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Numerical simulation of thermodynamic behavior of four components PNC including bare clay

K. Kim^{1, 2}, L. A. Utracki² and M. R. Kamal¹

¹ Dept. Chem. Eng., McGill University

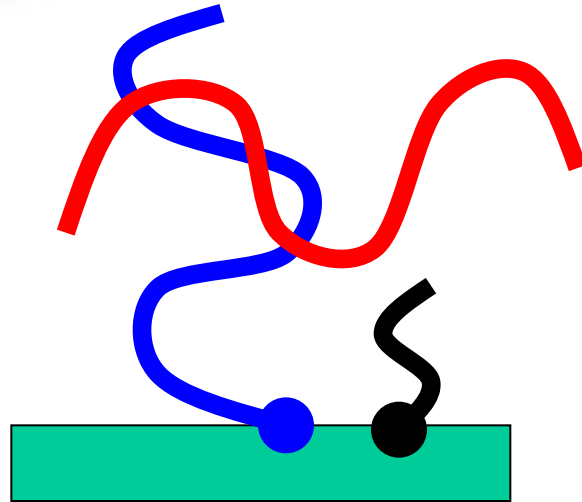
² NRCC/IMI .

NRCC/IMI, PNC-Tech Meeting, Boucherville, QC, 2004.06.10

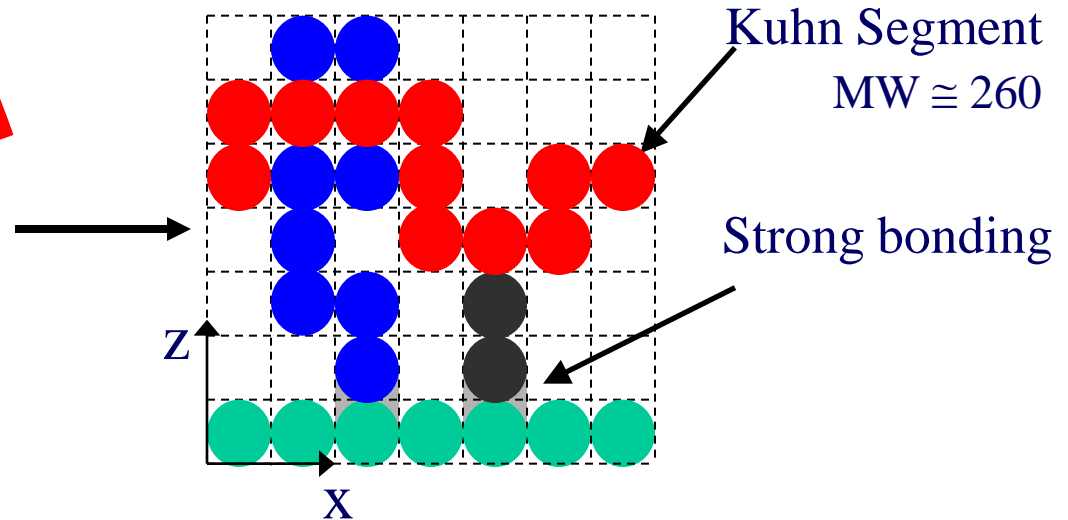
Overview

- Mathematical modeling and numerical simulation of PNC
⇒ Equilibrium thermodynamics
- More realistic 2D and 3D models, compromising four components and their interactions
⇒ The classical models: Fleer *et al.*, and Balazs *et al.*
- Research target
⇒ Analysis and optimization of PNC composition to assure system exfoliation (thermodynamic miscibility).

Numerical model for clay and macromolecules



Physical Chain model

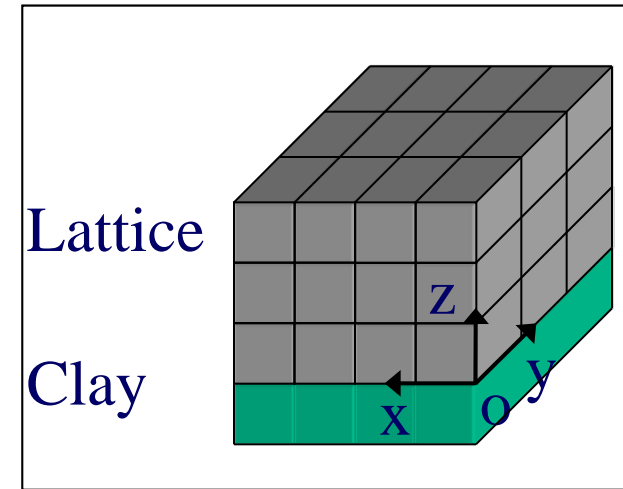


Statistical Representation

- Clay platelet: No conformational energy
- Host polymer: Conformational and mixing energy
- Compatibilizer: Strong bonding to the surface
- Organic modifier: Strong bonding to clay surface

1D vs. 2D or 3D model

- In principle, the lattice model of PNC is 3D
 - In 1D simulations it is assumed that properties of any lattice cell on a X-Y plane are identical, varying only with platelet separation in Z.
 - In 2D simulation it is assumed that properties depends on X and Z.
 - In 3D simulation variation of properties in all three dimensions is computed.
- The computed differences between 1D, 2D and 3D originate from the different probability for segment placement hence the configurational entropy.

