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

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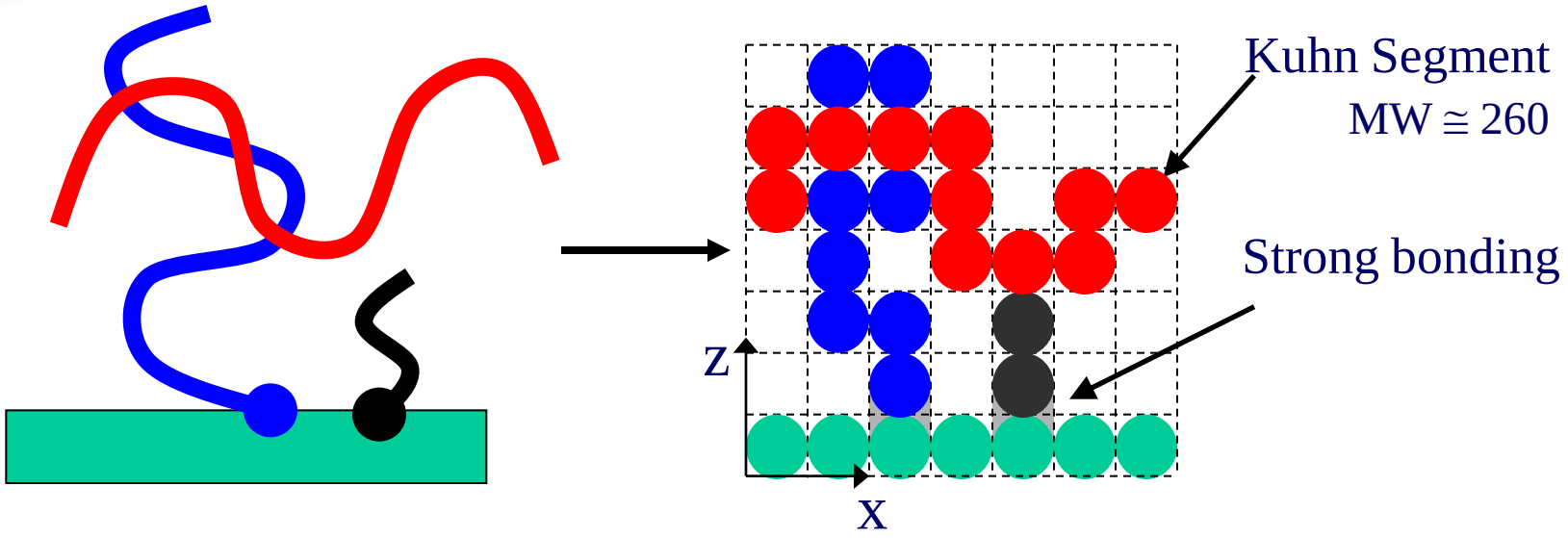
Overview

- 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).

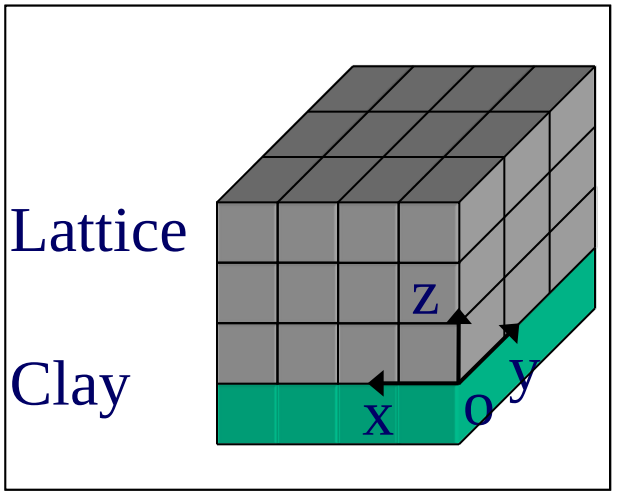
Numerical model for clay and macromolecules



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

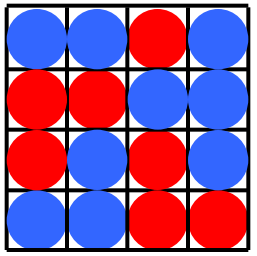
1D vs. 2D or 3D model



- 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.

Theory[1]

Excess free energy



Conformational Entropy:

Number of ways to occupy free lattice site

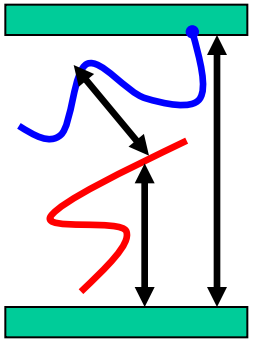
Mixing Enthalpy:

Huggins-Flory Theory

liquid-liquid : χ_{hg}, χ_{hg}, χ_{ho}

solid-liquid : χ_{hs}, χ_{hs} , χ_{os}

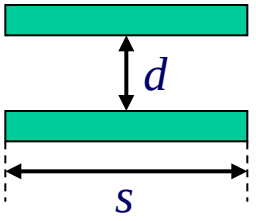
solid-solid



Long-range interaction:

