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Polymeric nanocomposites: flow and technology
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POLYMERIC NANOCOMPOSITES:
Flow and Technology

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·Amir Kabir University of Technology (**Polytechnic)**, Tehran, 2004

Outline

- **Introduction to the molten PNC structure**

- **#1. Thermodynamics**
  - Clay surface energy – adsorption & brushes
  - Free volume calculations from PVT data
  - Free volume – a measure of clay dispersion

- **#2. Rheology of PNC**
  - Flow of PNC based on PA-6, PP+PP-MA and PS
  - Liquid-crystal flow model
  - Fourier transform rheology

- **#3. Mathematical modeling PNC**
  - Self-consistent field (SCF) model
  - Criteria for optimization of clay dispersion

- **Global conclusions**

PNC Definitions

- *Polymeric nanocomposites (PNC)* = polymeric matrix + dispersed in it nanometer-size particles.

- *Nano-filler* of industrial interest is clay, in particular natural montmorillonite, MMT, with the platelet size: 1x100x300 nm.

- Two stages of clay dispersion are: *Intercalation* and *Exfoliation*.

- *Exfoliated clay* − individual platelets dispersed in a matrix polymer with the distance $d_{001} > 8.8$ nm. The platelets can be oriented, forming *Short stacks* or *Tactoids* or they can be randomly dispersed in the medium.

- *Intercalated clay* − *having* molecules inserted between *Platelets,* thus increasing the interlayer spacing between them to at least 1.5 nm.

- *Intercalant* − material sorbed between *Platelets* that binds with their surfaces to form an *Intercalate*.

- *Interlayer spacing or d-spacing*, d_{001}, is the thickness of the repeating layers as seen by the XRD.

- *Compatibilizer* − material grafted to the clay surface, miscible with the polymeric matrix.

