow$
colloid physics

Polymer $\leftrightarrow$ self-avoiding walk (SAW)





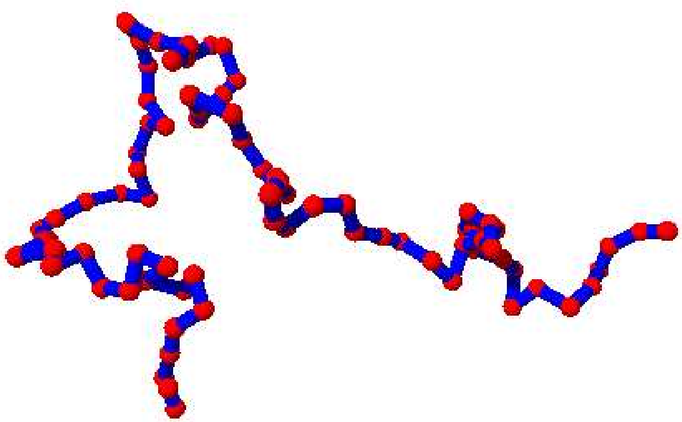
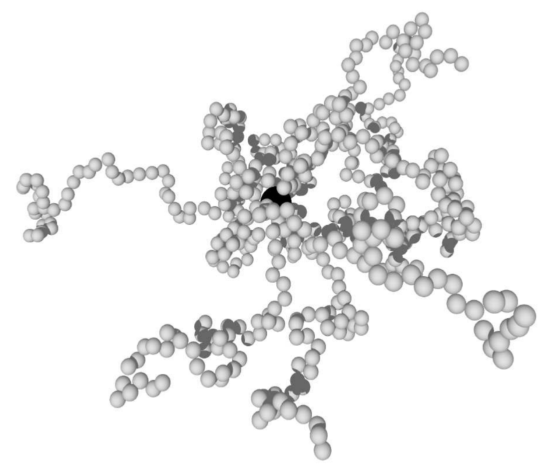
Polymer:

- continuous space
- C–C bonds (109.47°)
- non-trivial energy surface
- compl. mon.-mon. interaction

SAW:

- discrete lattice
- 90°. 180°
- indep. on angle energy
- self-avoidance

Scaling exponents

Chain polymers		Star polymers
		
	$N \to \infty$:	
$Z_1(N) \propto e^{\mu N} N^{\gamma_{\text{saw}}-1}$	partition func.	$Z_{*f}(N) \propto e^{\mu f N} N^{\gamma_f - 1}$
$< r^2 > \propto N^{2\nu_{\text{saw}}}$	size	

Phenomena influenced by star exponents

- Short distance force between star polymers:

$$< F(r) > \sim \Theta_{ff}/r, \quad \nu\Theta_{ff} = 2\gamma_f - \gamma_{2f} - 1$$

H. Löwen, C.N. Likos *et al.*, '98-.

- Diffusion limited reactions involving polymers:

$$nA + B \rightarrow B, \qquad \text{reaction rate: } k_n \sim (r/\ell)^{-\lambda_n}.$$

C. von Ferber, Yu.H.,'01.

- Multifractality of Laplacian field for fractal boundary conditions:

$$\frac{< \phi^n(\vec{x}+\vec{r}) >}{< \phi(\vec{x}+\vec{r}) >^n} \sim (R/r)^{-\tau_n}, \quad \vec{x} \in \partial X.$$

M.E. Cates, T. Witten, '86

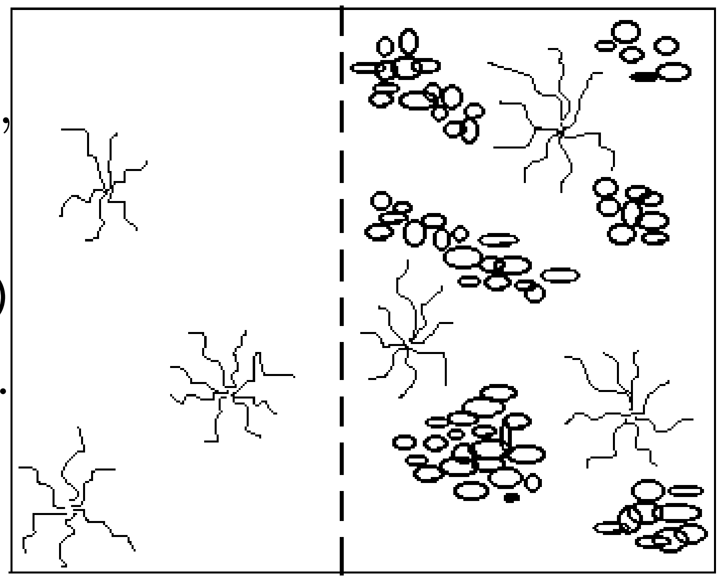
- DNA denaturation — Y. Kafri, E. Carlon, '02