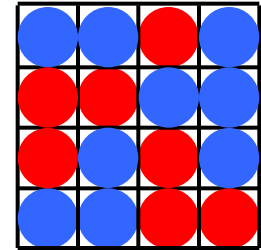


Theory¹

Excess free energy

Conformational Entropy:

Number of ways to occupy free lattice site



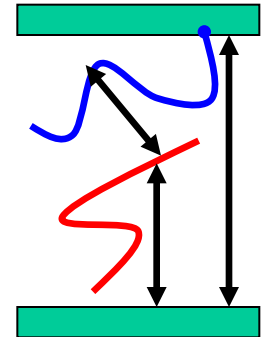
Mixing Enthalpy:

Huggins-Flory Theory

liquid-liquid : $\chi_{hg}, \chi_{hg}, \chi_{ho}$

solid-liquid : $\chi_{hs}, \chi_{hs}, \chi_{os}$

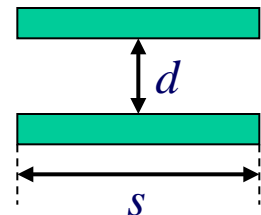
solid-solid



Long-range interaction:

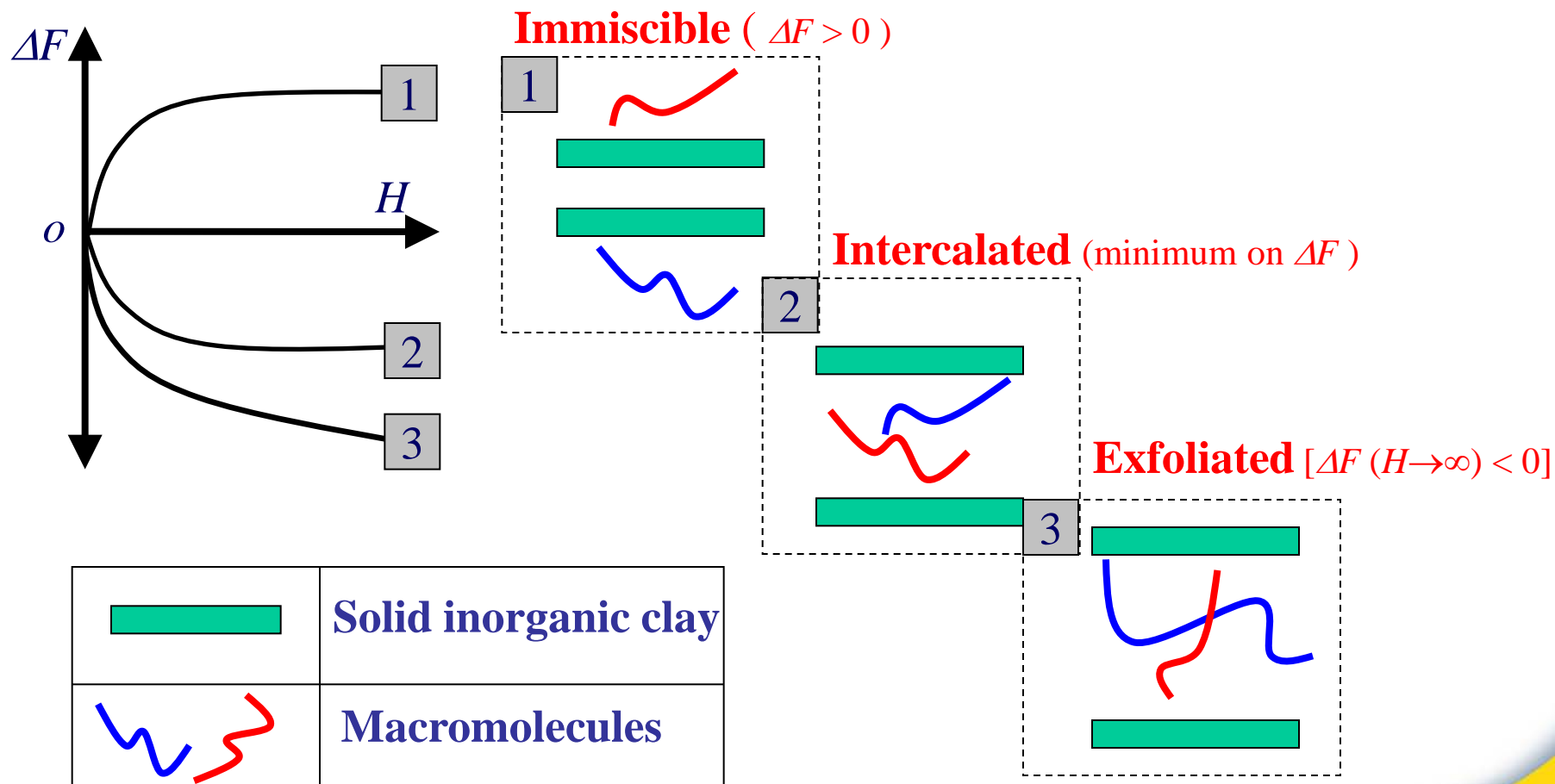
Van der Waals force between a pair of clay plates

$$F = \frac{-A s}{12\pi d^2}$$



Theory²

Equilibrium Thermodynamics.