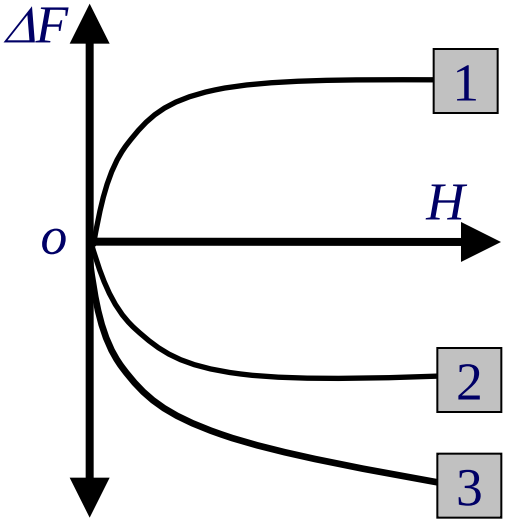
Van der Waals force between a pair of clay plates

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



Theory²

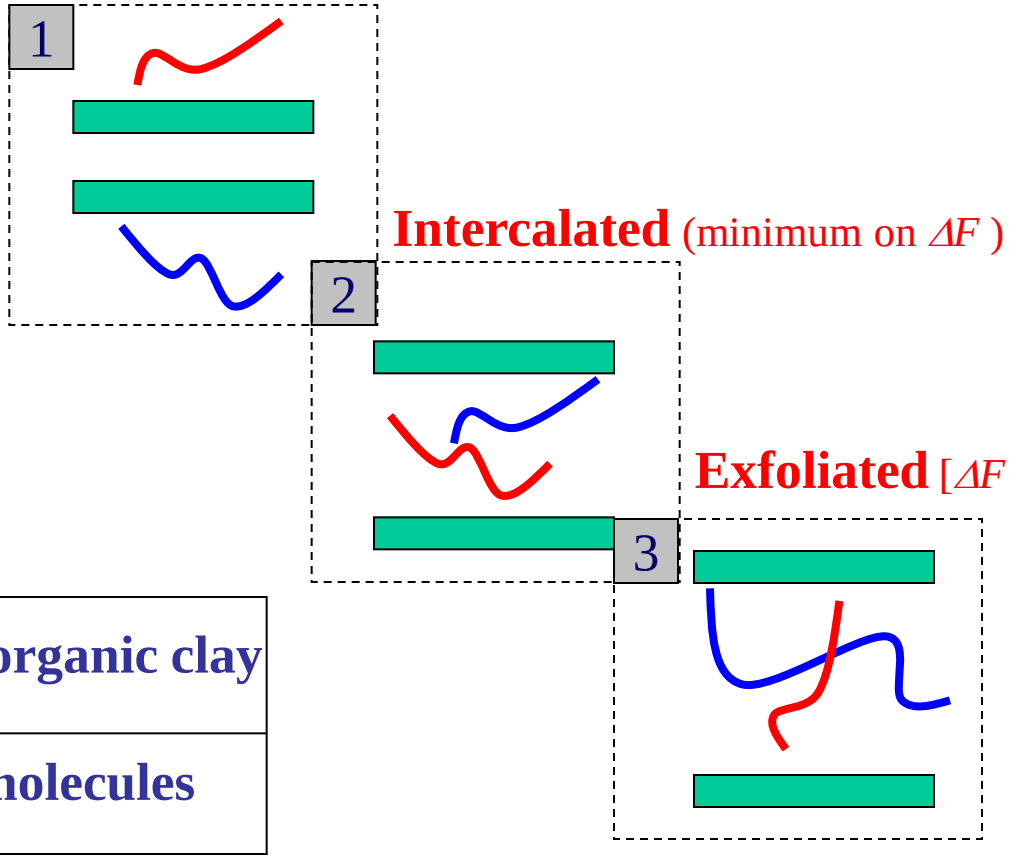
- Equilibrium Thermodynamics.



Immiscible ($\Delta F > 0$)

Intercalated (minimum on ΔF)

Exfoliated [$\Delta F\ (H \rightarrow \infty) < 0$]