Phenomenon of current interest

Consider star polymers immersed in a good solvent, part of which is in a porous medium:

$Z_{*f}(N) \propto e^{\mu f N} N^{\gamma_f - 1}$,

$\mathcal{F} = -\mu f N - (\gamma_f - 1) \ln N$.



$Z_{*f}(N) \propto e^{\mu' f N} N^{\gamma'_f - 1}$,

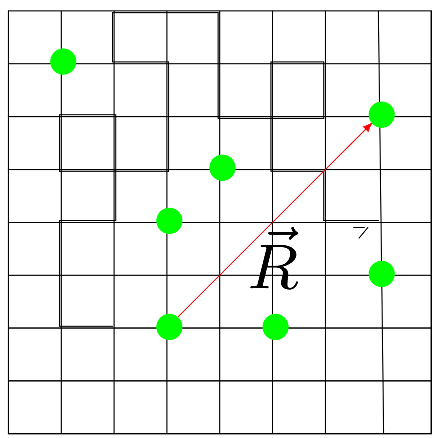
$\mathcal{F} = -\mu' f N - (\gamma'_f - 1) \ln N$.

How will star polymers of different architechture behave?

Is static segregation possible? Dependence on correlation of the medium?

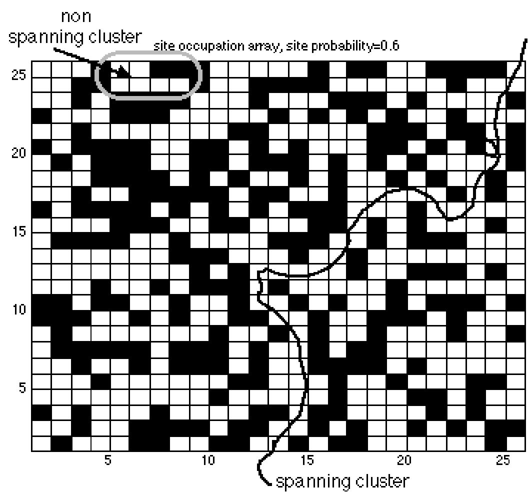
Choice of the model for the porous medium

A. Weak disorder, $c_{\rm perc} < c \leq 1$



$g(R) \sim R^{-a}$, $R \to \infty$

B. Strong disorder, $c = c_{\rm perc}$



$\delta \leq \varepsilon/2$ ($\varepsilon = 4 - d$, $\delta = 4 - a$):
$\nu = \nu^{\rm saw} = 1/2 + \varepsilon/16$,

$\varepsilon/2 \leq \delta \leq \varepsilon$: $\nu = 1/2 + \delta/8$.
V. Blavats'ka *et al.*'01

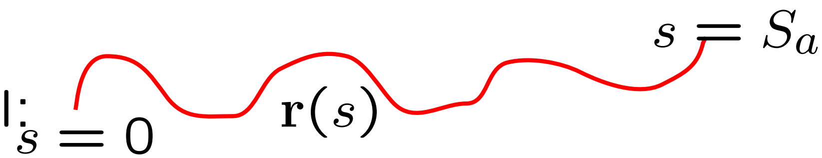
$\epsilon > 0$ ($\epsilon = 6 - d$):
$\nu = 1/2 + \epsilon/42$,

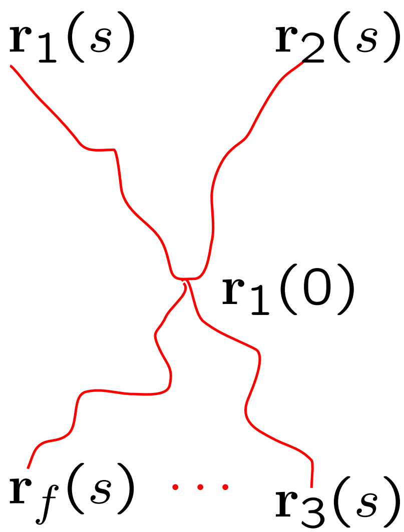
Y. Meir, A. B. Harris'89,
C. von Ferber *et al.*'04