- *The three principal methods for PNC preparation are:*
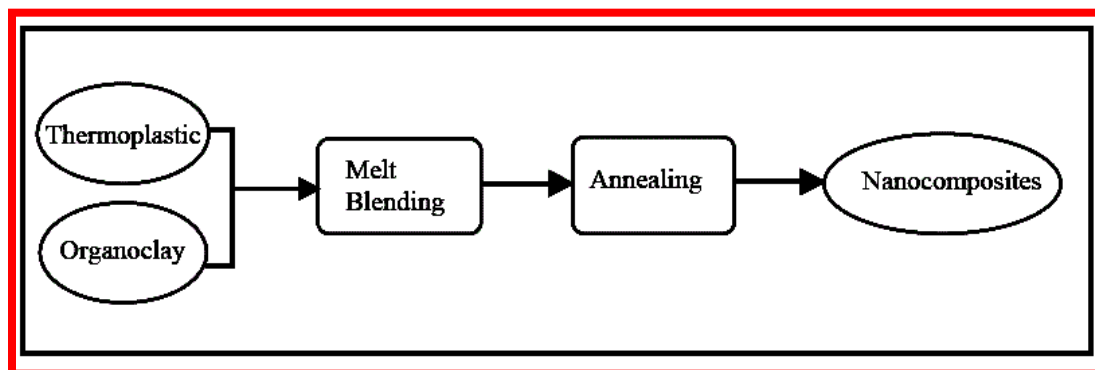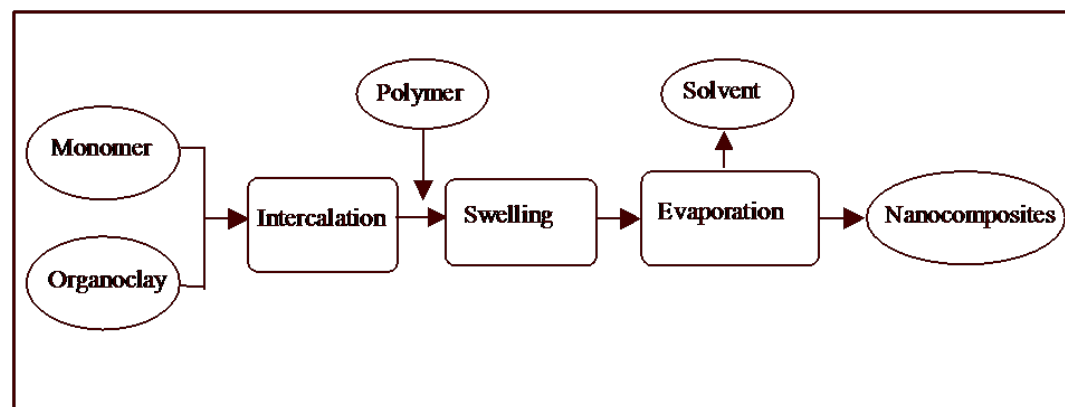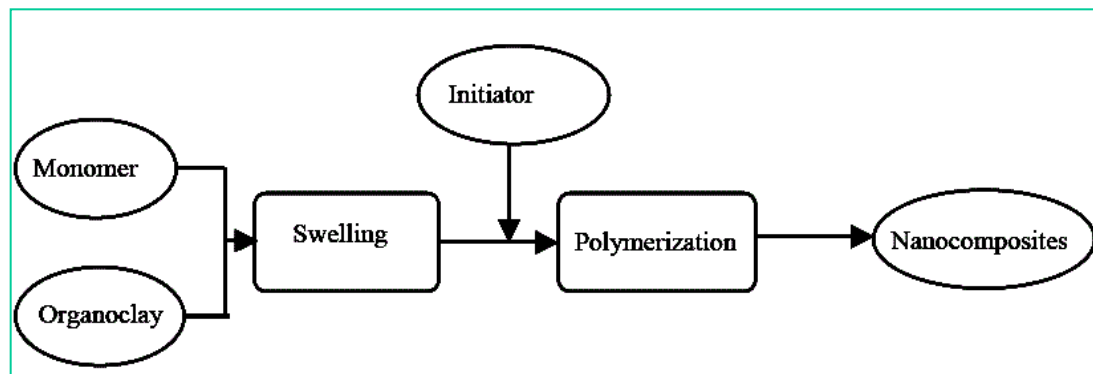
1. REACTIVE (*in situ* polymerization)

2. SOLUTION (dispersing organoclay in polymer solution)

3. MELT COMPOUNDING

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Montmorillonite (MMT)

Ca. 40% atoms on the surface

Cell unit MW (g/mol.)	540.46
Density (g/mL)	2.3 to 3.0
Mohs Hardness @20°C	1.5- 2.0