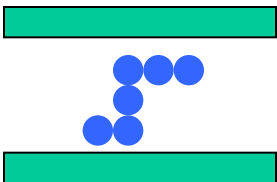
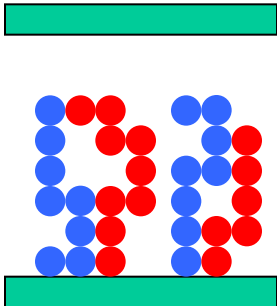

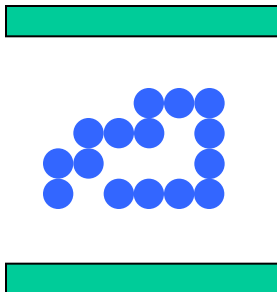
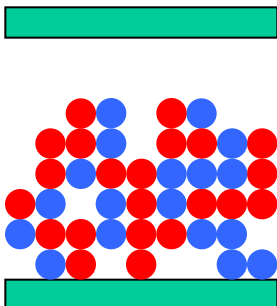
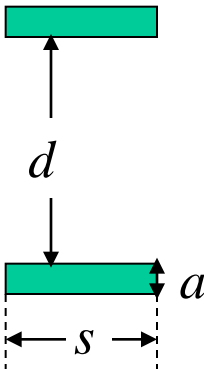


Theory³

Enthalpy

Entropy

Solid energy

 <p>Short chain Thin gap</p>	 <p>Poor solubility</p>	 <p>High area-lattice ratio</p>
 <p>Long chain Thick gap</p>	 <p>Good solubility</p>	 <p>Low area-lattice ratio</p>

Unfavorable
 $F \rightarrow (+)$

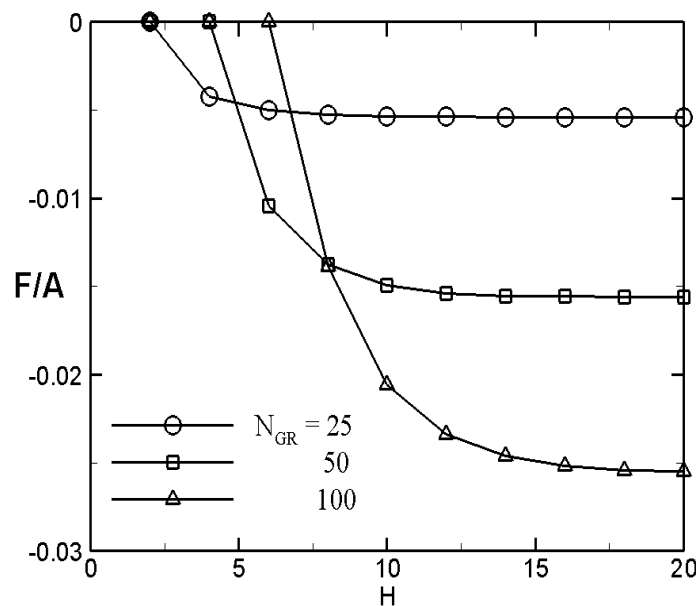


Favorable
 $F \rightarrow (-)$

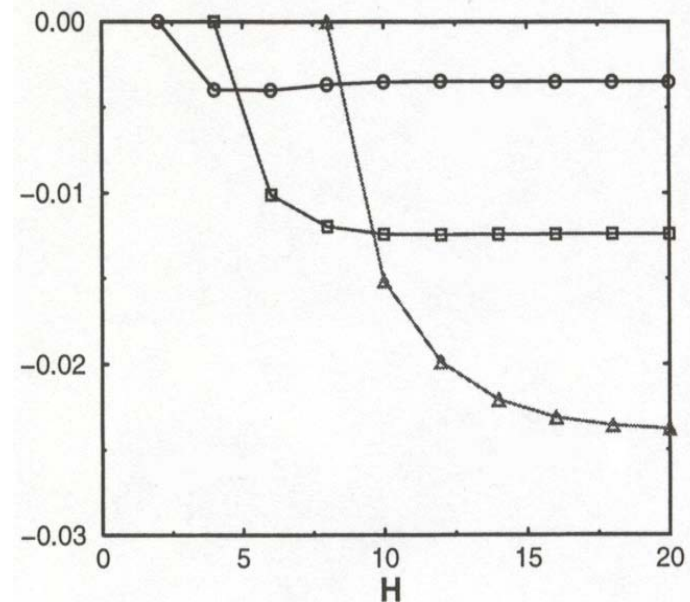
* Area-lattice ratio : $\varepsilon = s / a$

Result¹⁻¹

- Influence of statistical chain length on the excess free energy ($N_h = 100$, $N_g \in [25, 100]$, $\rho_g = 0.04$, $\chi_{gh} = 0$) for 1D:



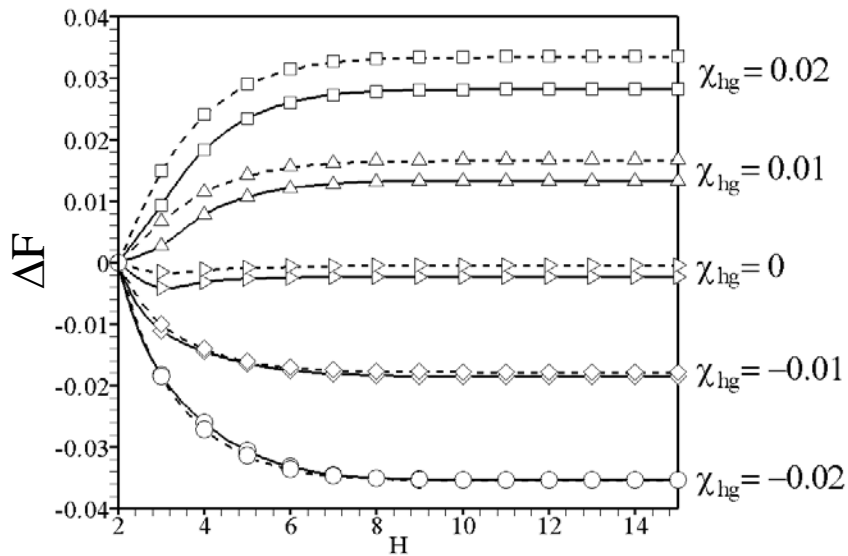
(a) Kim *et al.* (1D)



