Molecular migration in complex formulations: *Role of elasticity in binary polymer gels*

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Outline

- Introduction and Background

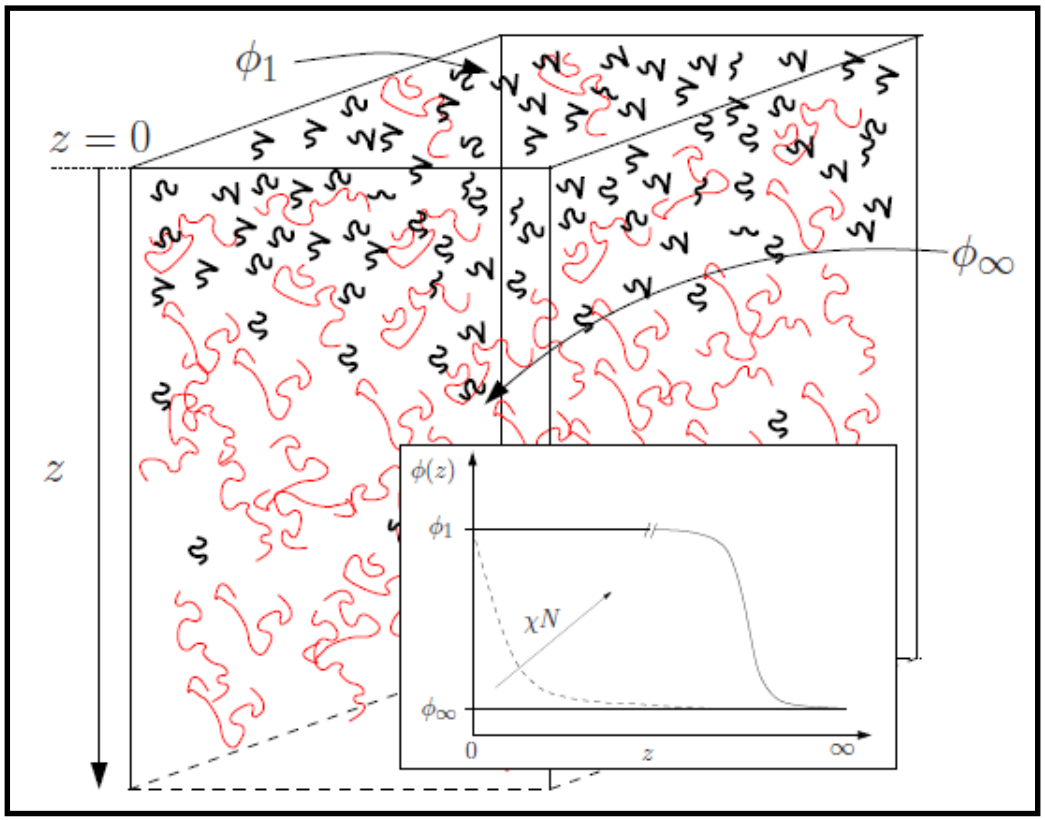
  Surface segregation in polymer mixtures

  - Experiment
  - Theory (Schmidt-Binder-MFT, SCFT)
- Our work

  Surface segregation in binary polymer gels

  - Model and Results
  - Experimental data fitting → limitations of the model
- Conclusions and new directions (LCL)

What is the problem?



- Low molecular weight component migrates to the surface
- A balance between loss of translational entropy and gain in surface free energy dictates the process

- How to determine what fraction of the material leeches to the surface?
- Can this “blooming” process be controlled?

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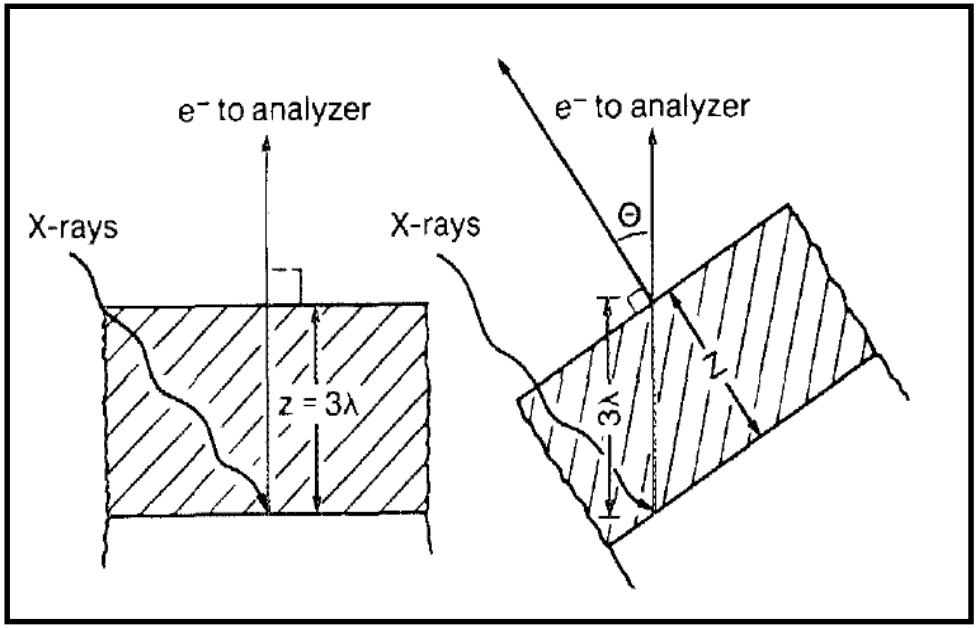
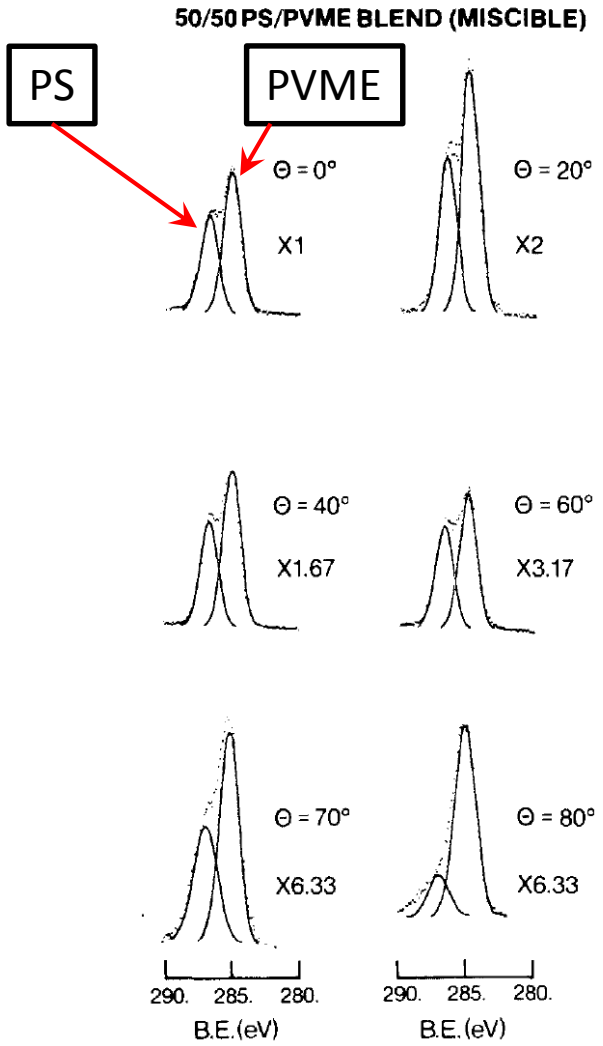
XPS on PS/PVME blends

- Angular dependence of scattered e^-
- Depth profile ≈ 10 A
- Measure emission spectra from Hydrogen Carbon and Oxygen Carbon
- Calibrate for pure PS and PVME blends
- Measure surface enrichment of low surface energy component