Cleavage	Perfect in one direction, lamellar
Characteristic	Expands up to 30 times in volume in H_2O
Appearance	Light yellow with dull luster
Field Indicators	Softness, and soapy feel

Silicon
Oxygen
Aluminum
Hydroxyl

0.96 nm
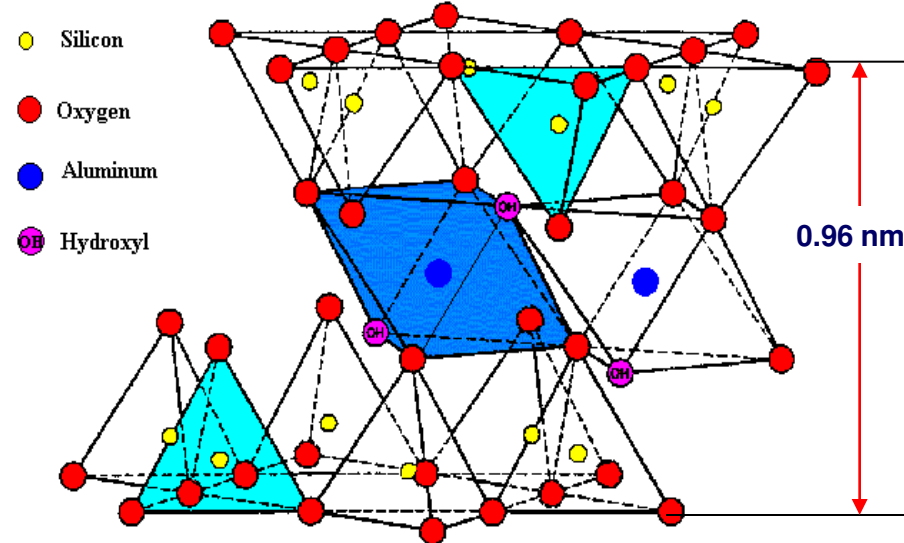
- At $T <$ 500°C smectites have 4 layers:
  - Outer layer with H_2O and Na^+, K^+, Ca^{++}, Mg^{++} ions.
  - 3-layer sandwich: octahedral central between two tetrahedral: SiO_2-(Al/Mg)-SiO_2; 0.956 nm thick.