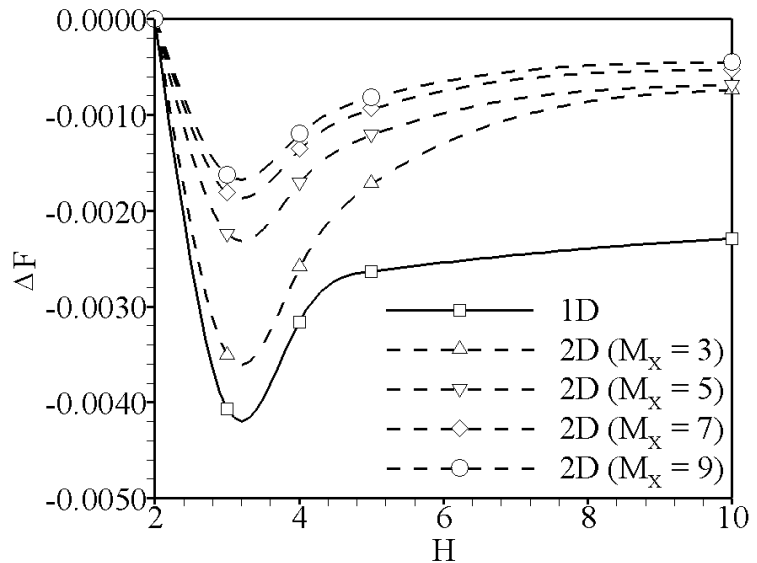
(b) Balazs *et al.* (1D)

Result¹⁻²

- The influence of dimensionality on excess free energy



(a) Kim *et al.* (1D&2D)

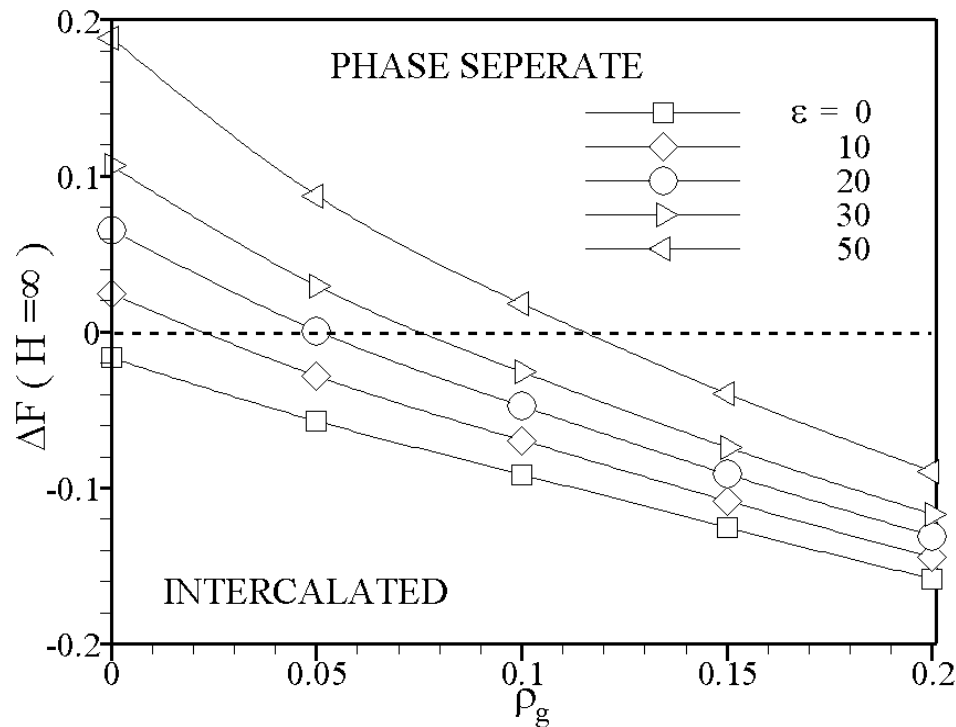


(b) Kim *et al.* (1D&2D)

Statistical chain length: $N_g = 25$, $N_h = 100$, **Surface property:** $\rho_g = 0.04$
Binary Interaction parameter: $\chi_{hg} \in [-0.02, 0.02]$

Result²⁻¹

- The influence of the area-lattice ratio (ε) and binary interaction (χ_{hg}) on the excess free energy