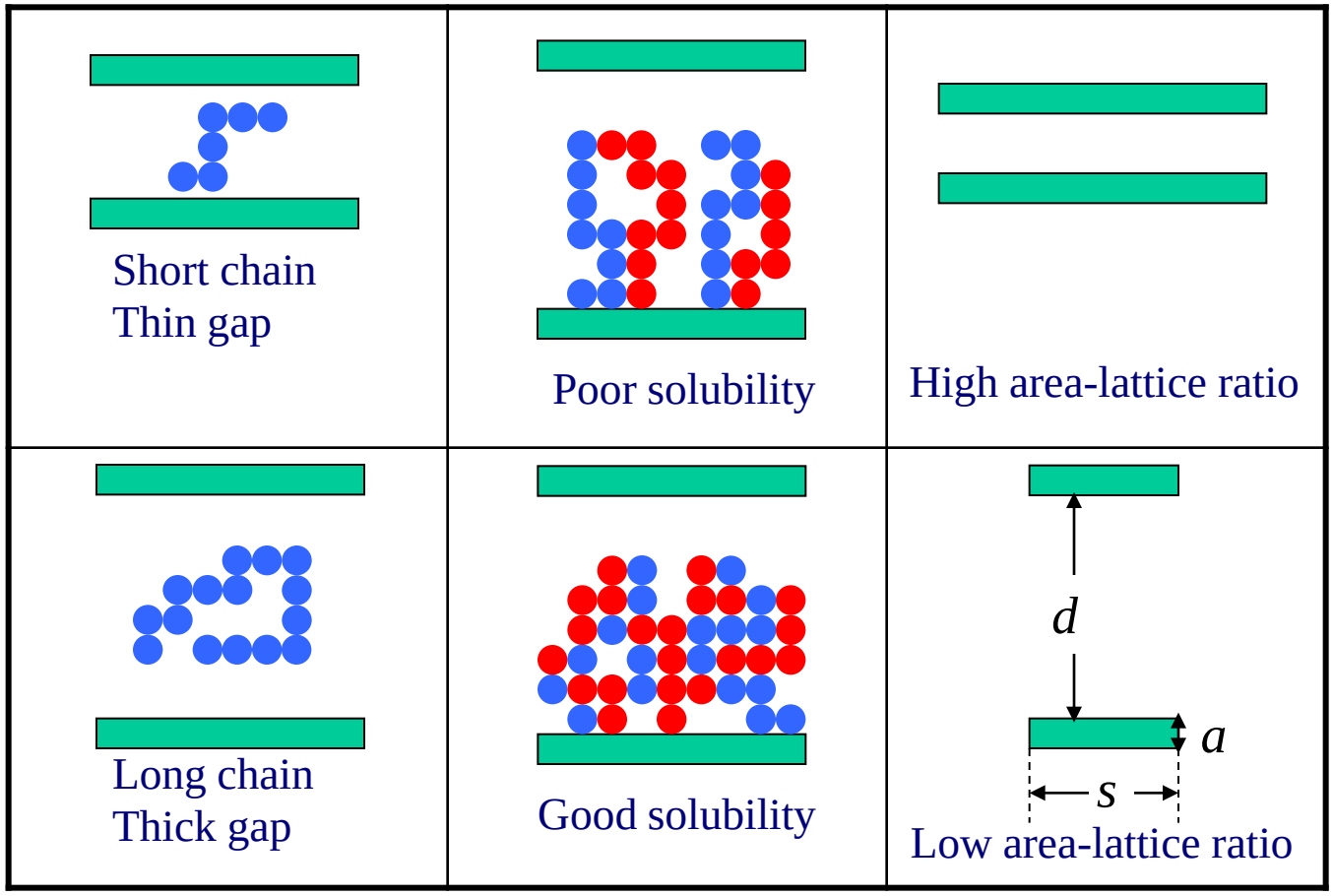
	Solid inorganic clay
	Macromolecules

Theory[3]

Enthalpy

Entropy

Solid energy



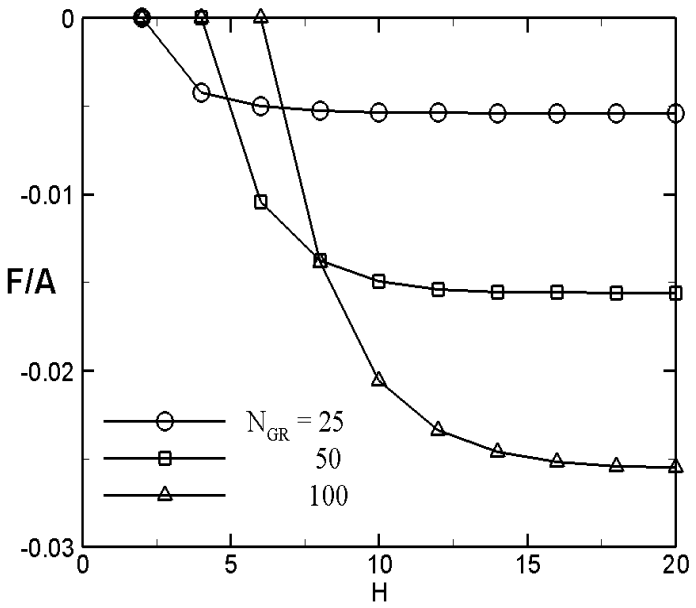
Unfavorable
F→(+)

Favorable
F→(–)

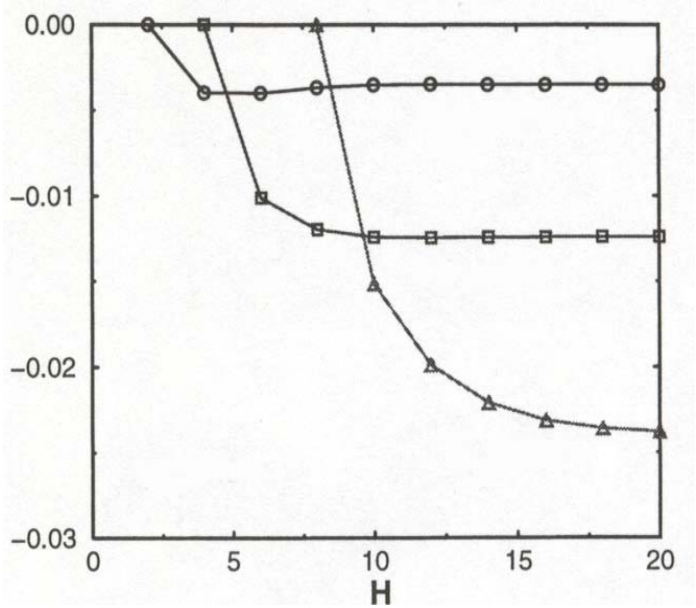
* Area-lattice ratio : ε = s / a

Result[1-1]