- MMT: monoclinic, contains ca.:
  $(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6$-$nH_2O$], has:
  Al = 10, Si = 21, H = 4, and O = 65 (wt%); aspect ratio: $p \cong$ 100 to 300; sp. surface area,
  $A_{sp} \cong$ 750 to 800 m²/g; Cation exchange capacity:
  CEC $\cong 1.0 \pm 0.2$ meq/g.

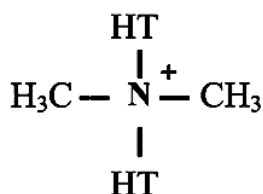- Reactive sites: **anions** and –OH groups on the surface; and **cations** and –OH groups at the rim.

TEM of MMT

Organoclays

Cloisite 15A
Cloisite 20A

2M2HT
Dimethyl dihydrogenatedtallow ammonium

Where HT = hydrogenatedtallow (~65% C18, ~30%C16, ~5% C14)

Anion: chloride

Cloisite 10A

2MBHT
Dimethyl benzyl hydrogenated-tallow ammonium

Where HT = hydrogentated tallow (~65% C18, ~30%C16, ~5% C14)

Anion: chloride

Cloisite 25A

2MHTL8
Dimethyl hydrogenated-tallow (2-ethylhexyl) ammonium
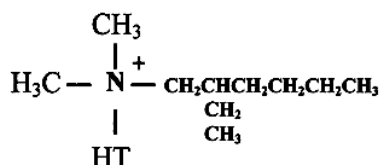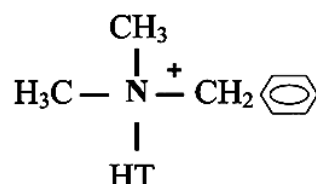
Where HT = hydrogenated tallow (~65% C18, ~30%C16, ~5% C14)

Anion: methyl sulfate

Cloisite 30B

MT-2EthOH
Methyl Tallow bis2hydroxyethyl ammonium
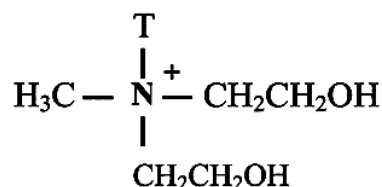
Where T = tallow (~65% C18, ~30%C16, ~5% C14)

Anion: chloride

- Commercial intercalated clays contain **quarternary** amines (*Southern Clay Products, 2000*).

- The cation exchange capacity of MMT: CEC = 100 ± 20 meq/100 g.

- Equilibrium of NaMMT reaction with ammonium salt is shifted left, hence excess of onium salt is often used, i.e., 0.9 to 1.4 meq/g or 23 to 40 % of the organic modifier.

- Intercalated clay contains 2 to 4 % water and up to 40 wt% of organic compounds.

- Intercalation increases the cost of clay from US$2,000 to US$7,000/ton.