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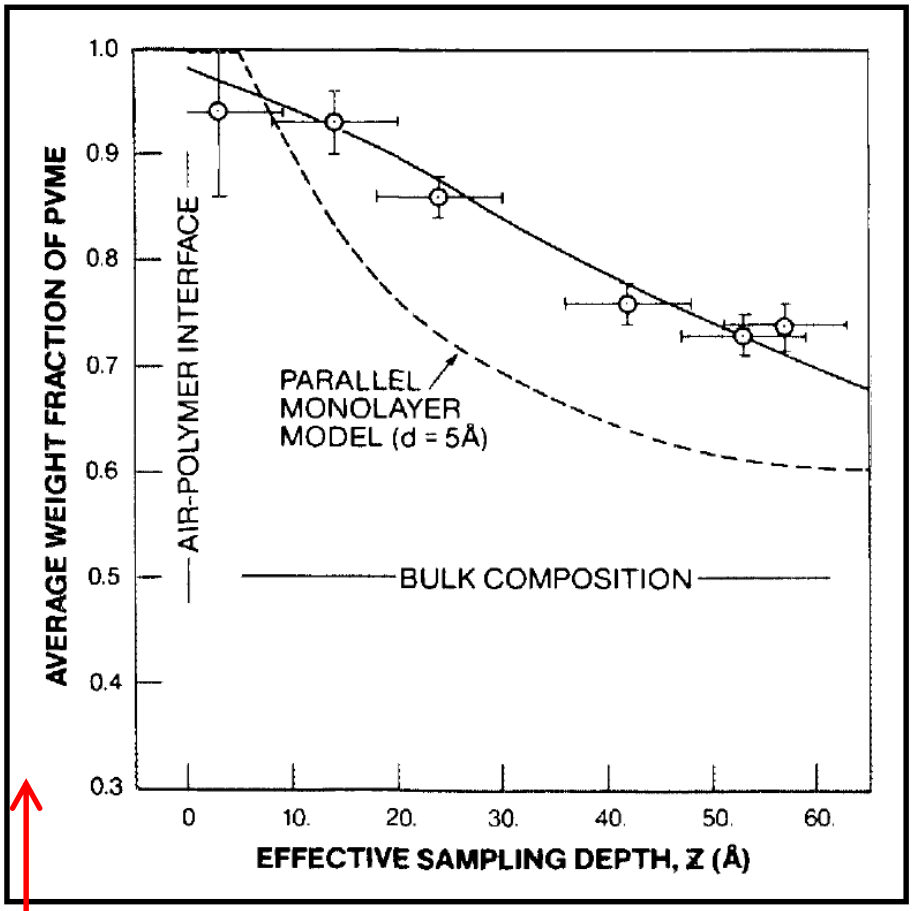
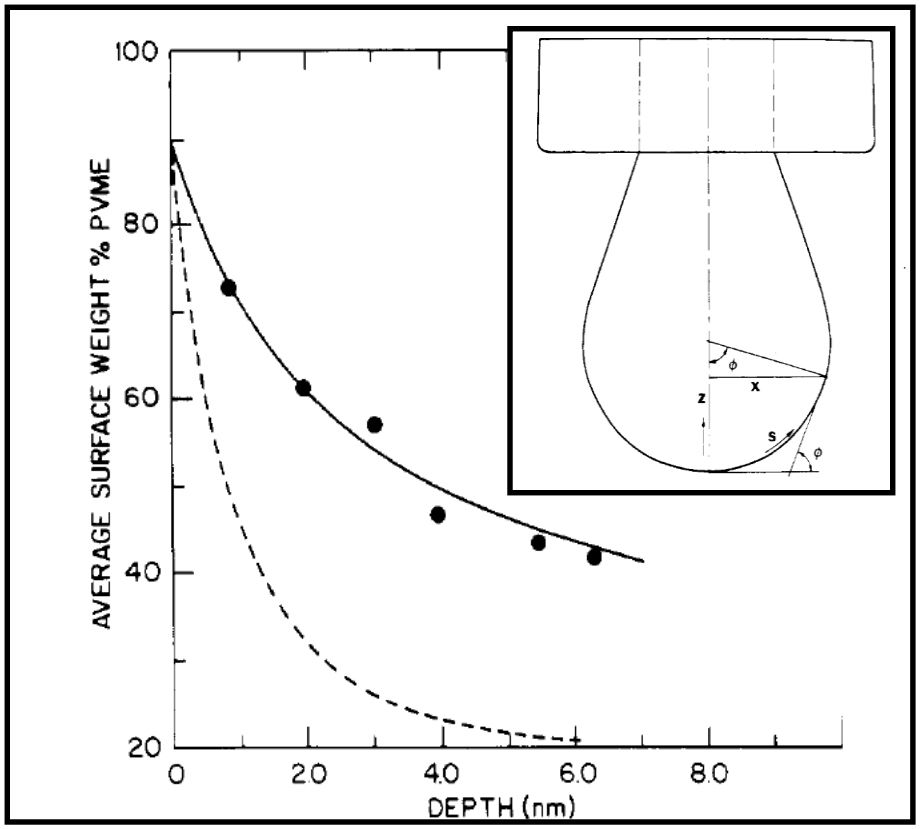
Surface enrichment of PVME in PS/PVME blends





D.H.–K. Pan and W.H. Prest Jr. *J. Appl. Phys.* **58**, 2861 (1985)
Q. S. Bhatia, D. H. Pan, J. T. Koberstein, *Macromol.* **21**, 2166 (1988)

- Measured surface tension via pendant drop technique
- Surface Enrichment in 80/20 PS-PVME blends
- γPVME = 21.9 dyn/cm at 150 ^{o}C
- γPS = 29.7 dyn/cm at 150 ^{o}C

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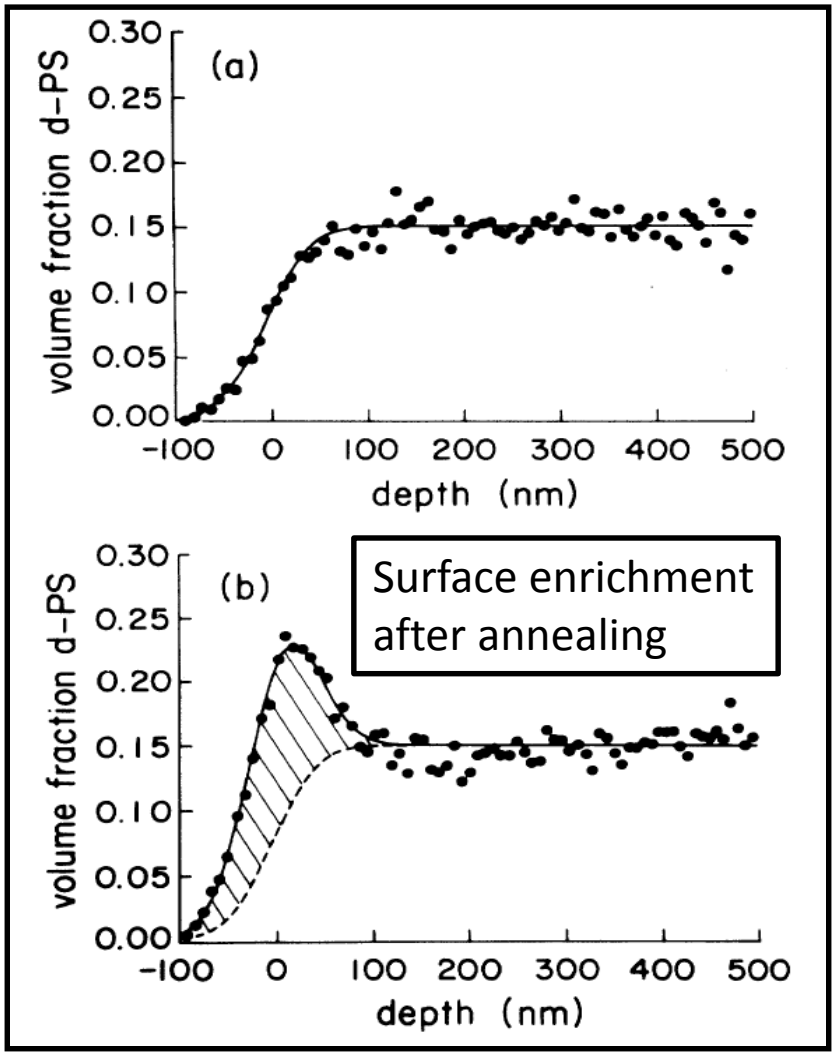
NR on d-PS/PS blends



- Neutron Reflectivity
- Forward recoil spectrometry
- Depth resolution ≈ 80 nm

- Theoretical predictions roughly agree with experiments
- Detailed analysis of profiles show deviations from mean field theory
- NR and Secondary Ion Mass Spec.

R. A. L. Jones *et al.*, *Phys. Rev. Lett.*, **62**, 2166 (1988)
R. A. L. Jones *et al. Europhys. Lett.*, **12**, 41 (1990)

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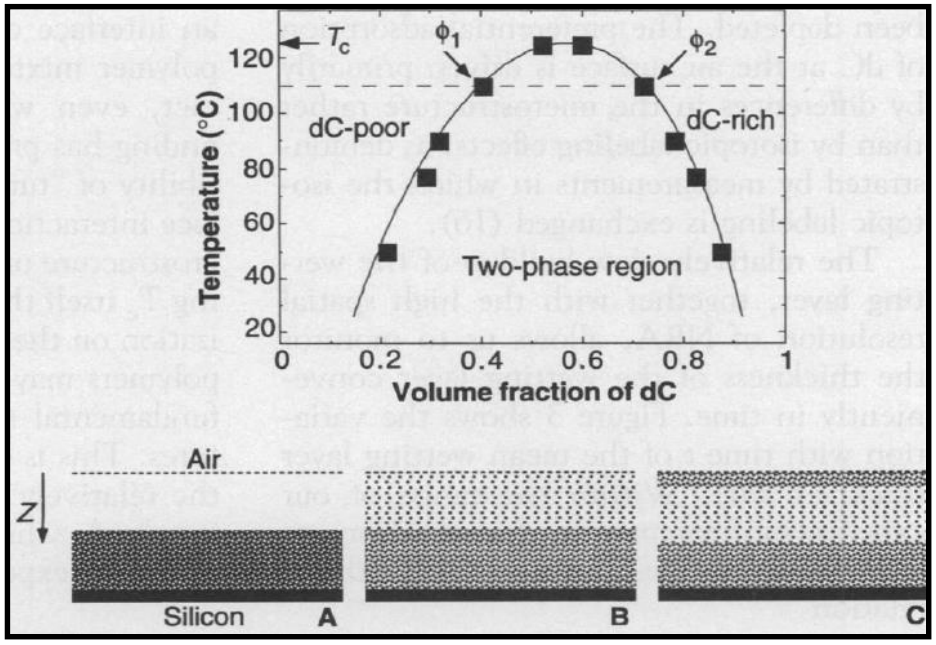
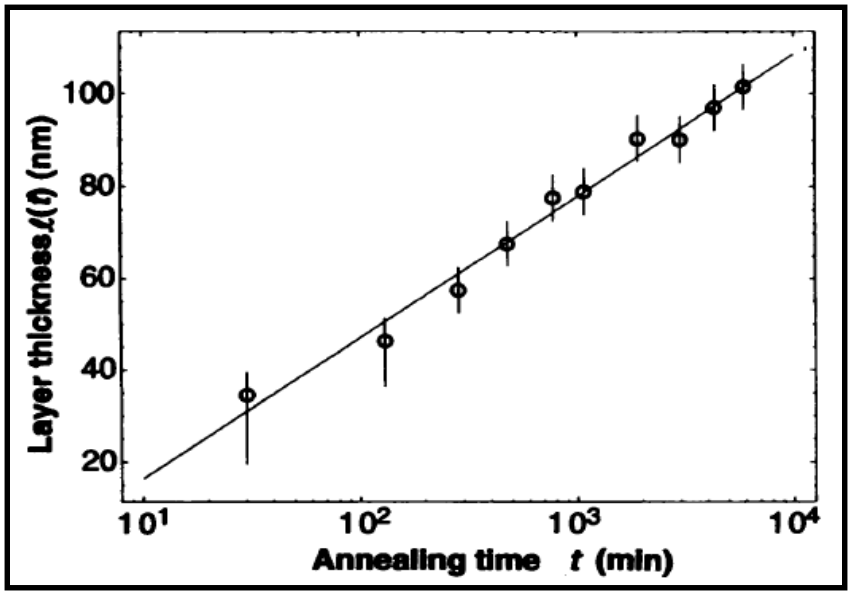
Wetting Transition in immiscible blends