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



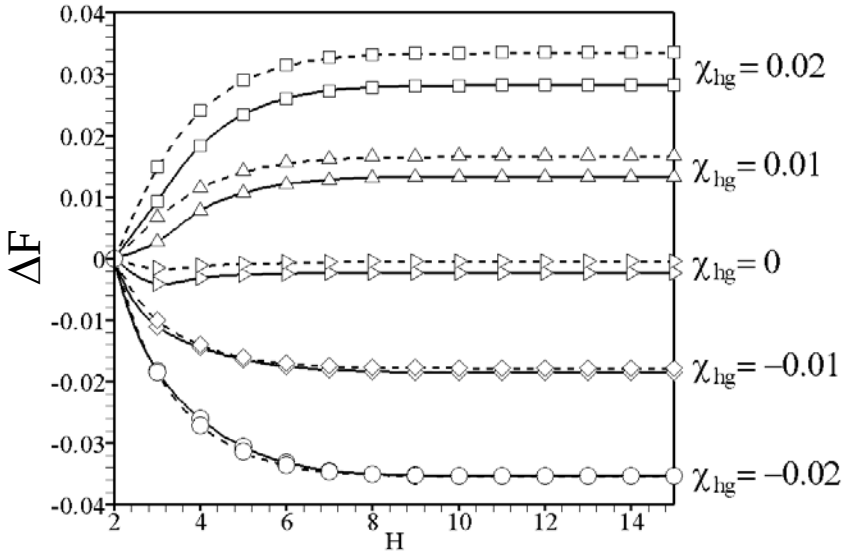
(a) Kim *et al.* (1D)



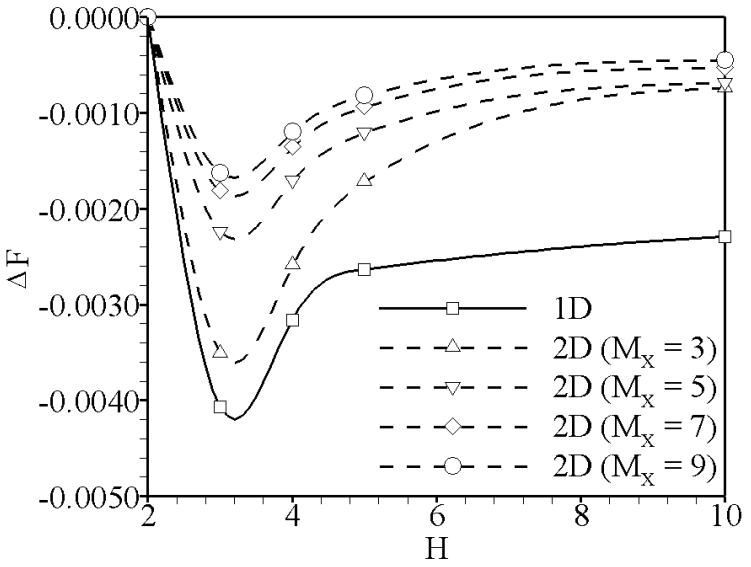
(b) Balazs *et al.* (1D)

Result[1-2]