Statistical chain length

$$N_g = 200, N_h = 400, N_o = 10$$

Surface property

$$\rho_g = 0 \sim 20\%, \rho_o = 70\%, \rho_v = 2 \sim 5\%$$

Solid influence

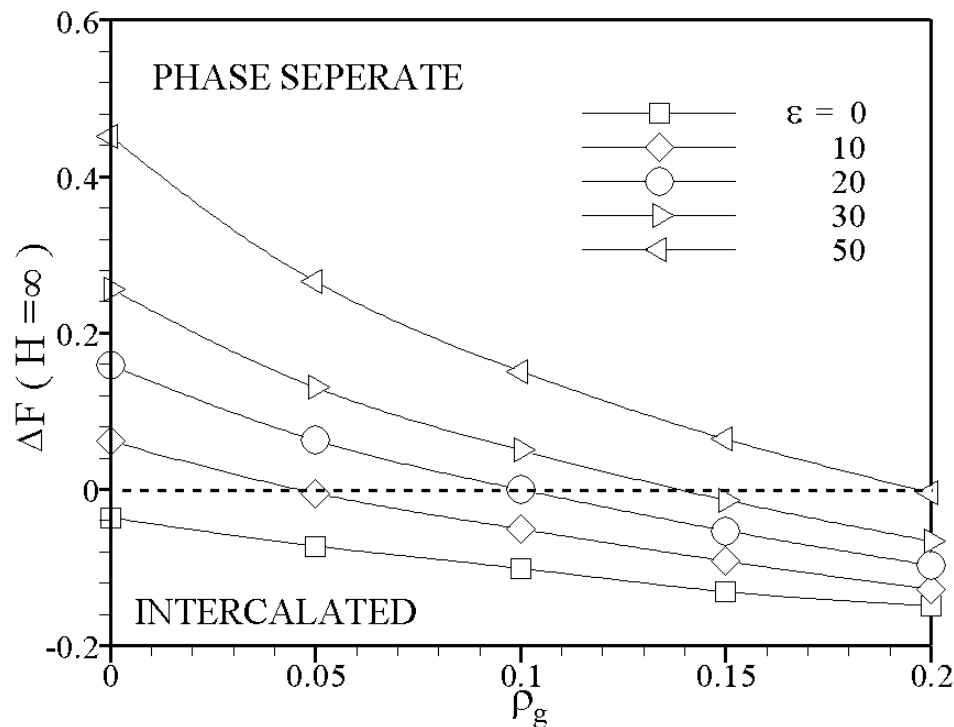
$$A = 20(k_B T), \varepsilon = 0 \sim 50$$

Binary Interaction parameter

$$\chi_{hg} = 0, \chi_{ho} = 0, \chi_{go} = 0, \\ \chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02$$

Neutral ($\chi = 0$; as in PP type PNC) liquid-liquid interactions, solid-liquid and solid-solid interactions included (lower vacancy fraction)

Result²⁻²



Statistical chain length

$$N_g = 200, N_h = 400, N_o = 10$$

Surface property

$$\rho_g = 0 \sim 20\%, \rho_o = 70\%, \rho_v = 5 \sim 10\%$$

Solid influence

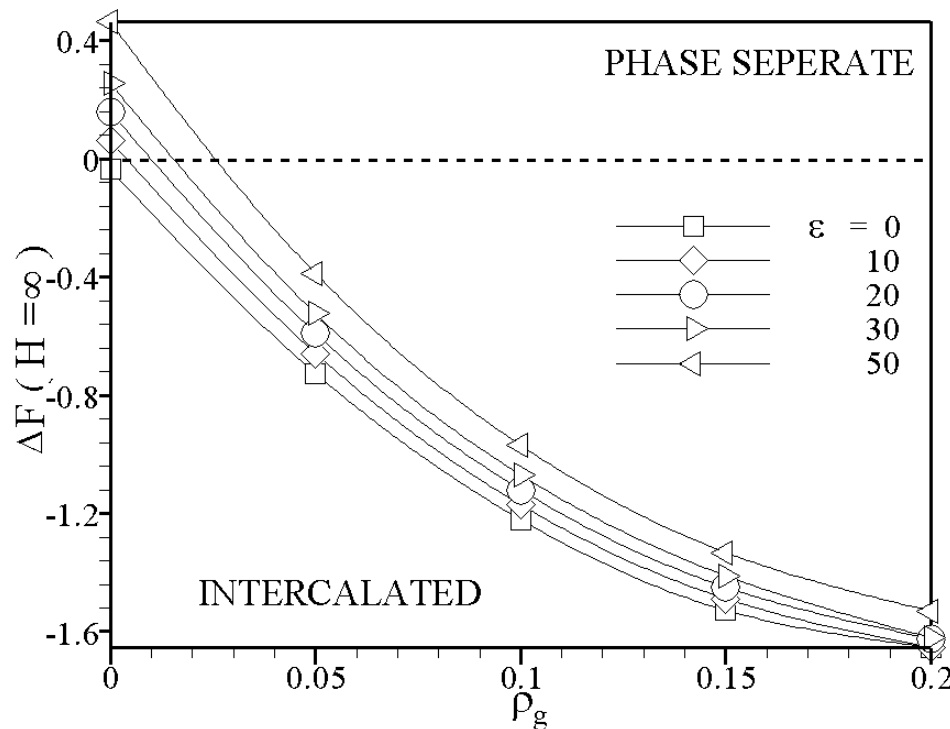
$$A = 20(k_B T), \varepsilon = 0 \sim 50$$

Binary Interaction parameter

$$\chi_{hg} = 0, \chi_{ho} = 0, \chi_{go} = 0, \\ \chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02$$

Neutral liquid-liquid interaction, solid-liquid and solid-solid interactions included (higher vacancy fraction)