Spin coated | Mixing | Wetting

U. Steiner *et al.*, Science, **258**, 1126 (1992)

- First observation of wetting transition in binary polymer mixture at interface
- Wetting layer grows as $log(t)$



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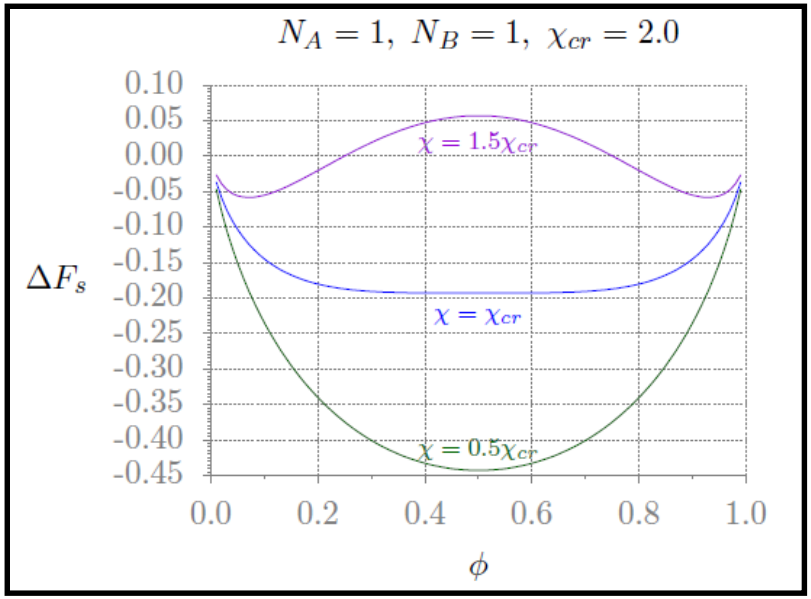
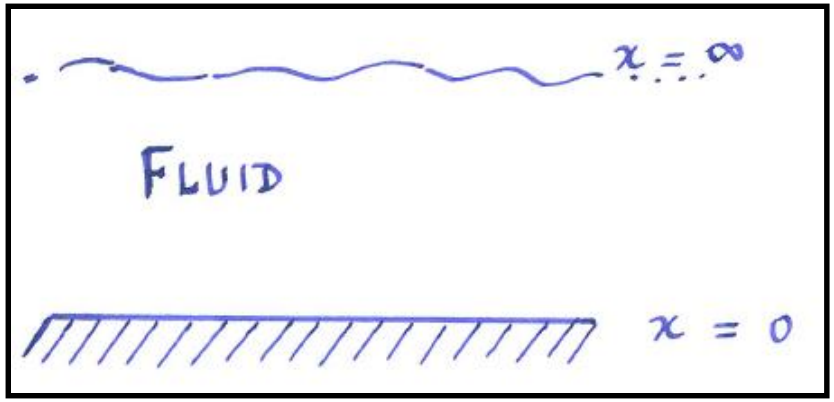
Theory: What was known

Flory-Huggins Theory



Cahn's Theory



Thermodynamics of polymer solutions + Wetting of a wall by a fluid = Schmidt-Binder Theory of surface segregation in polymer blends

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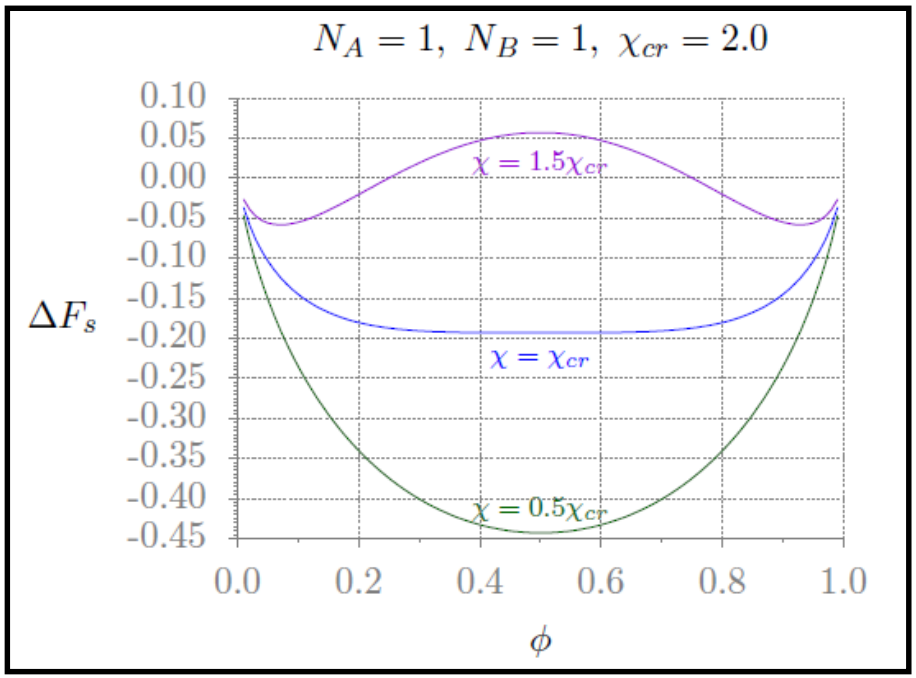
Flory-Huggins Theory

$$F_{FH} = \frac{\Delta F_{mix}}{k_B T} = \left[\frac{\phi_A \log(\phi_A)}{N_A} + \frac{\phi_B \log(\phi_B)}{N_B} + \chi \phi_A \phi_B \right]$$



N_A, N_B : degree of polymerisation

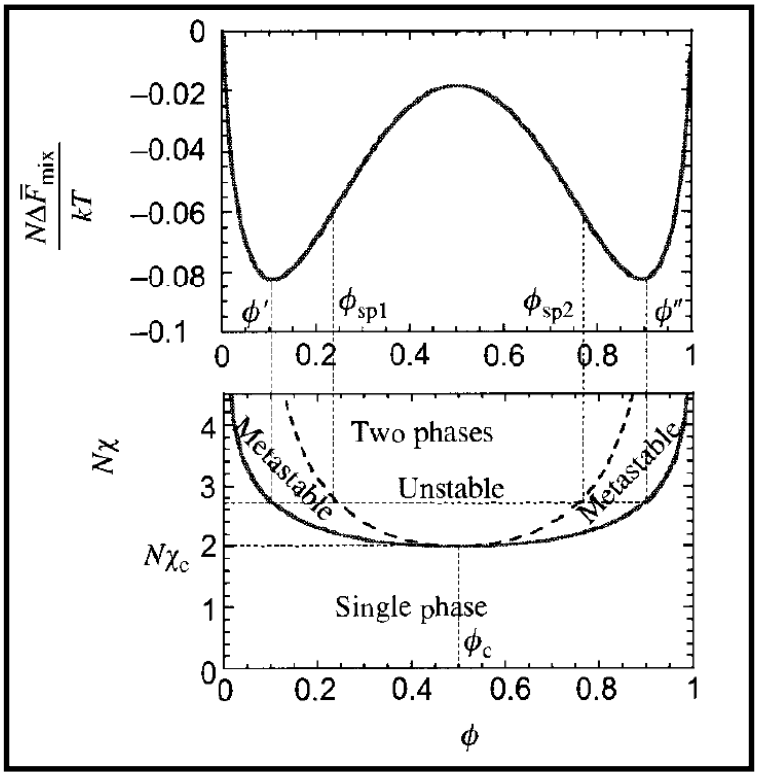
ϕ_A, ϕ_B : volume fraction of A and B

X : miscibility parameter

Can compute Binodals/Spinodals to find conditions for which the mixed phase is metastable and unstable

Flory-Huggins Theory: Phase Diagram

$$\Delta \bar{F}_{\text{mix}} = kT\left[\frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi) + \chi\phi(1-\phi)\right]$$



$$\left(\frac{\partial \Delta \bar{F}_{\text{mix}}}{\partial \phi}\right)_{\phi=\phi'} = \left(\frac{\partial \Delta \bar{F}_{\text{mix}}}{\partial \phi}\right)_{\phi=\phi''}$$