- The influence of dimensionality on excess free energy



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

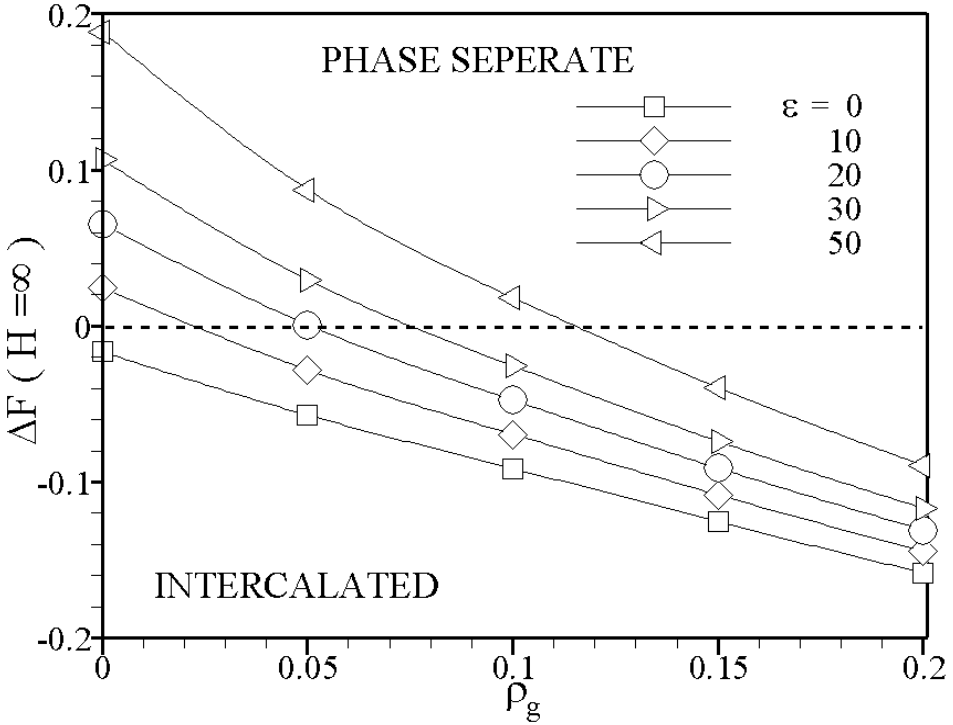


(b) Kim *et al.* (1D&2D)

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

Result[2-1]

- 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

$\rho_g = 0\sim20\%$, $\rho_o = 70\%$, $\rho_v = 2\sim5\%$

Solid influence

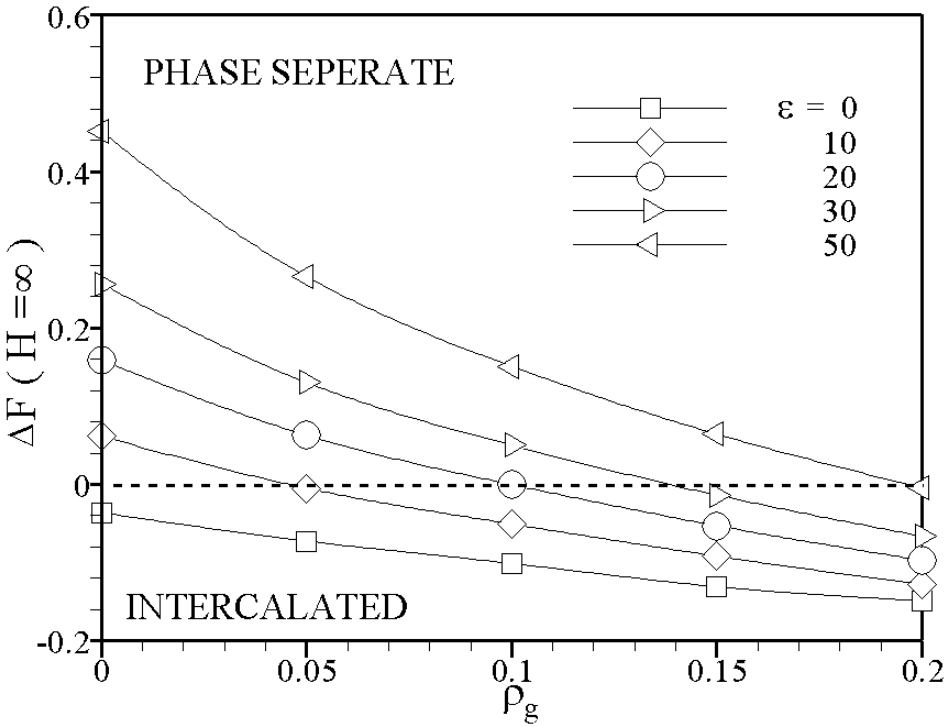
$A = 20(k_BT)$, $\varepsilon = 0 \sim 50$

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

ρ_g=0~20%, ρ_o= 70%,**ρ_v = 5~10%**

Solid influence

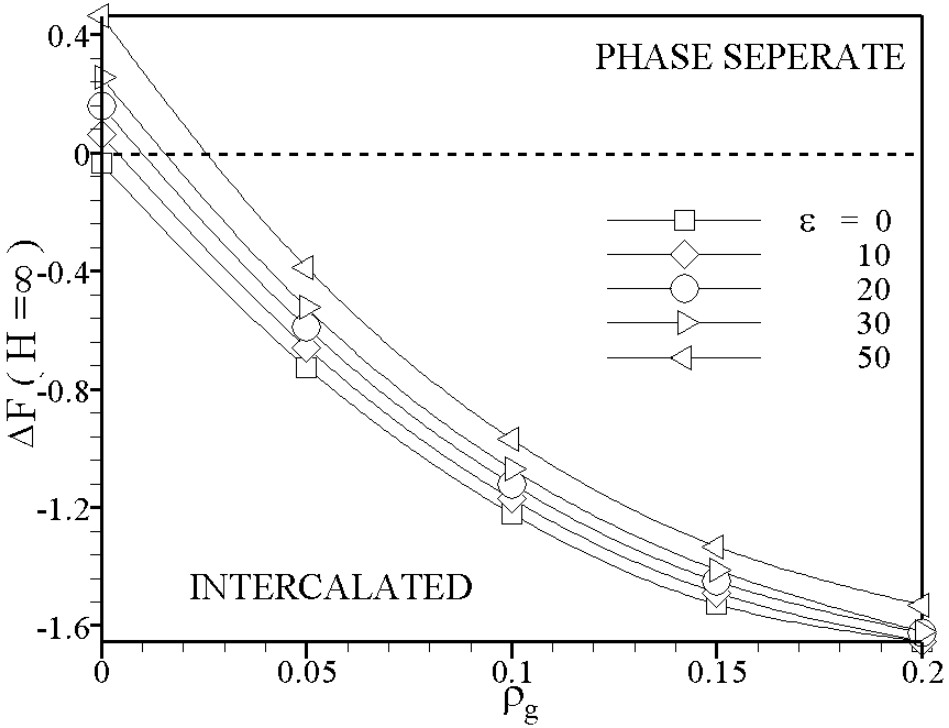
$A = 20(k_BT)$, $\varepsilon = 0 \sim 50$