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Clay surface energy

- The surface energy, $\sigma^s = \nu_1 A$, depends on the **nature and structure** of material.
  - Polymer surface tension coefficients at 20°C: $\nu_1 = 10$ to 49 mN/m
  - The surface tension coefficient of crystalline solid: $\nu_1 = 1\text{-}8$ N/m
  - The high surface energy causes **molecular adsorption**
  - ν_1 of freshly cleaved mica is 4,500 that exposed to air is 375 mN/m.

- Molecular adsorption causes **solidification** of organic molecules on the clay surface.
  - The solid layer is ca. 6 nm thick, thus <u>it increases clay platelet thickness from 1 to about 13 nm</u> (see next slide).
 - Molecular mobility is retarded up to ca. 100 nm from the clay surface.

- Another consequence of high surface energy is the **aggregation** of solid powders.
  - According to Johnson *et al.* [1971], the force between two interacting spheres of radius R is: $\left.\varepsilon\right|_{V=const} = N \times \left(\nu_{11}\pi R / 2\right) \propto \nu_{11} / R^2$

Owing to high surface energy of crystals (100 x of liquids) the macromolecules are readily adsorbed [Israelachvili, 1991].

$$G \equiv 6\pi R^2 \dot{D} / F_H = D / \eta_o$$
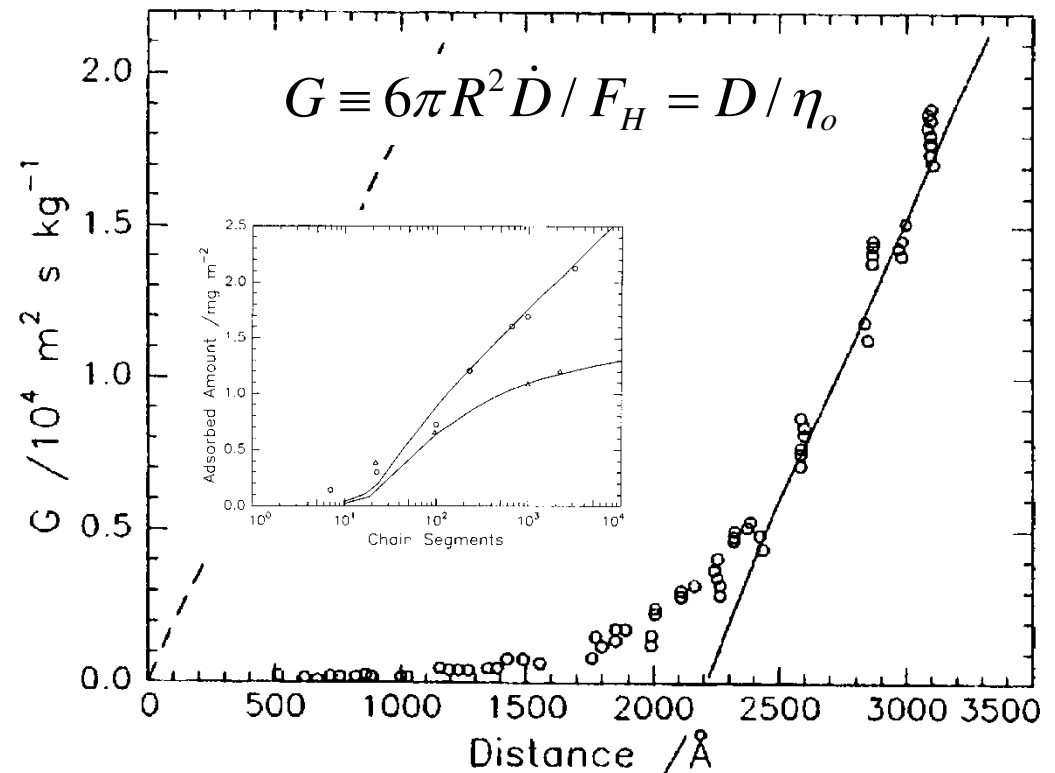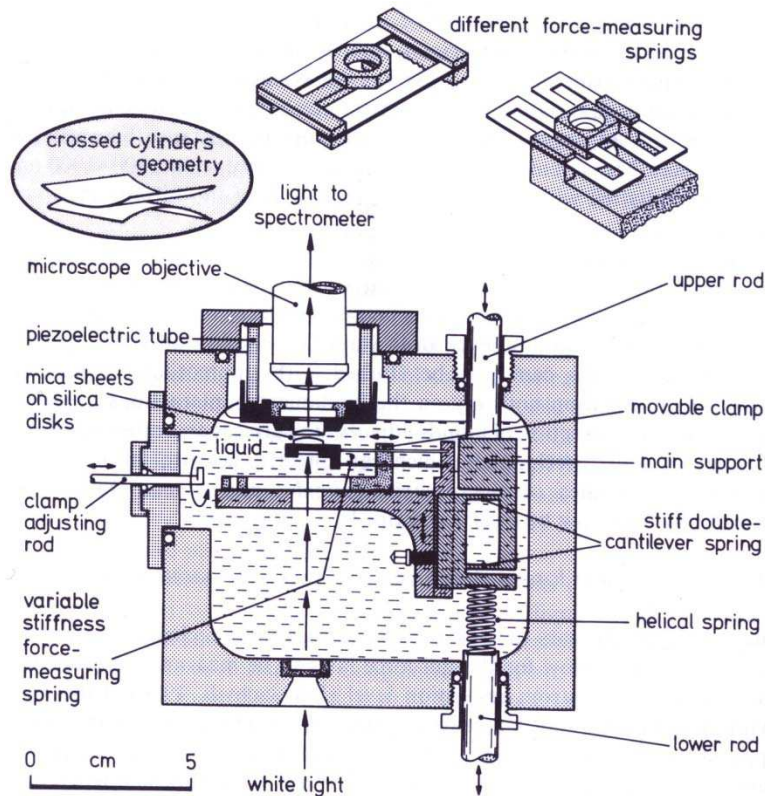
- The surface force analyzer (SFA) measured the mobility profile of adsorbed PS from a good solvent (toluene) – bulk mobility at *D/2* > 110 nm!
- The amount of adsorbed polymer depends on PS molecular weight and χ
  [see insert; Linden & van Leemput, 1978].