Binodal Line

Symmetric blend

$$kT\left[\frac{\ln\phi}{N} - \frac{\ln(1-\phi)}{N} + \chi(1-2\phi)\right] = 0$$

Spinodal Line

$$\frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} = kT\left[\frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)} - 2\chi\right] = 0$$

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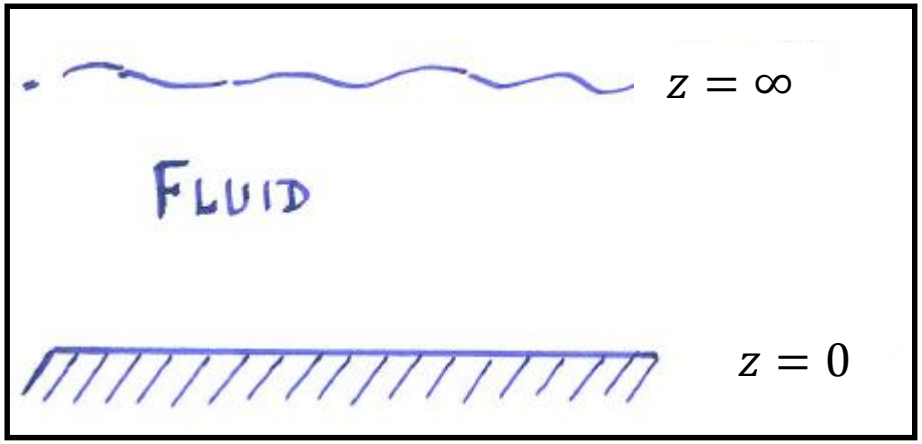
Cahn's Theory of Wetting



Objective: Obtain composition profile and excess free energy due to surface by finding profile ρ that minimizes excess free energy per unit area.
ρ_s: limiting composition of fluid at z=0

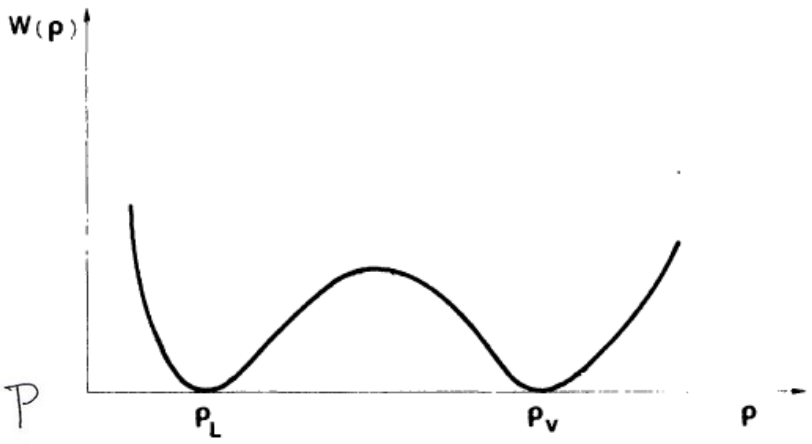
Concentration profile near the wall

- Assume vapour adsorption on to solid surfaces describable in terms of a continuum theory
- Solid–liquid interactions are short ranged described by $\gamma_c(\rho_s)$
- Treat fluid statics via mean field theory with a square gradient functional

J. Cahn, *J. Chem. Phys.*, **66**, 3667 (1977)

$$\gamma_c = \gamma_0 - \gamma_1 \rho_s + \frac{1}{2}\gamma_2 \rho_s^2 + \cdots$$

$$\gamma_d = \int dz \left[\frac{1}{2} L \left(\frac{d\phi}{dz} \right)^2 + W(\rho) \right]$$



$$W(\rho) = F(\rho) - \rho\mu - P,$$

E. L. eqn.

$$- \frac{d}{dz} \left[\frac{\partial \gamma_d}{\partial \rho'_z} \right] + \frac{\partial \gamma_d}{\partial \rho} = 0.$$

$$- L \frac{d^2\rho}{dz^2} + \frac{dW(\rho)}{d\rho} = 0.$$

$$\Rightarrow \quad W'(\rho) = L \frac{d^2\rho}{dz^2}$$

$$\left(\frac{\partial \rho}{\partial z}\right)\left[L\left(\frac{\partial \rho}{\partial z}\right)\right] - \gamma_d = 0.$$

$$\frac{1}{2} L \left(\frac{\partial \rho}{\partial z}\right)^2 = W(\rho) + \text{const.}$$

choose a point in bulk $\rho = \rho_b$

$$\frac{d\rho}{dz} = 0 \quad \& \quad W(\rho_b) = 0.$$

$$\Rightarrow \quad \text{constant} = 0.$$

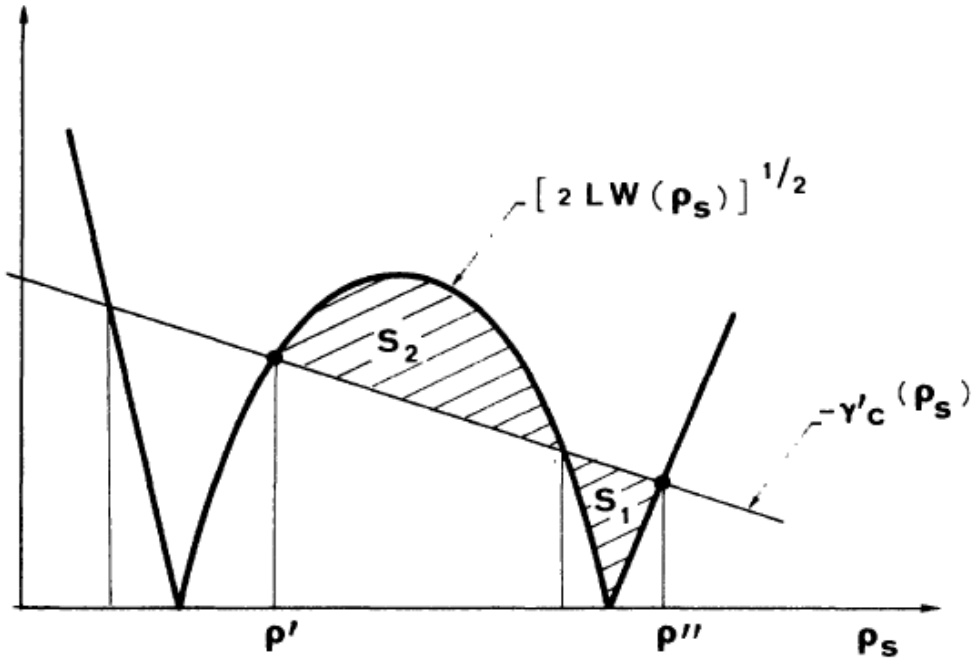
$$\text{Thus} \cdot \int_{\rho_s}^{\rho_b} \left[\frac{L}{2W(\rho)}\right]^{1/2} d\rho = \int_{z=0}^{z} dz'$$

$$\gamma_s(\rho_s, \rho_b) = \int_{\rho_b}^{\rho_s} L\left(\frac{\partial \rho}{\partial z}\right) d\rho$$

$$= \int_{\rho_b}^{\rho_s} \left[2 L W(\rho)\right]^{1/2} d\rho$$

$$\gamma_{tot} = \gamma_d + \gamma_c(\rho_s)$$

$$-\gamma_c'(\rho_s) = \left[2 L W(\rho_s)\right]^{1/2}$$



Schmidt-Binder formalism

$$\frac{F_b + F_s^b}{A k_B T} = \int_0^\infty dz \left\{ G(\phi) + \kappa(\phi)[d\phi/dz]^2 \right\} + \mu_1 \phi_1 - \frac{1}{2} g \phi_1^2$$

Surface free energy → F_S

$$G(\phi) = \frac{\phi \log(\phi)}{N_A} + \frac{(\phi - 1)\log(\phi - 1)}{N_B} + \chi\phi(\phi - 1) - \Delta\mu\phi$$

Flory-Huggins energy of mixing of polymers

$$\frac{\delta}{\delta\phi}\left[\frac{F_b + F_S^b}{A k_B T}\right] = 0$$

First variation of functional gives equations of motion at equilibrium

Schmidt-Binder formalism

Concentration Profile

$$\frac{6z}{a} = \int_{\phi_1}^{\phi(z)} \frac{d\phi'}{\sqrt{\phi'(1-\phi')[G(\phi',\chi) - G(\phi_\infty,\chi) - \Delta\mu\,(\phi' - \phi_\infty)]}}$$

$$\phi_m = \frac{\phi_\infty + \phi_1}{2}$$

Layer Thickness

Surface excess

$$z^\star = \int_0^\infty (\phi(z) - \phi_\infty)\mathrm{d}z$$

Combination of Flory-Huggin's theory and Cahn's wetting

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Schmidt-Binder: generating profiles