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)

Result[2-3]



Statistical chain length

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

Surface property

$\rho_g = 0\sim20\%$, $\rho_o = 70\%$, $\rho_v = 5\sim10\%$

Solid influence

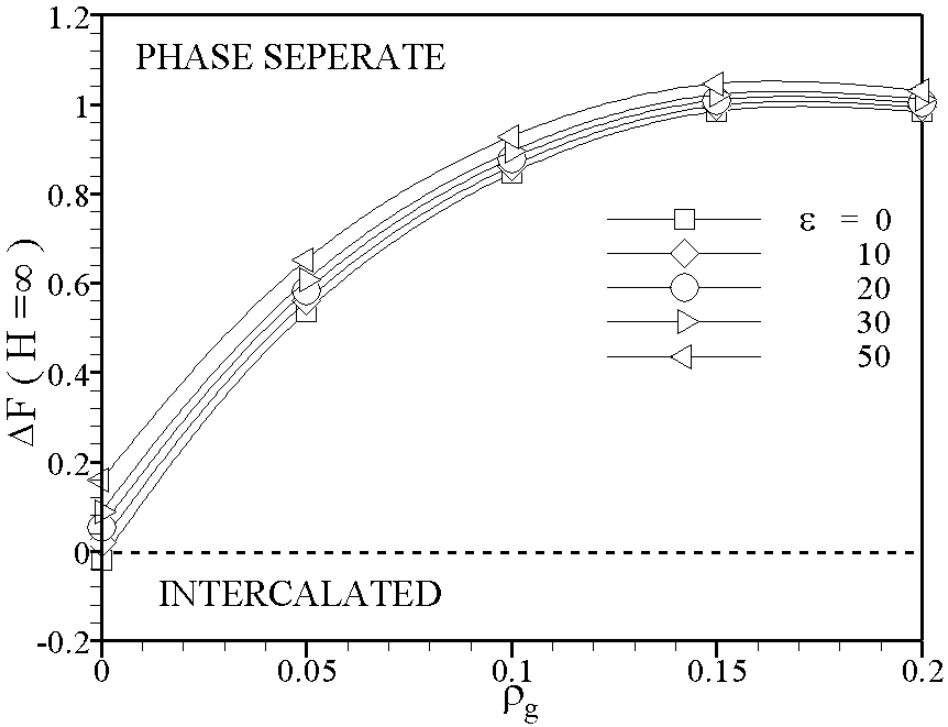
$A = 20(k_BT)$, $\varepsilon \in [0,50]$

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).

Result[2-4]



Statistical chain length

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

Surface property

$\rho_g = 0\sim20\%$, $\rho_o = 70\%$, $\rho_v = 2\sim5\%$

Solid influence

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

Binary Interaction parameter

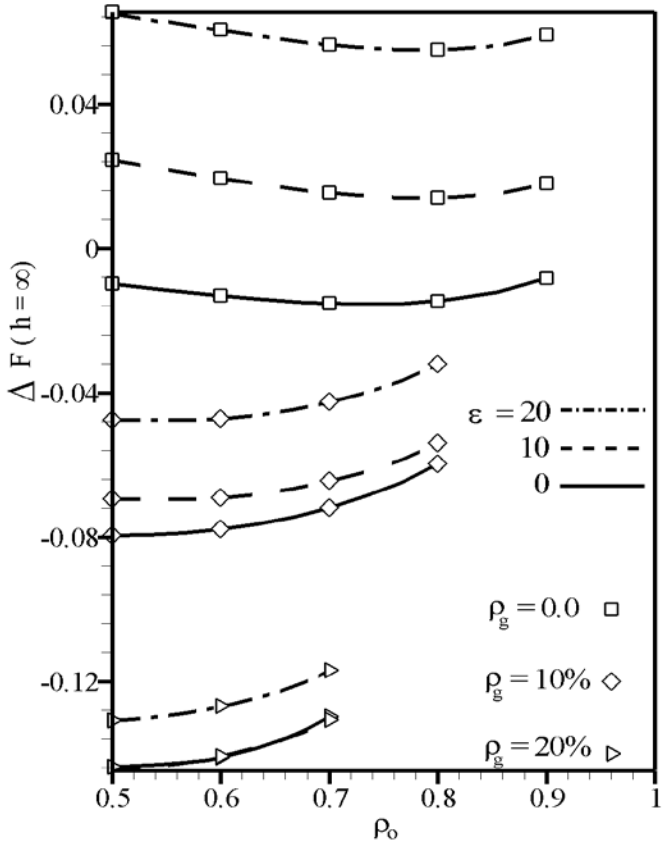
χ_{hg}=0.02, $\chi_{ho} = 0$, $\chi_{go} = 0$,

