Surface segregation of conformationally asymmetric polymer blends

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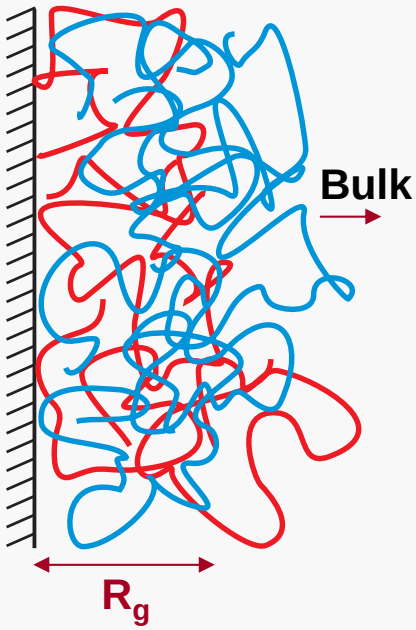
S. Stepanow, A. Fedorenko, Phys. Rev. E 73, 031801 (2006)



The problem: An incompressible polymer blend in the vicinity of a neutral surface

- $l_A > l_B$ Two chemically different polymers
- $l_A = l_B, N_A < N_B$ Difference only in degrees of polymerization

Aim: Computation of the concentration profile of an incompressible athermal blend as a distance to the surface

Results:

- Excess of stiffer polymers in the vicinity of the hard wall
- Excess of shorter polymers at the wall for polymers differing only in lengths
- The effects are controlled by gyration radii of polymers

Boundary conditions in polymer solutions and melts

(Neutral surfaces)

Polymer solution:

- Solution is an (almost) incompressible fluid
- Competion between solvent molecules and the polymer
- Excess of solvent molecules in the vicinity of the wall

Adsorbing (Dirichlet) boundary condition

$$G(z, N; z')|_{z,z'=0} = 0$$

Polymer melt & Surface:

- Incompressible fluid
- Screening of monomer interactions
- Overlapping Gaussian chains
- Constant monomer density across the surface

Reflecting (Neumann) boundary condition

$$\partial_z G(z, N; z')|_{z=0} = 0$$

Qualitative discussion of BCs

Polymer melts (& semi-dilute polymer solutions):

The relevant quantity governing the properties of the system: the number of monomers between two subsequent cross-links along the chain (~1), but not the chain length N

↓

The effect of the wall on the monomers is similar to that on solvent molecules in solution

Monomers are classical objects, which are described in the relaxational regime

↓

$$\rho_{monomer}(z) \simeq \exp(-U_{wall}(z)/k_BT) \simeq$$

uniform in the space between two walls

↓

The Dirichlet boundary condition is irrelevant in dense polymeric systems

Implication for quantum liquids? **Polymer configuration ↔ The trajectory of a quantum particle**

↓

The problem of the boundary condition in polymer melts is expected to have its counterpart in quantum fluids in the presence of a neutral boundary

While the wave functions of single particles obey the Dirichlet boundary condition at the wall, the density of the fluid is not required to be zero at the wall

Collective description of the polymer blend

Individual description: Description in terms of individual conformations $r_i(s)$

Collective description: Description in terms of the monomer densities $\rho_A(r)$ and $\rho_B(r)$

(S. F. Edwards)

$$\rho_A(r) = l^{-1} \sum_{m=1}^{n_A} \int_0^L ds\delta(r - r_m(s)), \qquad \rho_B(r) = l^{-1} \sum_{m=n_A+1}^{n_A+n_B} \int_0^L ds\delta(r - r_m(s))$$

Average monomer density: $\langle \rho_\alpha(r) \rangle = \frac{\int D\Phi \phi_\alpha(r) Z(\Phi)}{\int D\Phi Z(\Phi)}$

Φ_α (α =A,B): collective fields conjugated to $\rho_\alpha(r)$

The partition function: $Z(\Phi) = \exp(-\mathcal{F}(\Phi)), \quad \mathcal{F}(\Phi)$: **The effective Ginzburg-Landau Hamiltonian**

Computations are similar to those in the theory of polymer solutions:
replace the bare interactions in Feynman diagramsby the Edwards´ effective potentials

$$\mathbf{V}^{\mathrm{eff}} = (\mathbf{V}^{-1} + \mathbf{S}_0)^{-1}$$

Pecularities of the collective description in the half-space

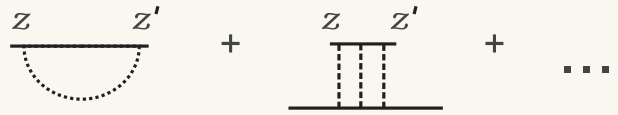
- The description in terms of $r_i(s)$ is gas like → The Dirichlet BC for the bare Green's function