Here: case A

Field-theoretical description of a polymer star

- Edwards continuous chain model:





The partition function of the f-arm polymer star: $\mathcal{Z}_f\{S_a\} = \int D[\mathbf{r}_1, \ldots, \mathbf{r}_f] \times$

$$\exp\left[-\mathcal{H}_f\right] \prod_{a=2}^{f} \delta^d(\mathbf{r}_a(0) - \mathbf{r}_1(0)).$$

$$\mathcal{H}_f = \frac{1}{2} \sum_{a=1}^{f} \int_0^{S_a} \mathrm{d}\, s \left(\frac{\mathrm{d}\, \mathbf{r}(s)}{\mathrm{d}s}\right)^2 + \frac{u_0}{4!} \sum_{a,b=1}^{f} \int_0^{S_a} \mathrm{d}s \int_0^{S_b} \mathrm{d}s' \delta^d(\mathbf{r}_a(s) - \mathbf{r}_b(s')).$$

- Mapping to the $m = 0$ limit of the field theory:

$$Z_f\{\mu_a\} = \int \prod_{b=1}^{f} \mathrm{d}\, S_b \exp[-\mu_b S_b] \mathcal{Z}_f\{S_a\} = \int D[\phi] \exp[-\mathcal{L}]|_{m=0},$$

$$\mathcal{L} = \frac{1}{2} \int \mathrm{d}^d x \, [\, (\mu_0^2 |\vec{\phi}(x)|^2 + |\nabla \vec{\phi}(x)|^2) + \frac{u_0}{4!} S_{i_1,\ldots,i_4} \phi^{i_1}(x) \ldots \phi^{i_4}(x) \,]\,.$$

- A polymer star $\Longleftrightarrow$ the traceless local composite operator:

$$\sum_{i_1,\ldots,i_f=1}^{m} N^{i_1,\ldots,i_f} \phi^{i_1}(x) \ldots \phi^{i_f}(x), \text{ with } \sum_{i=1}^{m} N^{i,i,\ldots,i_f} = 0.$$

- Quenched disorder: $\mu_0^2 \to \mu_0^2 + \delta\mu_0(x)$, with

$$\langle\langle \delta\mu_0(x) \rangle\rangle = 0, \qquad \langle\langle \delta\mu_0(x) \delta\mu_0(y) \rangle\rangle = g(|x - y|).$$

● Replicated effective Lagrangean (Weinrib, Halperin'83):

$$\mathcal{L}_{\text{eff}} = \frac{1}{2}\sum_{\alpha=1}^{n}\int \mathrm{d}^d x[(\mu_0^2|\vec{\phi}_\alpha(x)|^2 + |\nabla\vec{\phi}_\alpha(x)|^2) + \frac{u_0}{4!}S_{i_1,\ldots,i_4}\phi_\alpha^{i_1}(x)\ldots\phi_\alpha^{i_4}(x)]$$
$$+ \sum_{\alpha,\beta=1}^{n}\int \mathrm{d}^d x \mathrm{d}^d y g(|x-y|)\vec{\phi}_\alpha^2(x)\vec{\phi}_\beta^2(y), \qquad m,n\to 0.$$

For small k: $\tilde{g}(k) \sim v_0 + w_0|k|^{a-d}$.

● Further reduction: $(u_0+v_0)\to u_0$ (Kim'83, Blavats'ka *et al.'01*):

$$\mathcal{L}(\vec{\phi}) = \sum_k \sum_{\alpha}^{n}\frac{1}{2}(\mu_0^2+k^2)(\vec{\phi}_k^\alpha)^2 + \frac{u_0}{4!}\sum_{\alpha}^{n}\sum_{\{k\}'}(\vec{\phi}_{k_1}^\alpha\vec{\phi}_{k_2}^\alpha)(\vec{\phi}_{k_3}^\alpha\vec{\phi}_{k_4}^\alpha)$$

$$+\frac{w_0}{4!}\sum_{\alpha\beta}^{n}\sum_{\{k\}''}|k|^{a-d}(\vec{\phi}_{k_1}^\alpha\vec{\phi}_{k_2}^\alpha)(\vec{\phi}_{k_3}^\beta\vec{\phi}_{k_4}^\beta).$$