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

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

Result[3]

- 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

ρ_g= 0~20%, ρ_o= 50~90%, ρ_v= 2~5%

Solid influence

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

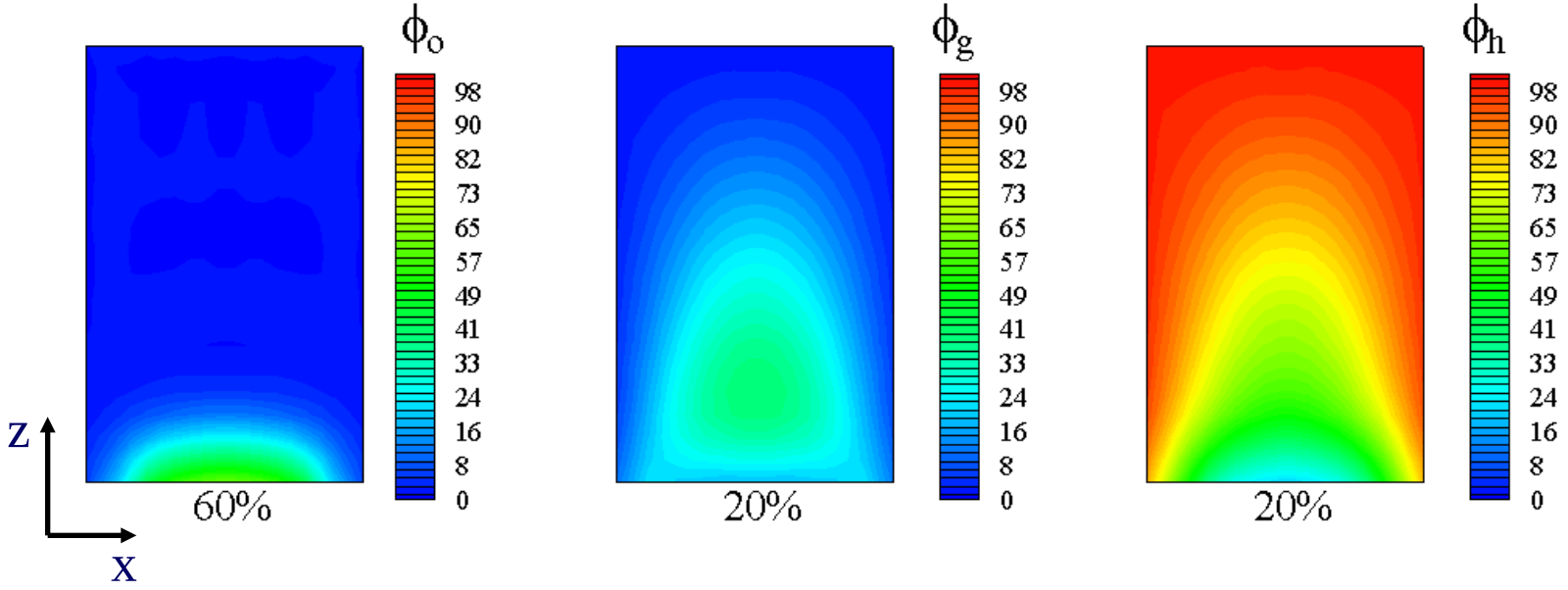
Binary Interaction parameter

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

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

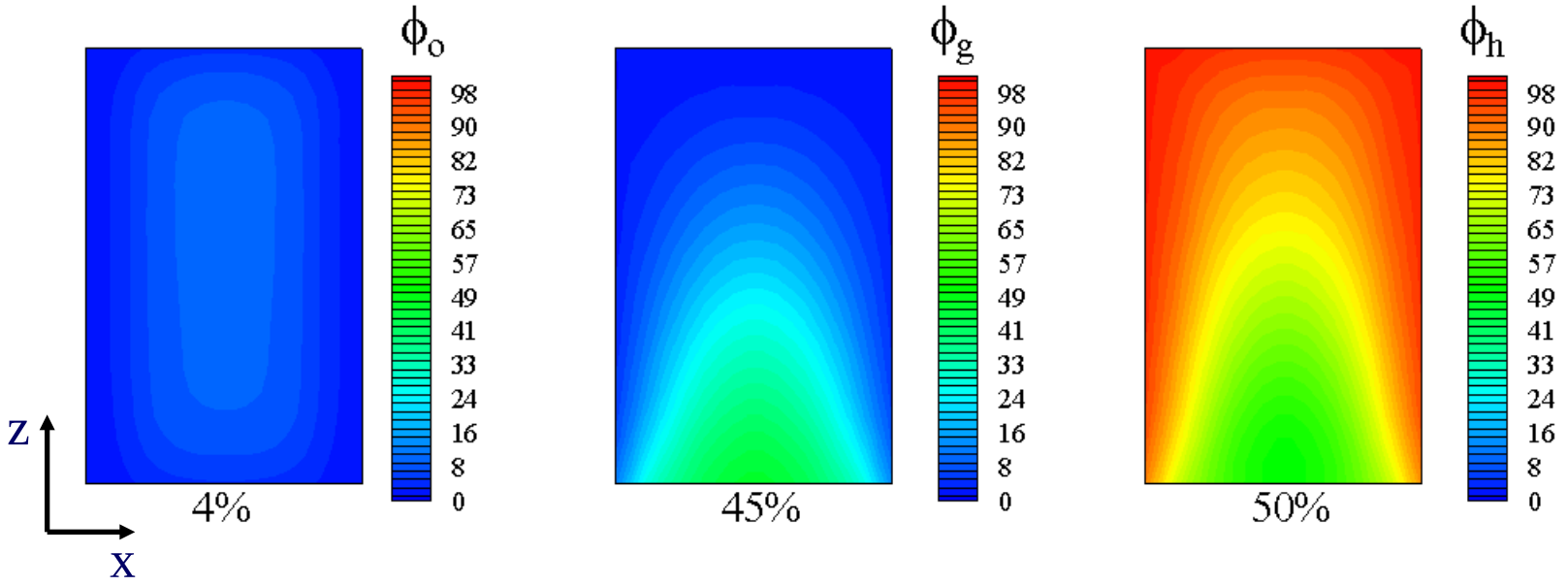
Result[4-1]