8
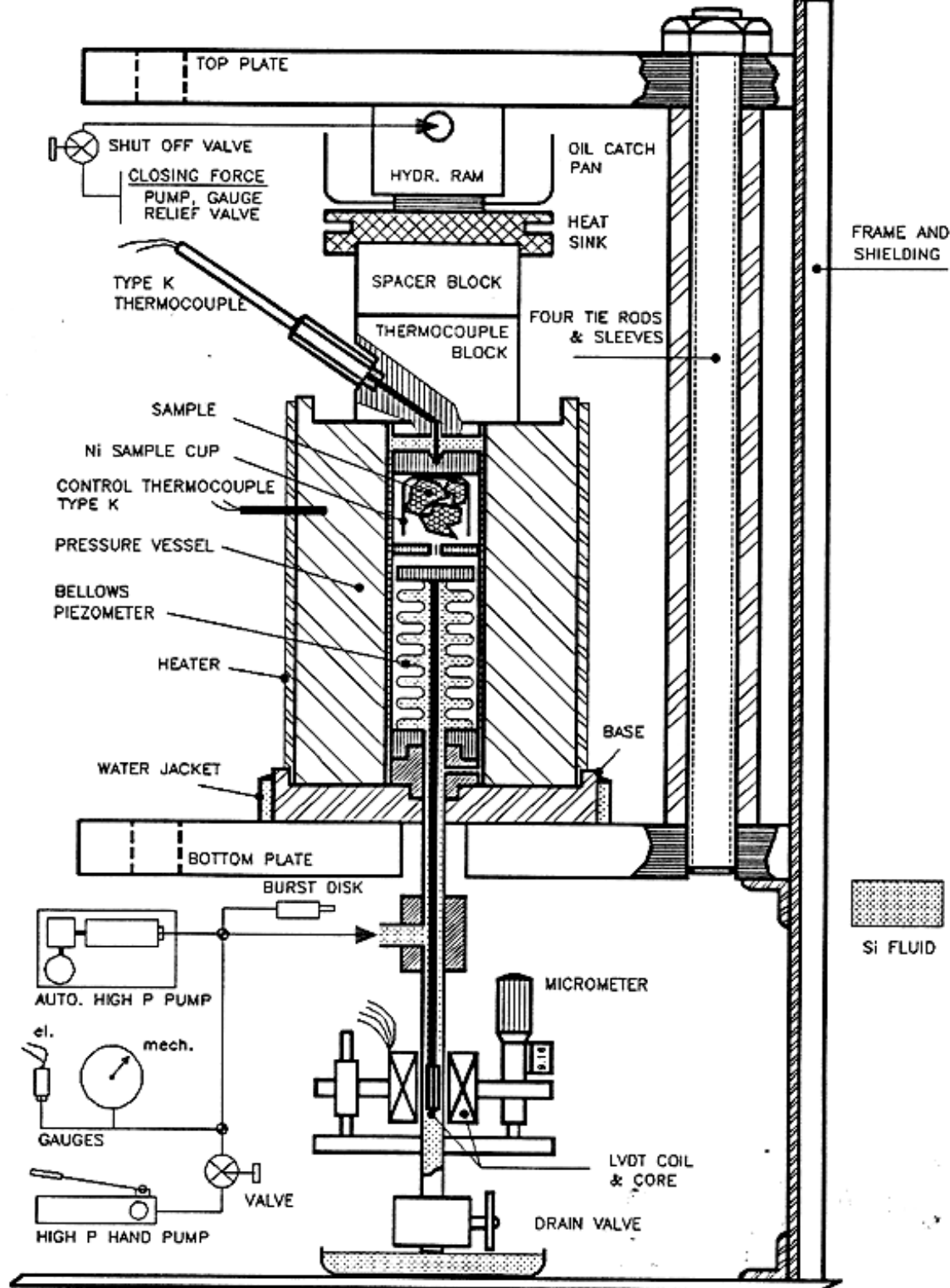
Gnomix® PVT instrument
T = 25-400°C, P = 10- 200 MPa