Result²⁻³



Statistical chain length

$$N_g = 200, N_h = 400, N_o = 10$$

Surface property

$$\rho_g = 0 \sim 20\%, \rho_o = 70\%, \rho_v = 5 \sim 10\%$$

Solid influence

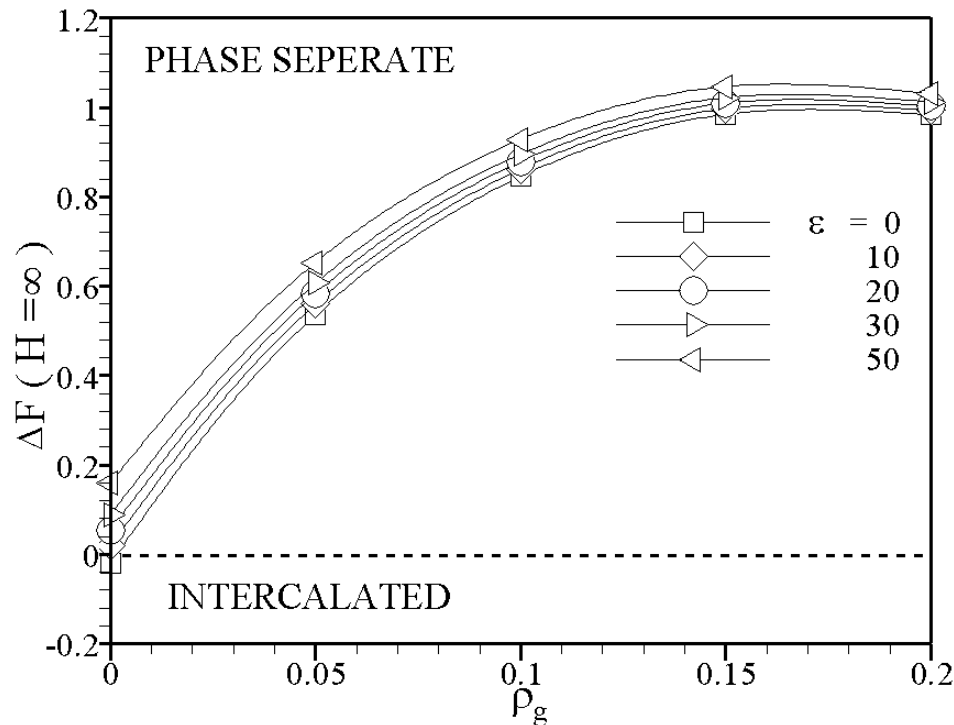
$$A = 20(k_B T), \varepsilon \in [0, 50]$$

Binary Interaction parameter

$$\chi_{hg} = -0.02, \chi_{ho} = 0, \chi_{go} = 0, \\ \chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02$$

Favorable liquid-liquid interaction, solid-liquid and solid-solid interactions included (higher vacancy fraction).

Result²⁻⁴



Statistical chain length

$$N_g = 200, N_h = 400, N_o = 10$$

Surface property

$$\rho_g = 0 \sim 20\%, \rho_o = 70\%, \rho_v = 2 \sim 5\%$$

Solid influence

$$A = 20(k_B T), \varepsilon \in [0, 50]$$

Binary Interaction parameter

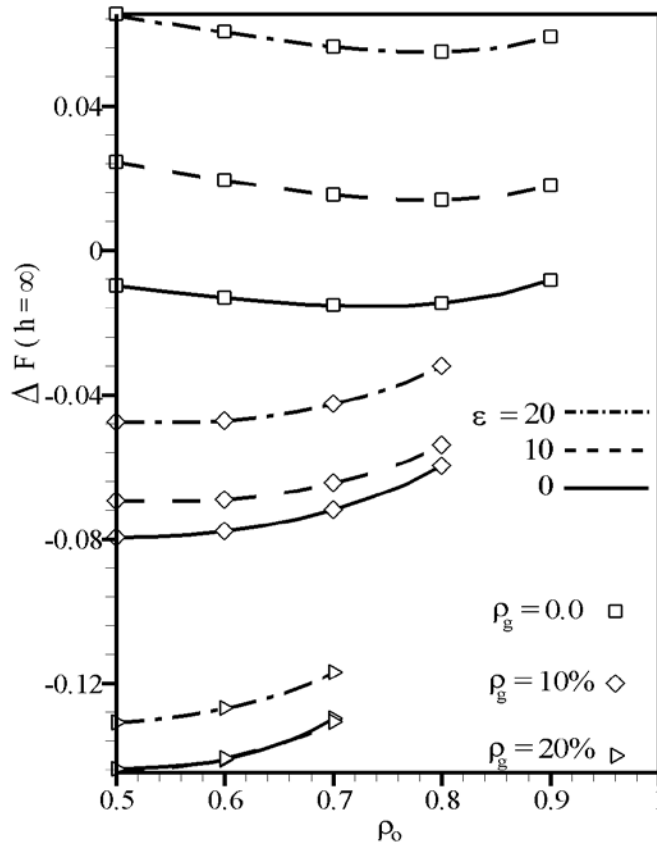
$$\chi_{hg} = 0.02, \chi_{ho} = 0, \chi_{go} = 0,$$

$$\chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02$$

Unfavorable liquid-liquid interaction, solid-liquid and solid-solid interactions included (lower vacancy fraction).

Result³

- The influence of the area-lattice ratio (ε) and grafting density (ρ_g, ρ_o) on the excess free energy