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



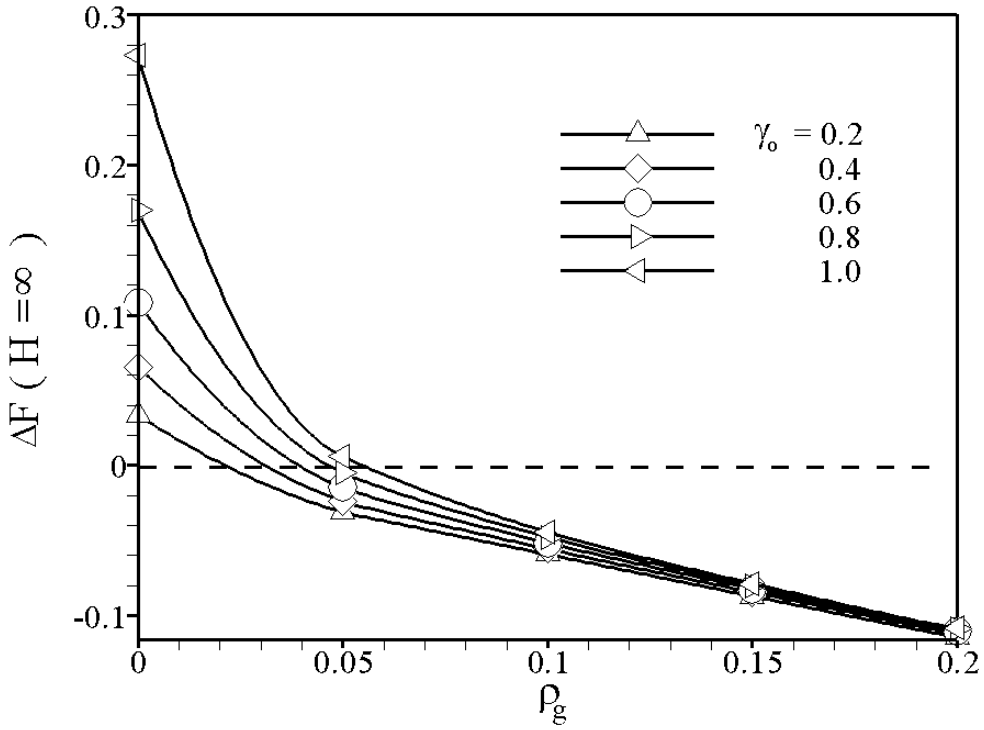
$N_g = 200$, $N_h = 400$, $N_o = 100$, $\rho_g = 15\%$, $\rho_o = 80\%$, **ρ_v = 2~5%,** $A = 20(k_BT)$,
$\chi_{hg} = 0$, $\chi_{ho} = 0$, $\chi_{go} = 0$, $\chi_{hs} = 0.01$, $\chi_{gs} = -0.01$, $\chi_{os} = -0.02$, **γ_g = 0.0**

Result[4-4]



$N_g = 200$, $N_h = 400$, $N_o = 100$, $\rho_g = 15\%$, $\rho_o = 80\%$, **$\rho_v = 2\sim5\%$,** $A = 20(k_BT)$,
$\chi_{hg} = 0$, $\chi_{ho} = 0$, $\chi_{go} = 0$, $\chi_{hs} = 0.01$, $\chi_{gs} = -0.01$, $\chi_{os} = -0.02$, **$\gamma_o = 100\%$**

Result[4-5]



Statistical chain length

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

Surface property

$\rho_g = 0\sim20\%$, $\rho_o = 70\%$, $\rho_v = 2\sim5\%$

Solid influence

$A = 20(k_BT)$, $\varepsilon = 10$, $\gamma_o \in$ **[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)	- 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

- **The work has been supported by NSERC strategic grant on “Polymeric Nanocomposites”.**