1) Input of $\phi_\infty, \phi_1, N_a, N_b, \chi, a$

2) Calculation of $z(\phi)$

3) Inversion of $z(\phi)$ to $\phi(z)$

4) Analysis of data/plot

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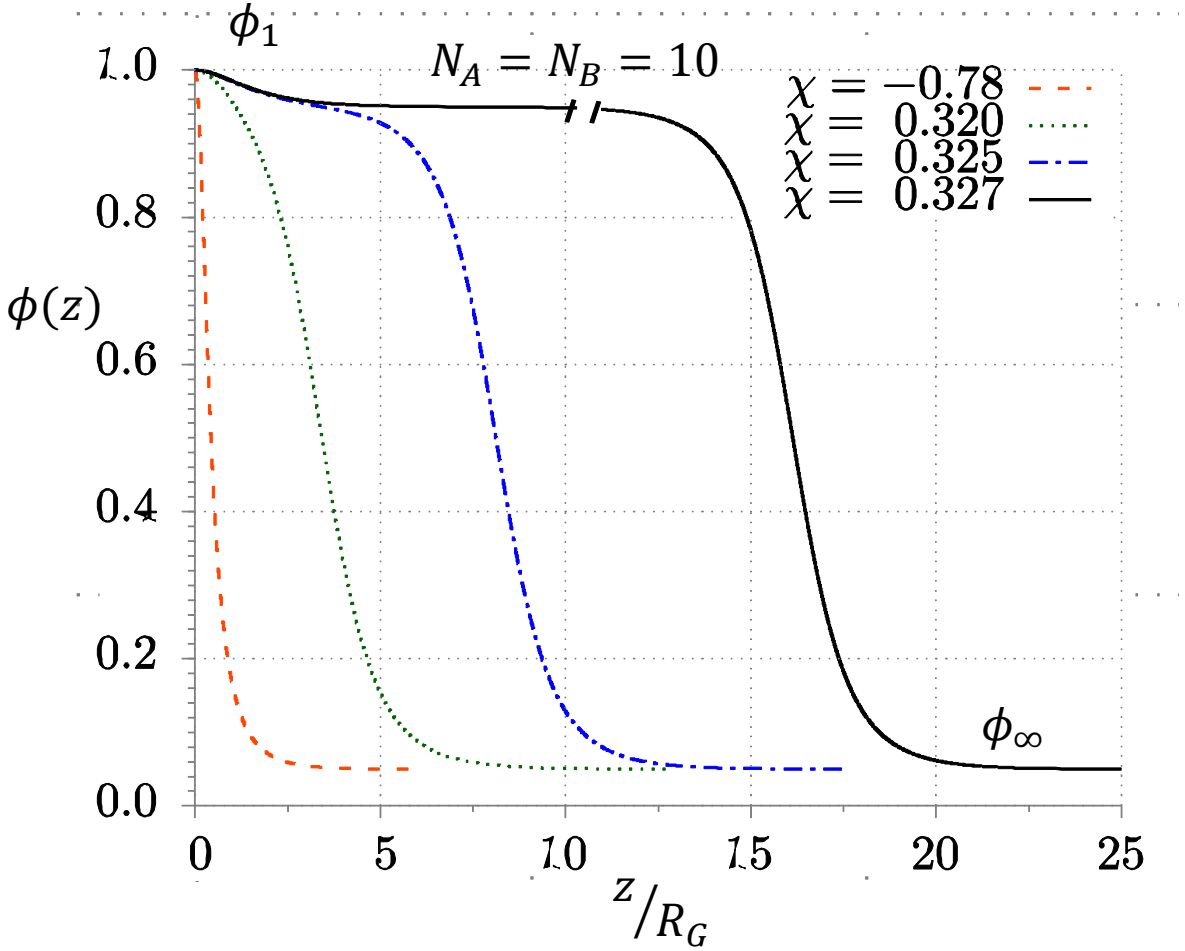
Segregation and wetting profiles from Schmidt-Binder theory (SBMFT)



ϕ_∞: Bulk concentration
ϕ_1: Surface concentration

- Surface segregation for low values of χ
- Wetting transition for large values of χ
- Predictive tool against which to compare experimental data

- ϕ_1 is an input not an output
- Infinite reservoir

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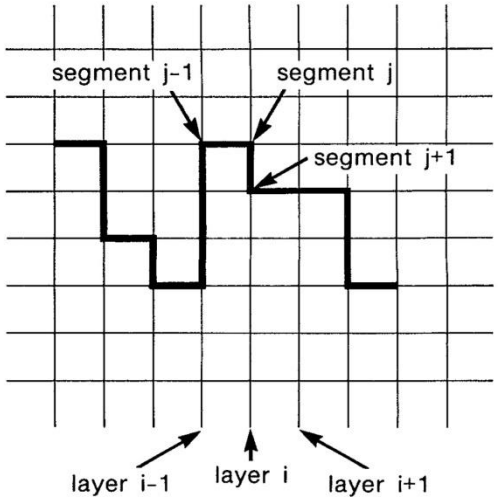
Self Consistent Field theory

Diffusion equation for a polymer distribution

$$\frac{\partial q_{a/b}(\mathbf{r},t)}{\partial t} = R_g^2 \nabla^2 q_{a/b}(\mathbf{r},t) - \beta w_{a/b}(\mathbf{r})$$

- $q_{a/b}(\mathbf{r},t)$ probability distribution for a single monomer, where $\mathbf{r}$ is the distance from the surface (in one dimension $\mathbf{r} = z$), t a segment of the chain;
- $R_g^2 = N_{a/b}\frac{a^2}{6}$, where $N_{a/b}$ is the degree of polimerization, a the Khun length;
- $w_{a/b}(\mathbf{r})$ mean field of interaction between the species;
- In the schematic (Shull 1991) $j = t$ and $i = z \rightarrow$



SCFT Equations

$$w_{a/b}(\mathbf{r}) = \frac{\mu_{a/b}(\mathbf{r}) - k_b T \log\left(\phi_{a/b}(\mathbf{r})\right)}{N_{a/b}} - \Delta w(\mathbf{r}) \tag{1}$$

$$\mu_{a/b}(\mathbf{r}) = N_{a/b} F_{mix} + N_{a/b}\phi_{b/a}(\mathbf{r}) \left[\frac{\partial F_{mix}}{\partial \phi_{a/b}(\mathbf{r})} - \frac{\partial F_{mix}}{\partial \phi_{b/a}(\mathbf{r})} \right] \tag{2}$$

$$\phi_{a/b}(\mathbf{r}) = e^{\beta \mu_{a/b}(\mathbf{r})} \int_0^{N_{a/b}} dt \; q_{a/b}(\mathbf{r}, t) q_{a/b}(\mathbf{r}, N_{a/b} - t) \tag{3}$$

- $\mu_{a/b}$ chemical potential of a single species;
- F_{mix} bulk free energy (i.e. Flory-Huggins);
- $N_{a/b}$ degree of polimerization of a single species;

R.Schull J.Chem.Phys.,Vol. 94, 5723(1991)

Mean field and chemical potential calculated with Flory-Huggins theory!

Initial conditions

Boltzmann probability:

Probability of placing a single monomer on the surface:

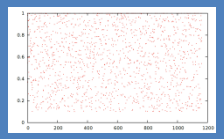
$$q(\mathbf{r},t) = e^{-F_s} \ , \ F_s/\beta = -\mu\phi_1 - g\frac{\phi_1^2}{2}$$

where:

- F_s surface free energy;
- ϕ_1 surface volume fraction;
- μ surface field;
- g surface interaction;

Algorithm for generating profiles using SCFT

Initial conditions for Parameters χ, N_i, F_s, T And monomer distribution q(r,t)



Random volume fractions

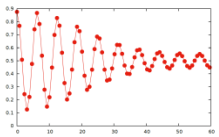
Chemical potential and mean field

Calculation of q(r,t)
Volume fraction
Chemical potential
Mean field

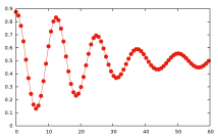
(n-1)

n

Check difference between volume fractions at (n-1) and n iteration

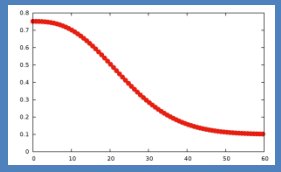


vs

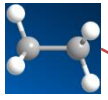


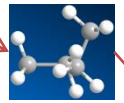
(n-1) n

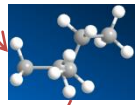
Difference less than setted precision

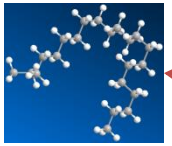


Profiles!









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Building process of a polymer chain