Statistical chain length

$$N_g = 200, N_h = 400, N_o = 10$$

Surface property

$$\rho_g = 0 \sim 20\%, \rho_o = 50 \sim 90\%, \rho_v = 2 \sim 5\%$$

Solid influence

$$A = 20(k_B T), \varepsilon \in [0, 20]$$

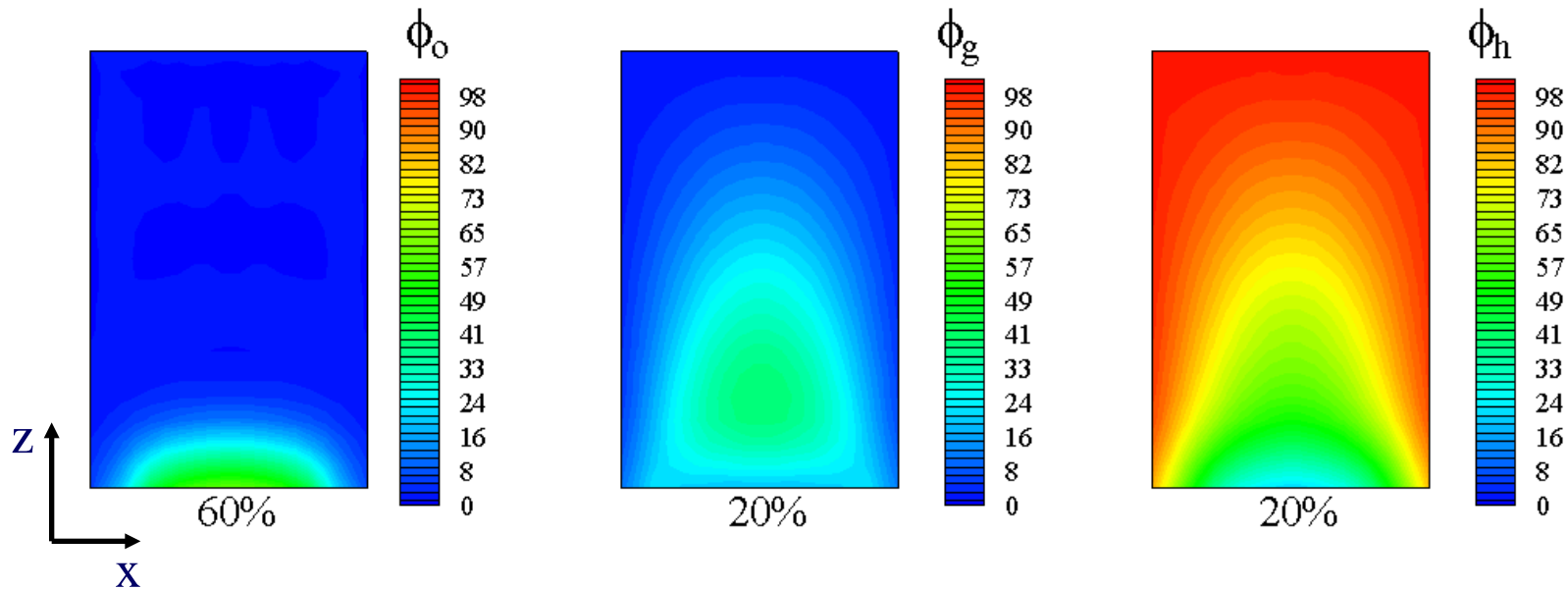
Binary Interaction parameter

$$\chi_{hg} = 0, \chi_{ho} = 0, \chi_{go} = 0,$$

$$\chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02$$

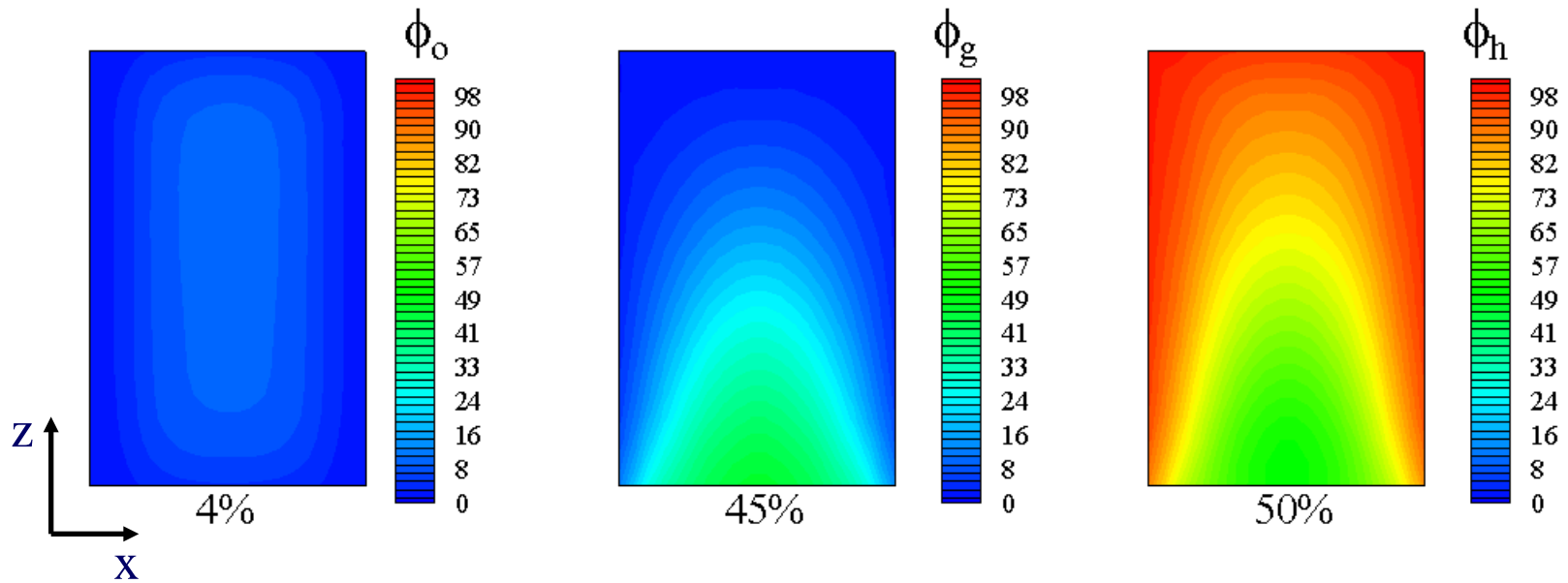
Result⁴⁻¹

- The influence of degradation of organic modifier on the volume fraction of species in 2D lattice.