Renormalization

- Correlations: renormalized vertex functions

$$Z_\phi \Gamma^{(2)},\ Z_u \Gamma_u^{(4)},\ Z_w \Gamma_w^{(4)},\ Z_{\phi^2}\Gamma^{(2,1)},\ Z_f \Gamma^{(*f)}, .$$

- Change of scale κ: RG functions

$$\beta_u(u,w) = \frac{\mathrm{d}}{\mathrm{d}\kappa} \ln Z_u,\ \beta_w(u,w) = \frac{\mathrm{d}}{\mathrm{d}\kappa} \ln Z_w,$$

$$\eta_\phi(u,w) = \frac{\mathrm{d}}{\mathrm{d}\kappa} \ln Z_\phi, \qquad \eta_{\phi^2}(u,w) = \frac{\mathrm{d}}{\mathrm{d}\kappa} \ln Z_{\phi^2}, \qquad \eta_f(u,w) = \frac{\mathrm{d}}{\mathrm{d}\kappa} \ln Z_f.$$

- Scale invariance: fixed points $\beta_u(u^*,w^*) = \beta_w(u^*,w^*) = 0$.

- Scaling exponents (in the stable accessible FP)

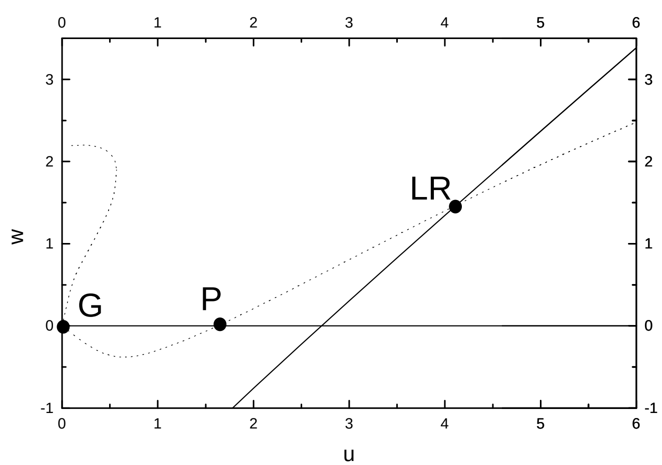
$$\eta = \eta_\phi(u^*),\ \nu = [2 - \eta_\phi(u^*) + \eta_{\phi^2}(u^*)]^{-1},\ \eta_f = \eta_f(u^*,w^*).$$

Results for a polymer chain: scaling is governed by a new law

- ε, δ-expansion, with $\varepsilon = 4 - d$, $\delta = 4 - a$ (Blavats'ka *et al.*'01):

$$\nu = \begin{cases} \nu^{\text{pure}} = 1/2 + \varepsilon/16, & \delta < \varepsilon/2, \\ \nu^{\text{LR}} = 1/2 + \delta/8, & \varepsilon/2 < \delta < \varepsilon, \end{cases}$$

- fixed d, a technique (Blavats'ka *et al.*'02):



The lines of zeroes of the d=3 two-loop β-functions resummed by the Chisholm-Borel method at $a = 2.9$. The fixed point **LR** is stable.

Results for a polymer star: ε, δ-expansion

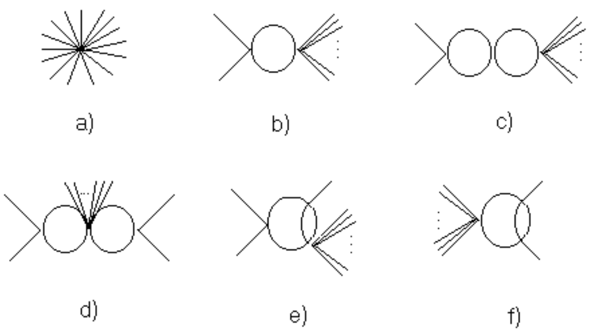


Diagram contributions to the vertex function $\Gamma^{(f)}$ up to the 2-loop order. (a): f-point vertex $N^{i_1,\ldots,i_f}\phi^{i_1}\ldots\phi^{i_f}$, (b): one-loop contribution, (c)-(f): two-loop contributions.

$$\gamma_f = 1 + \nu\eta_f(u^*, w^*) + (\nu(2-\eta)-1)f.$$

$$\eta_f = \begin{cases} \eta_f^{\text{pure}} = -\frac{1}{8}\varepsilon f(f-1), \\ \eta_f^{\text{LR}} = -\frac{1}{4}\delta f(f-1), \end{cases} \quad \gamma_f = \begin{cases} \gamma_f^{\text{pure}} = 1 - \frac{1}{16}\varepsilon f(f-3),\ \delta < \varepsilon/2, \\ \gamma_f^{\text{LR}} = 1 - \frac{1}{8}\delta f(f-3),\ \varepsilon/2 < \delta < \varepsilon. \end{cases}$$