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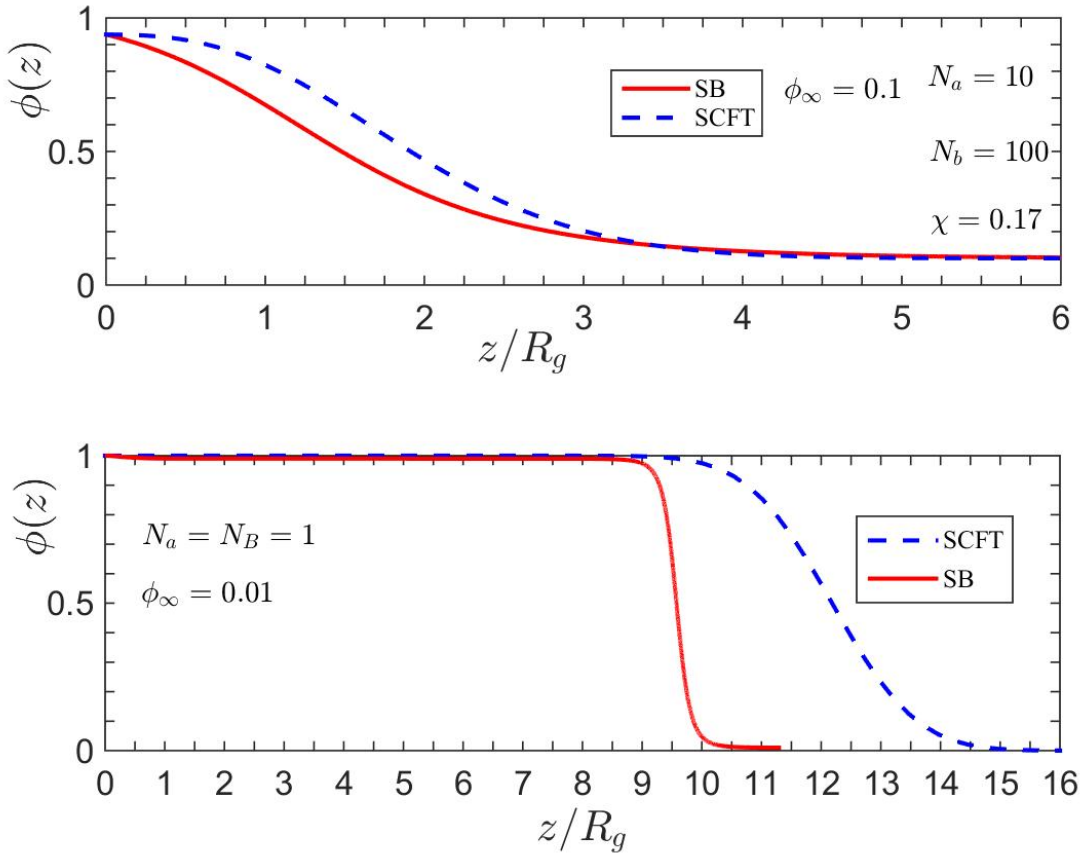
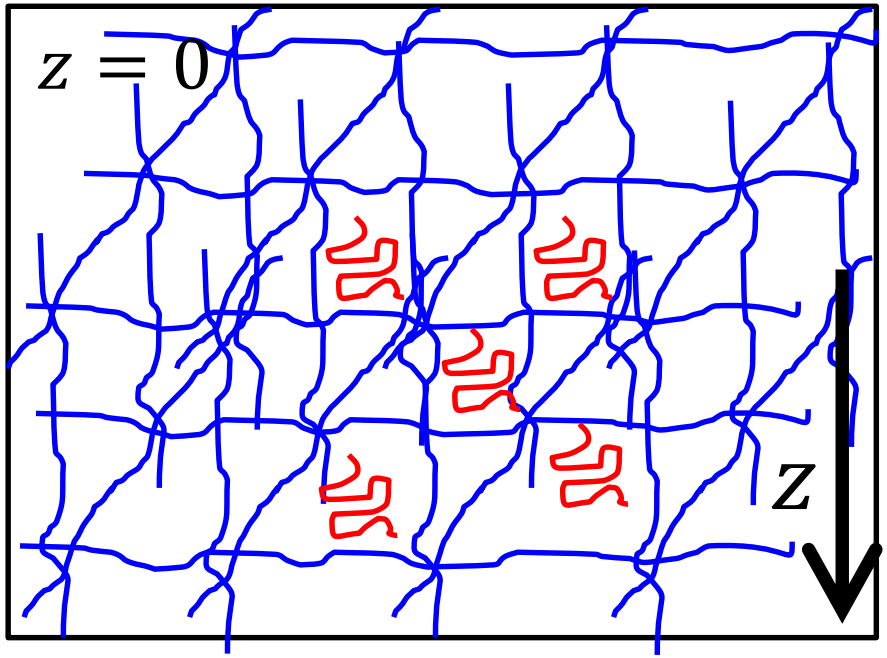
Comparison of surface profiles using Schmidt-Binder and SCFT



SCFT smoothens out the transition !!

Comparison SB-SCFT(top) and wetting transition (bottom) with $\chi \sim 2.1$.

What was lacking in existing models



Elastic effects of the polymer matrix through which the small molecule migrates ignored in previous studies

Important length scales

- R_G: radius of gyration of the polymer
- a: mesh size (for a gel)

Is this a question of kinetics/dynamics or thermodynamics?

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The Elastic Flory-Huggins Functional

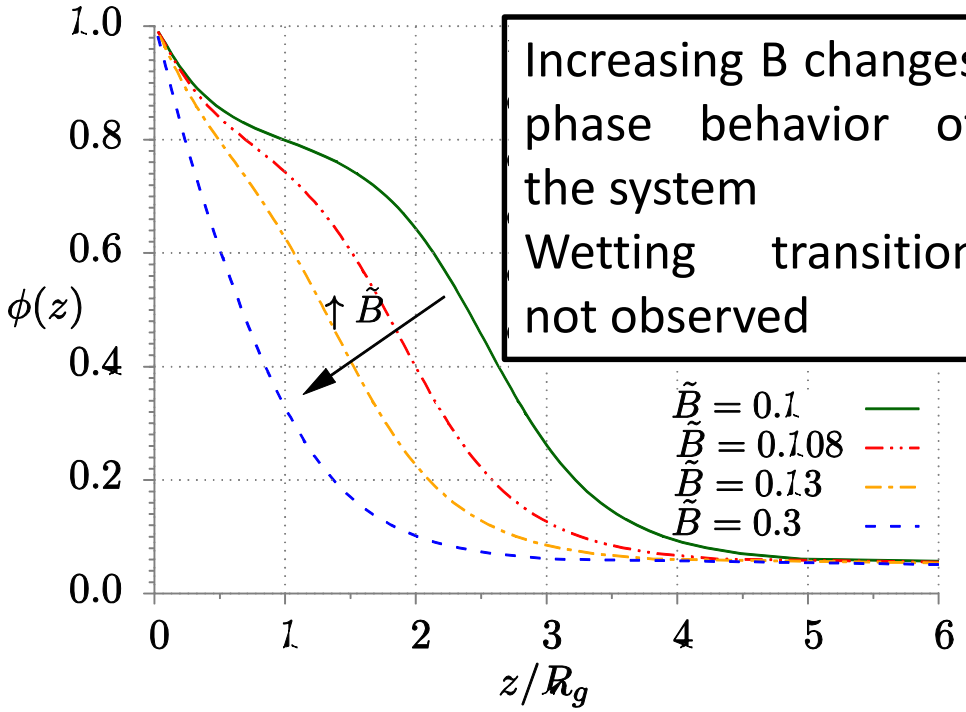
New free energy:

$$\beta F_{mix} = \frac{1}{N_a}\phi \log \phi + \frac{B}{2}(1-\phi_\infty)\left[\left(\frac{1-\phi}{1-\phi_\infty}\right)^{\frac{2}{3}} + 2\left(\frac{1-\phi_\infty}{1-\phi}\right)^{\frac{1}{3}} - 3\right] + \chi\phi(1-\phi)$$

$$\Rightarrow$$

- $N_b \to \infty$, $(1-\phi)\log(1-\phi) \to 0$;
- uniaxial entropy S_{el};
- B elasticity of the network;

Results from our model



Increasing B changes phase behavior of the system
Wetting transition not observed

Predictive tool with elastic moduli estimates that resemble rubbery polymers where effect should be observable.

If validated might pave the way to control migration in model (and perhaps industrial formulations)
Some initial skepticism !!

Incorporated elastic effects to understand small molecule migration in phase separating binary polymer mixtures