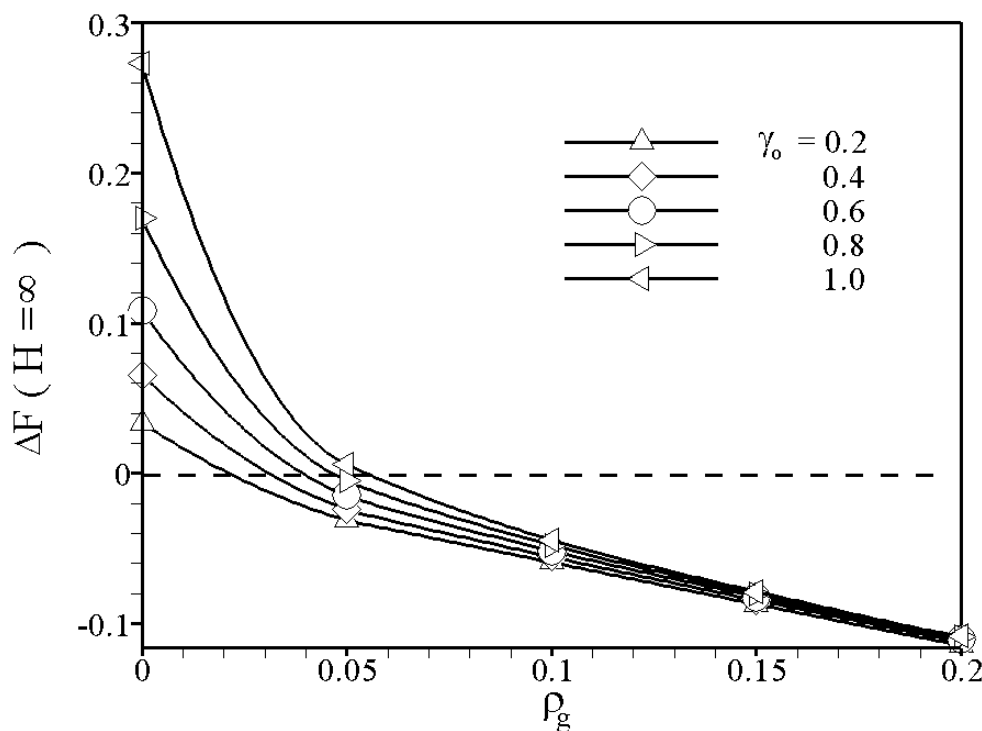
$$N_g = 200, N_h = 400, N_o = 100, \rho_g = 15\%, \rho_o = 80\%, \rho_v = 2\sim 5\%, A = 20(k_B T), \\ \chi_{hg} = 0, \chi_{ho} = 0, \chi_{go} = 0, \chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02, \gamma_g = 0.0$$

Result⁴⁻⁴



$N_g = 200, N_h = 400, N_o = 100, \rho_g = 15\%, \rho_o = 80\%, \rho_v = 2\sim 5\%, A = 20(k_B T),$
 $\chi_{hg} = 0, \chi_{ho} = 0, \chi_{go} = 0, \chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02, \gamma_o = 100\%$

Result⁴⁻⁵



Statistical chain length

$$N_g = 200, N_h = 400, N_o = 10$$

Surface property

$$\rho_g = 0 \sim 20\%, \rho_o = 70\%, \rho_v = 2 \sim 5\%$$

Solid influence

$$A = 20(k_B T), \varepsilon = 10, \gamma_o \in [0.2, 1.0]$$

Binary Interaction parameter

$$\chi_{hg} = 0, \chi_{ho} = 0, \chi_{go} = 0, \\ \chi_{hs} = 0.01, \chi_{gs} = -0.01, \chi_{os} = -0.02$$

Neutral liquid-liquid interaction, solid-liquid and solid-solid interactions with organic modifier degradation.

Summary of findings for SCF model

- To achieve exfoliation in 4-component system:
 - Clay: Intercalated, but with surface partially bare for interacting with a compatibilizer (functionalized polymer)
 - Stable intercalant; no thermal degradation or extraction
 - Compatibilizer
 - Strongly interacting with clay surface
 - High molecular weight
 - With non-positive ΔF of mixing with host polymer
 - Host polymer – MW comparable to that of compatibilizer.

Solutions of practical problems

Problem	Suggestion
The absence of specific interaction between host and grafted polymer ($\chi_{hg} = 0$)	Higher grafting density, and/or higher MW of compatibilizer and organic modifier (ρ_o , ρ_g , N_o and N_g)
Increased bare surface area (unfavorable solid-solid interaction)	Higher favorable interactions between clay and compatibilizer or intercalant (stronger negative values for χ_{gs} and χ_{os})
Thermal degradation of organic modifier (increasing γ_o)	<ul style="list-style-type: none"> - Better attraction between compatibilizer and solid surface and bigger ρ_g - Less unfavorable interaction between host polymer and solid
Unfavorable host polymer-solid interaction ($\chi_{hs} > 0$)	Decrease ρ_v High saturation of inorganic surface region with the compatibilizer and organic modifier

Conclusions

- Successful recovery of the 1D solutions based on the classical theory by Fleer *et al.* and that of Balazs *et al.*
- Validation of the 2D solution by comparison with the 1D approach.
- More realistic physical simulation by incorporating liquid-liquid, liquid-solid and solid-solid interactions, as well as binary interaction parameters.
- SCF approach requires less computational resources than molecular dynamics simulation.
- Successful identification of optimum operational parameters.

Acknowledgement

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