Results for a polymer star: fixed $d = 3$, a technique

a	$f=$ 1,2	3	4	5
(3) [1]	1.18	1.06	0.86	0.61
(3) [2]	1.1573(2)	1.0426(7)	0.8355(10)	0.5440(12)
3	1.17	0.99	0.83	0.57
2.9	1.25	0.87	0.78	0.46
2.8	1.26	0.81	0.76	0.43
2.7	1.28	0.74	0.72	0.40
2.6	1.30	0.73	0.70	0.37
2.5	1.34	0.71	0.70	0.35
2.4	1.35	0.70	0.70	0.31
2.3	1.38	0.70	0.69	0.29

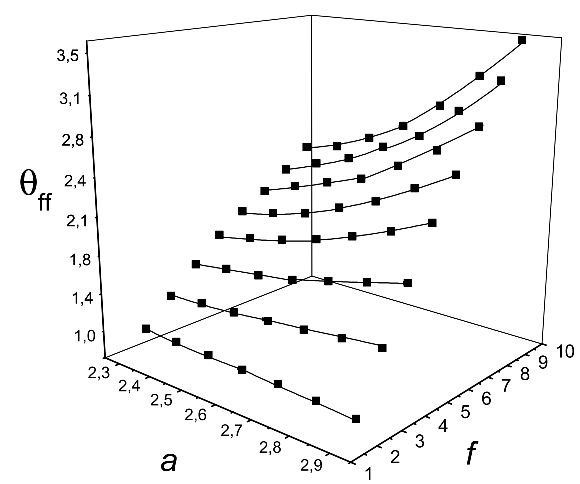
Critical exponents γ_f for the f-arm star in $d = 3$ and different values of a.
[1]: Pure system. Field-theoretical RG (three-loop): v. Ferber, Holovatch '95.
[2]: Pure system. Monte Carlo simulations, Hsu, Grassberger '04.

Contact exponents

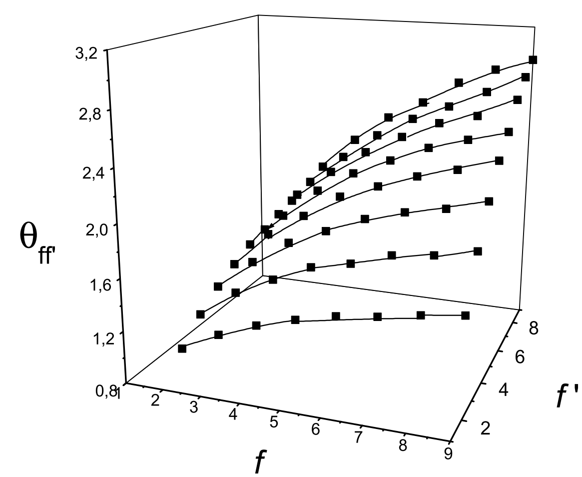
The mean force $F(r)$ between two star polymers of f and f' arms at distance r:

$$\frac{1}{k_B T} F^{(a)}(r) = \frac{\Theta^{(a)}_{ff'}}{r},$$

with $\Theta^{(a)}_{ff'} = \gamma^{(a)}_f + \gamma^{(a)}_{f'} - \gamma^{(a)}_{f+f'} - 1.$



$\Theta^{(a)}_{ff}$ as a function of f and a at $d = 3$.



$\Theta^{(a)}_{ff'}$ as a function of f and f' for $a = 2.7$ at $d = 3$.

What can be learned from these data?

Recall: Segregation behavior depends on $(\gamma_f^{(a)} - \gamma_f)$

- Strong segregation of:

  chain polymers, $f = 1, 2$ and star polymers, $f > 3$

  $(\gamma_1^{(a)} - \gamma_1) > 0$ $(\gamma_f^{(a)} - \gamma_f) < 0$

- For given a (given 'medium'):

$$\gamma_{f_1}^{(a)} > \gamma_{f_2}^{(a)}, \qquad f_1 < f_2.$$

- Entropy-induced softening of short distance star-star force:

$$< F^{(a)}(r) > \sim \ominus_{f_1 f_2}^{(a)} / r.$$