Flory-Huggins + Cahn + Gel elasticity = our proposed model

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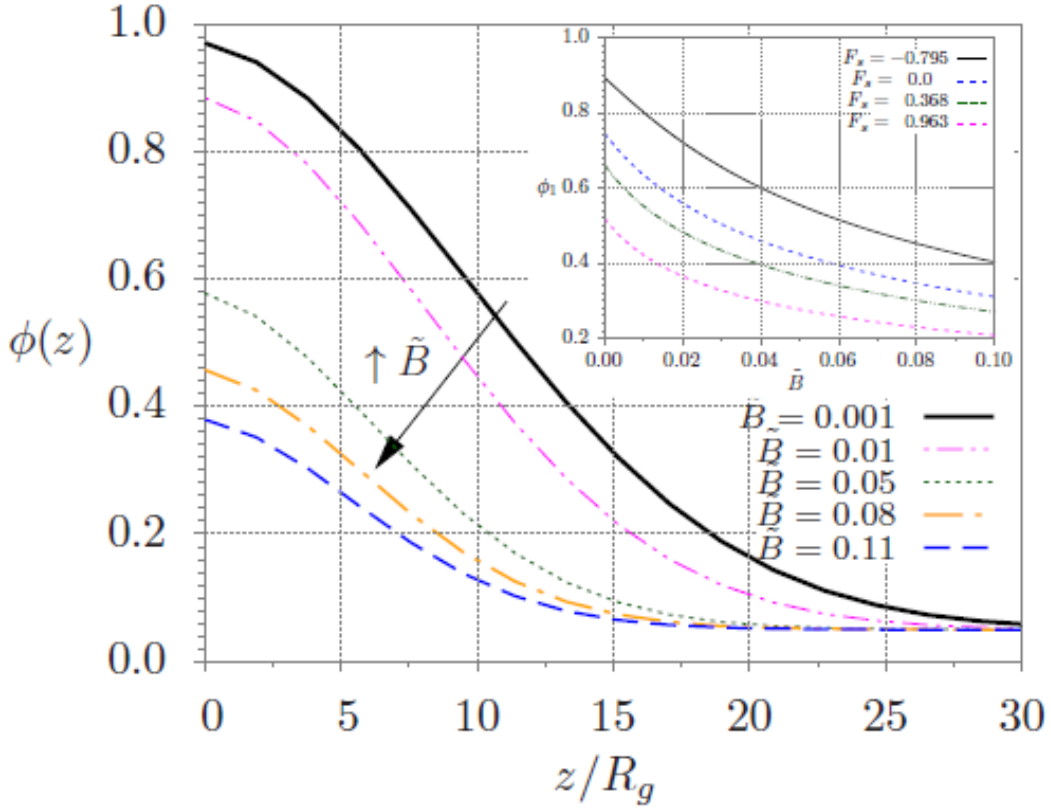
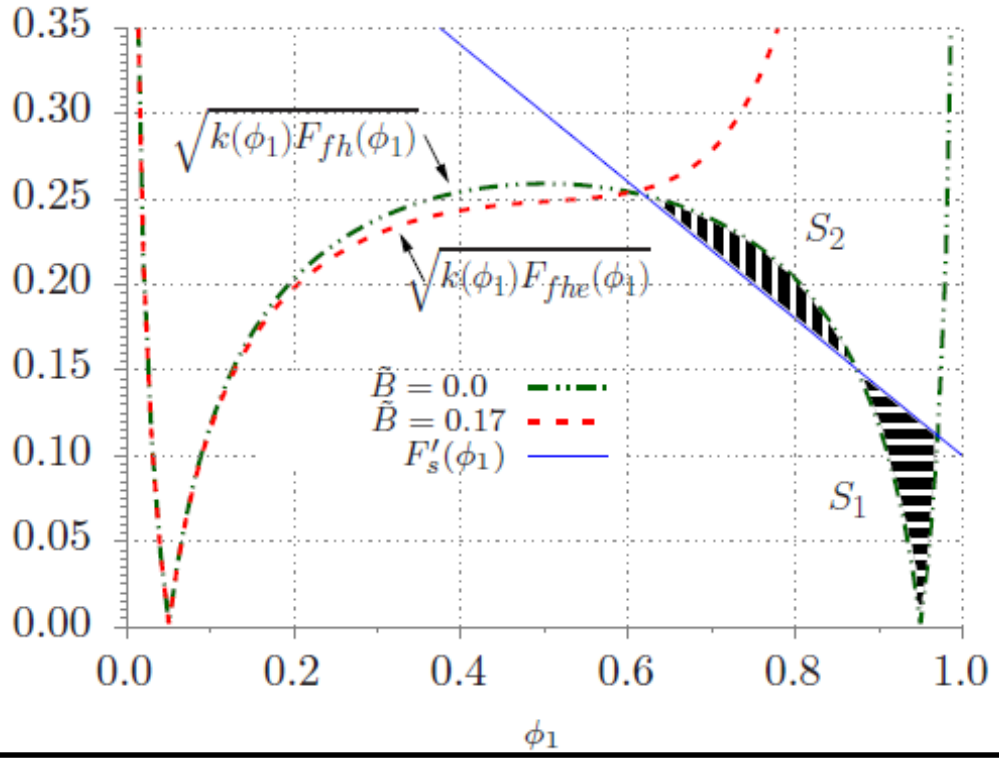
Surface profiles from SCFT



Developed a self-consistent field theoretic formulation. ϕ_1: Surface migrant fraction is an output of this method and no longer an input

Geometric construction to predict wetting



Used Cahn construction (a geometric criterion) to show that the wetting transition is absent for polymer mixtures with elastic interactions

Follows from mechanical equilibrium of a droplet + variational formulation having gradient terms in free energy close to a wall

We are therefore inclined to believe that our theoretical model predicts an observable effect. In order to validate this further we propose another approach at a lower length scale than the current theory.

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Conclusions

- Small molecules in polymer mixtures migrate to the interface exposed to atmosphere (*as a competition between entropy reduction and surface energy gain*)
- Elasticity dominates the physics in case one component is a cross-linked gel.
- Migrant fraction decreases with increasing bulk modulus
- Effect should be observable for rubber like polymers.

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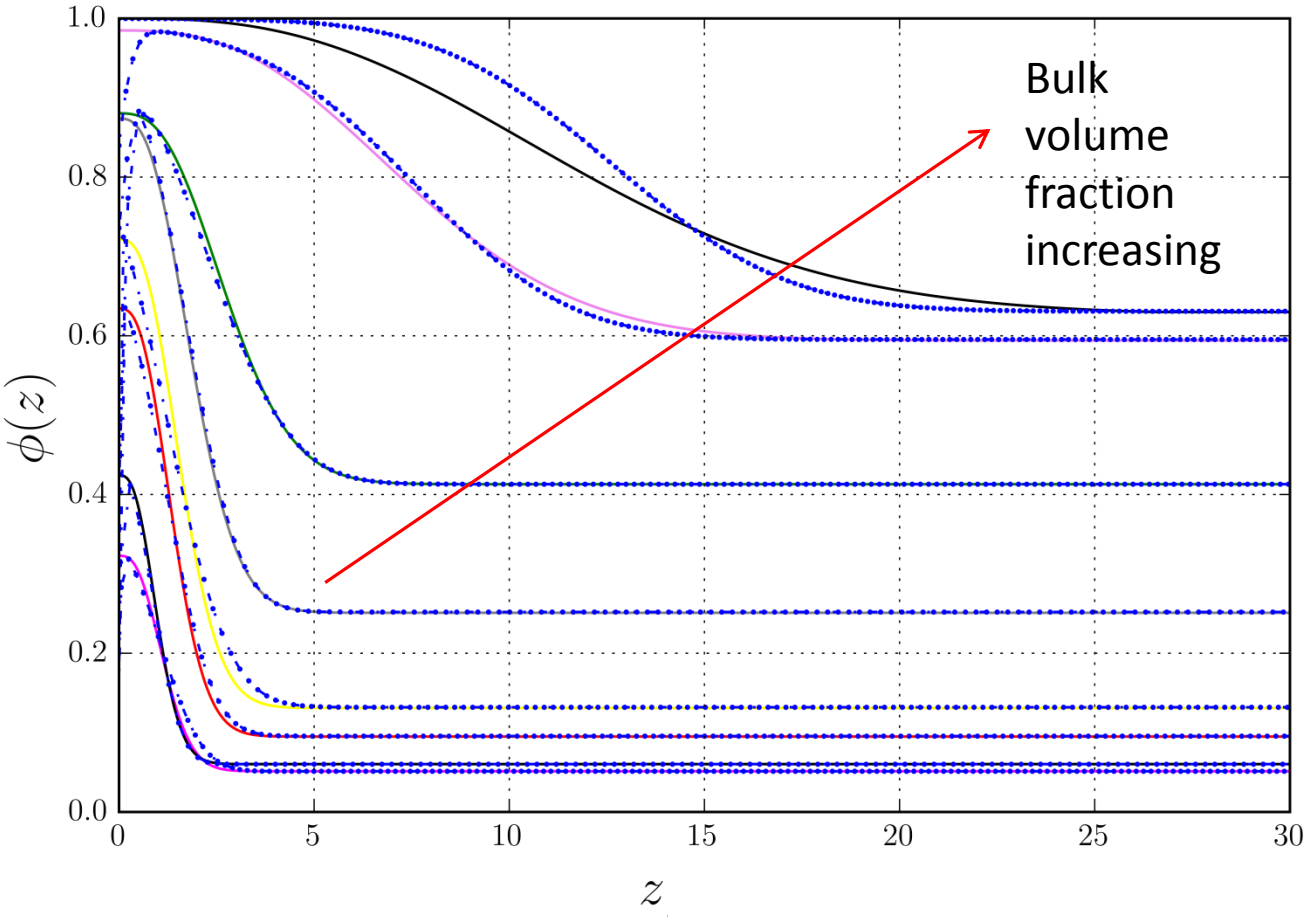
Comparison with NR experiments with scaling lattice parameter (a) for Px/Py



Experimental data:
Blue points

Theory fit:
Continuous lines

Working on a more refined theory that matches experimental data high volume fractions of the migrant

Good fit with a=k1+k2*volume fraction

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Going beyond Flory-Huggins theory

Limitations of Flory Huggins and related free energies:

- Mean field theory (volume changes in mixing not considered)
- Approximates polymers as Gaussian chains (only valid in the limit of long chains)
- Incompressible lattice
- Composition dependence of Flory-Huggins miscibility parameter not considered

Limitations of wetting theory:

- Viscoelastic effects at the interface is not considered

Higgins theory (Locally Correlated Lattice-LCL)-Concepts

- Introduction of compressible volume on lattice model("hard spheres" space and "holes-vacancies" space);
- Microscopic parameters for interaction of single components;
- Good comparison with PVT measurements;
- Large literature of different types of mixtures;

Free Energy-LCL for mixtures

Holes

$$\frac{A}{k_B T} = N_i \ln \phi_i + N_j \ln \phi_j + N_h \ln \phi_h + \frac{N_i q_i z}{2} \ln\left(\frac{\xi_i}{\phi_i}\right)$$

$$+ \frac{N_j q_j z}{2} \ln\left(\frac{\xi_j}{\phi_j}\right) + \frac{N_h z}{2} \ln\left(\frac{\xi_h}{\phi_h}\right)$$

Interaction between different monomers

$$- \frac{N_i q_i z}{2} \ln\left[\xi_i \exp\left(\frac{-\varepsilon_{ii}}{k_B T}\right) + \xi_j \exp\left(\frac{-\varepsilon_{ij}}{k_B T}\right) + \xi_h\right]$$

$$- \frac{N_j q_j z}{2} \ln\left[\xi_i \exp\left(\frac{-\varepsilon_{ij}}{k_B T}\right) + \xi_j \exp\left(\frac{-\varepsilon_{jj}}{k_B T} + \xi_h\right)\right]$$

Where:

$$N_h = (V/v) - N_i r_i - N_j r_j \qquad \phi_m = N_m r_m v / V$$

$$q_m z = r_m z - 2r_m + 2 \qquad \xi_m = N_m q_m / (N_i q_i + N_j q_j + N_h)$$

Lipson, J. Chem. Eng. Data (2014)

Key Parameters Higgins theory

- r_i number of segments per molecule;
- ν_i volume per lattice site;
- ϵ_{ii} non bonded segment-segment interaction;
- Total volume: $V = Nr\nu + N_h\nu_h$;
- $\epsilon_{ij} = g(\epsilon_{ii}\epsilon_{jj})^{\frac{1}{2}}$ -"chi parameter" with $g \simeq 1$;
- z lattice coordination number (z=6);

Offers a computationally cheaper way to match theoretical predictions with experimental data for systems that can be glassy or undergoing a phase transformation and thereby not accessible by computer simulations or SAFT.