Collective description: liquid ➡ Derivation of the boundary conditions appropriate for a liquid

⬇

Renormalization of the one-polymer Green´s function: $G \to G_r$

$$G_r^{-1} = G^{-1} - \Sigma \qquad \Sigma =$$



The Dyson equation

Homogeneous density $\to G_r$ obeys the reflecting boundary condition

- Presence of the wall ➡ Matrix inversion of $\langle \rho_\alpha(\mathbf{r}_2)\rho_\alpha(\mathbf{r}_1)\rangle_0$ Not translationally invariant due to the wall

⬇

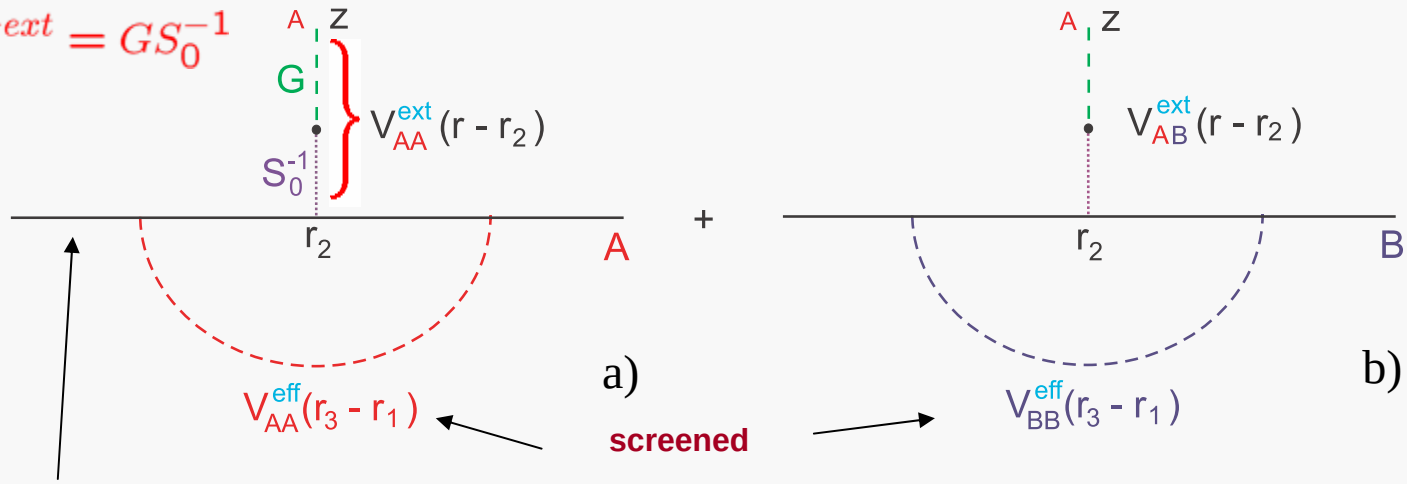
Take into account the Ghost Vertex

$$\langle \rho_\alpha(\mathbf{r}_2)\rho_\alpha(\mathbf{r}_1)\rangle_s =$$
$$\langle \rho_\alpha(\mathbf{r}_2)\rho_\alpha(\mathbf{r}_1)\rangle_0 - \langle \rho_\alpha(\mathbf{r}_2)\rho_\alpha(\mathbf{r}_1)\rangle_{0b}$$

Computation of the excess monomer concentration to the lowest order in effective potentials

$$V^{ext} = GS_0^{-1}$$

$$\langle \rho_A(z) \rangle = \frac{n_A N_a}{V} +$$



$$G_r(r, r_0, L-s_3) = G_0(r^{||}-r_0^{||}, L-s_3)[G_0(z - z_0, L - s_3) + G_0(z + z_0, L - s_3)]$$

Polymer Green´s function with the reflecting boundary condition

Analytical expression associated with the diagram a):

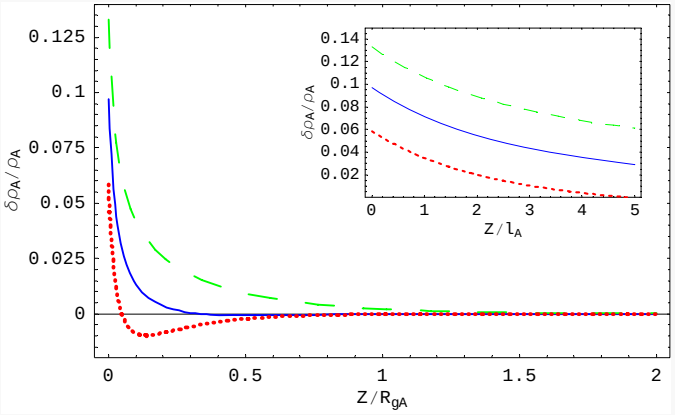
$$-\frac{\rho_A \tilde{V}_{AA}^{ext}}{8\pi^3 N_A} \int d^2q^{||} \int dq \tilde{V}_{AA}^{eff}(q^{||2} + q^2) \frac{q^2a^2e^{-2z\sqrt{p+x}/a} + 2qa\sqrt{p+x}\sin(qz)e^{-z\sqrt{p+x}/a} + p + x}{p^2(p+x)(p+x+q^2a^2)^2}$$

$$x = q^{||2}a^2, \quad a^2 = \frac{l^2}{6}$$

Laplace transformation with respect to the contour length N
(p is Laplace conjugate to N)

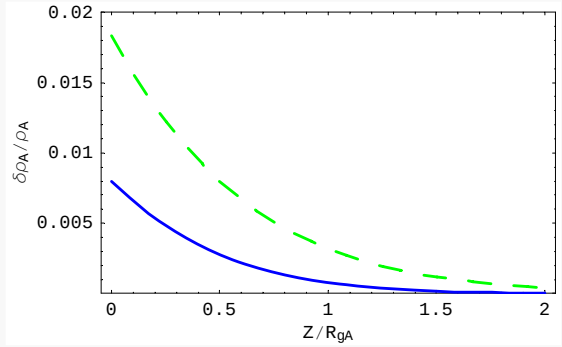
Concentration profiles as a function of the distance to the wall

$l_A > l_B$



Concentration profile of the A polymer as a function of the distance to the surface for different values of N_B, and l_A=1.5, l_B=1, Λ^{-1}=1.55. Continuous line: $N_A=N_B=10^4$; dashes: $N_B=5\cdot10^4$; dots: $N_B=2\cdot10^3$.

$l_A = l_B$, $N_A < N_B$



Concentration profile of the A polymer as a function of the distance to the surface for different values of N_B, and l_A=l_B=1.5, $N_A=10^4$, Λ^{-1}=1.55. Continuous line: $N_B=2\cdot10^4$; dashes: $N_B=5\cdot10^4$.

Analytical Results

- The excess of the stiffer polymer ($l_A > l_B$, $R^A_g = R^B_g$) at the surface ($z=0$)

$$\delta\rho_A(z=0) = \frac{27}{\pi^2}\Lambda\frac{\rho_A\rho_B l_A^2 l_B^2}{(\rho_A l_B^2+\rho_B l_A^2)^2}\left(\frac{1}{l_B^2}-\frac{1}{l_A^2}\right)\ln(a^2\Lambda^2 N) > 0$$

Qualitative: the stiffer polymer with the same R_g is less disturbed by the wall

- The excess of the shorter polymer (A=B, $N_A < N_B$) at the surface

$$\delta\rho_A(z=0) = \frac{3}{4\pi^2}\frac{\Lambda}{l^2}\frac{\rho_A\rho_B}{(\rho_A+\rho_B)^2}\ln\frac{N_B}{N_A}$$

Qualitative: compatible with the crossover to polymer solution, $N_A \to 1$

$\Lambda^{-1} \simeq l_{cs}$: length below of which the blend is not more incompressible

Summary

Study of the behaviour of polymer blends of two chemically different polymers in the vicinity of a neutral surface

Computation of the concentration profile of an incompressible athermal blend as a distance to the surface

- **Excess of stiffer polymers in the vicinity of the hard wall**
- **Excess of shorter polymers at the wall for polymers differig only in lengths**
- **The effects are controlled by gyration radii of polymers**

Outlook

- **The effect of the higher-order terms,**
- **Consideration of surfaces with different preferences,**
- **Behaviour of polymers with complicated architecture,**
- **…**