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Elasticity Dominated Surface Segregation of Small Molecules in Polymer Mixtures

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EPSRC
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P&G

erc
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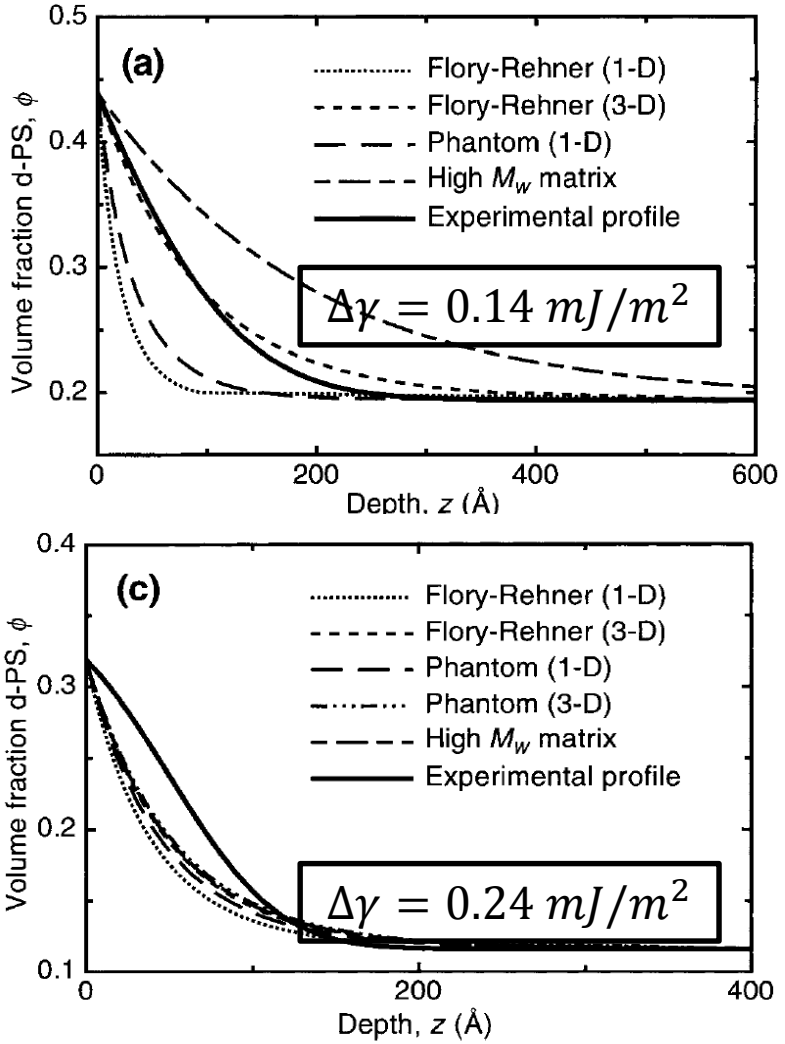
Thank You !!

BC: “What you asked me to do is not happening”
CDG: “Okay, if you do it, it will happen !!”

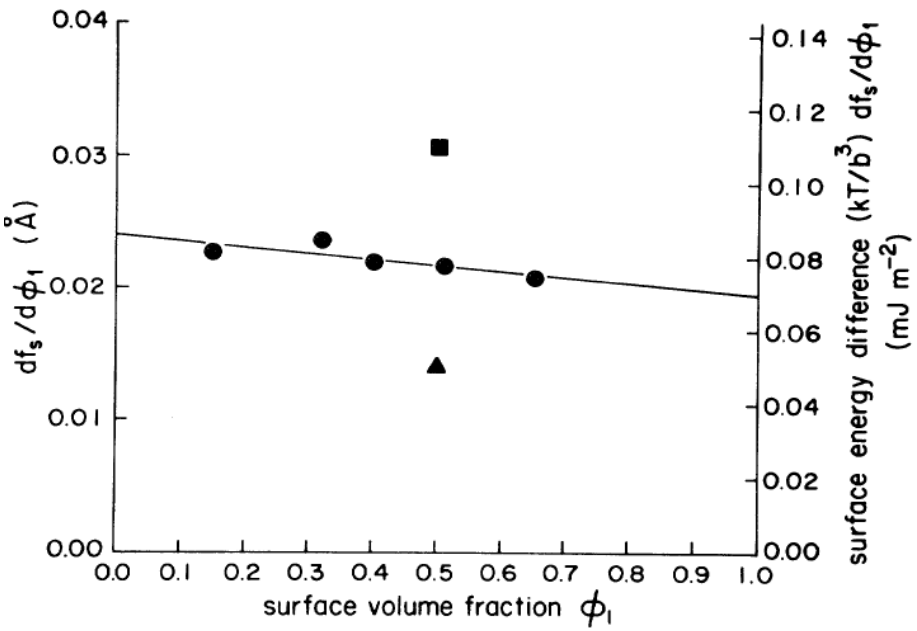
Segregation in d-PS/h-PS mixture

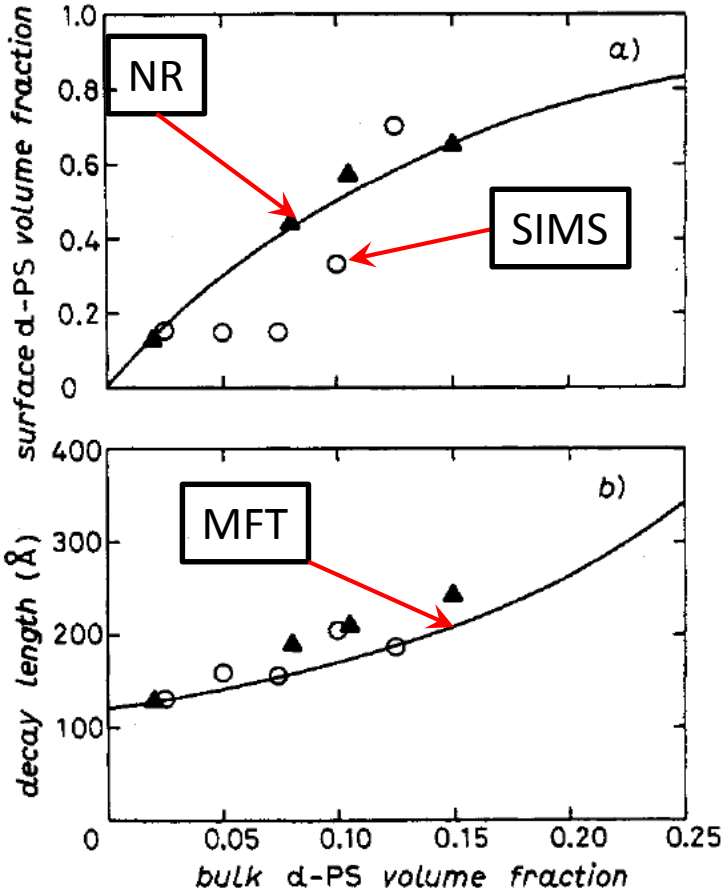
- Measured surface segregation in d-PS/h-PS (hydrogenated poly-styrene) network
- NR/Ion-beam profiling
- $\Delta\gamma$ dependent on network properties
- Fitted experimental profiles with 1D and 3D Flory-Rehner Theory, Phantom Networks (including swelling)
- None of the theories give good fits with 3D Flory-Rehner showing agreement in some regimes



M. Geogheghan *et al.*, *J. Phys. Cond. Mat.*, **12**, 5129 (2000)

NR and SIMS on d-PS/PS blends





- Uses Schmidt-Binder MFT to fit the surface excess as a function of ϕ_b (bulk concentration)
- Parameter estimates $\mu \approx 0.024\ A^{\circ}$, $g \approx -0.0046\ A^{\circ}$ (when surface free energy properly scaled)

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Cahn's Theory of Wetting: Details

$c(\infty) = c_0$ → Bulk composition of the fluid.

$K\left(\frac{\partial c}{\partial x}\right)^2$ → Energy contribution due to presence of a gradient

$\Delta f = f(c) - f(c_0) - (c - c_0)\left(\frac{\partial f}{\partial c}\right)_{c_0}$ → Free energy to create unit volume of uniform fluid of composition c, from a large reservoir of composition c_0

Calculus of variations: $\frac{\delta \Delta F}{\delta c(x)} = 0$ Functional minimisation.

$-\frac{d}{dx}\left[\frac{\partial \Delta F}{\partial c'(x)}\right] + \frac{\partial \Delta F}{\partial c} = 0.$ → Euler - Lagrange eq^{n}.

$\Delta f = K\left(\frac{\partial c}{\partial x}\right)^2 + \text{constant}$