Example of PVT data

- S-S theory provides good description of the observed PVT dependencies for PA as well as for its PNC.

Ube PA-6
- experimental
- computed from S-S
P = 0.1 - 200 MPa
V (mL/g)
T (K)

Ube PNC
- experimental
- computed from S-S
P = 0.1 - 200 MPa
T (K)

- Fitting the *PVT* data to the theoretical equations provides two main sets of information:
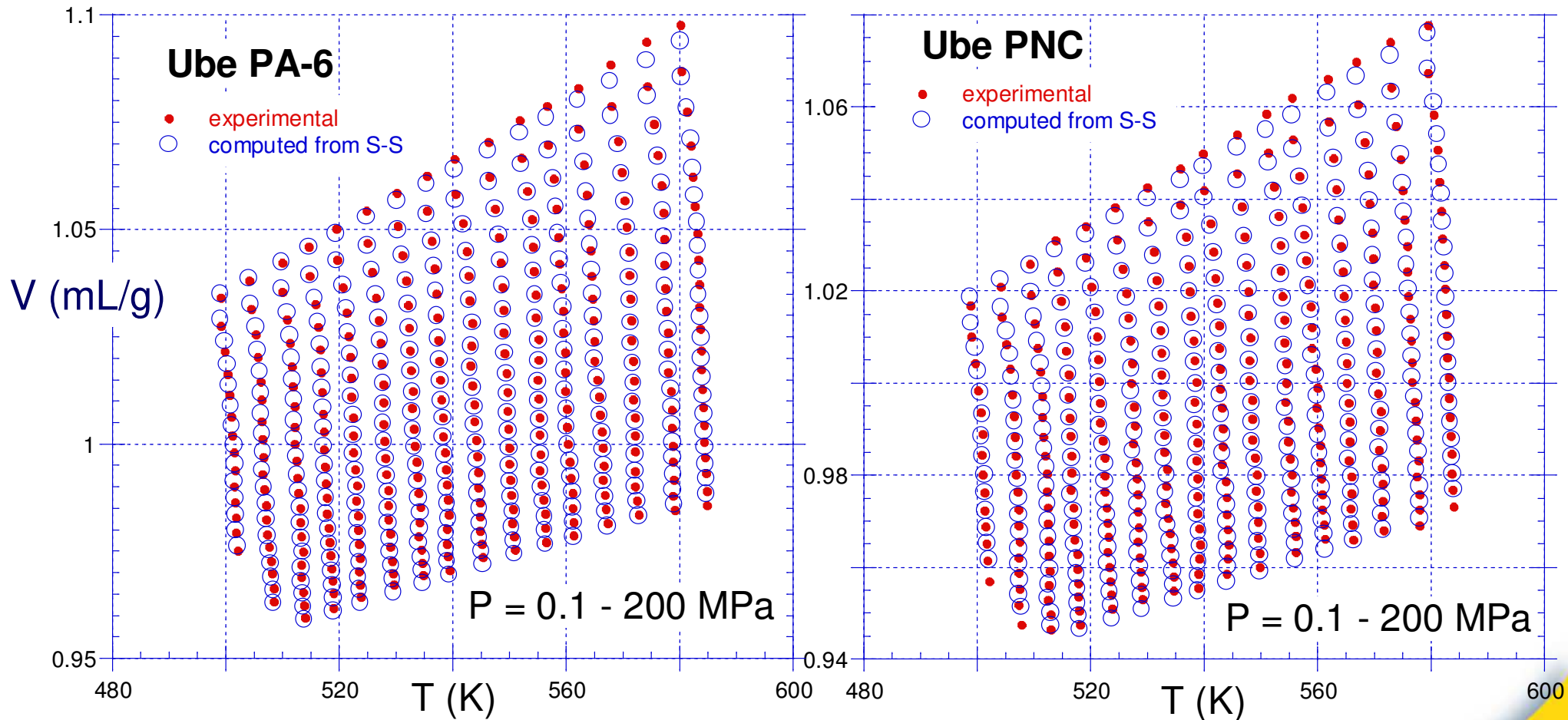 - The free volume (hole) fraction, $h = h(P, T)$, and
  - The reducing parameters: P^*, V^* and T^*, from which the bulk-average interaction parameters, $<\varepsilon^*>$ and $<v^*>$, may be computed.
- The temperature and pressure dependent free volume function h was shown to correlate with the degree of exfoliation, d_{001}.
- The concentration dependent interaction parameters have been used to examine the PNC structure on the molecular level.
  - Comparing the theoretical models with the bulk-average interaction parameters, $<\varepsilon^*>$ and $<v^*>$, indicates which one of them is the closest to reality.
  - The selected model yields the numerical values of the individual binary parameters, ε_{ij}^*, and v_{ij}^*.

S-S Quasi-lattice

- Hole fraction: *h = 1 − y(V, T)* is a measure of disorder.

Hole ○ →

$$\tilde{P} = P/P* ; \quad \tilde{T} = T/T* ; \quad \tilde{V} = V/V*$$

- Free energy →

$$\tilde{F} = \tilde{F}\left[\tilde{V}, \tilde{T}; y(\tilde{V}, \tilde{T}); c/s\right]$$

$$\text{Minimization} : \left(\partial \tilde{F}/\partial y\right)_{\tilde{V}, \tilde{T}} = 0$$

$$\text{Equation of state} : \tilde{P} = -\left(\partial \tilde{F}/\partial \tilde{V}\right)_{\tilde{T}}$$

Occupied sites
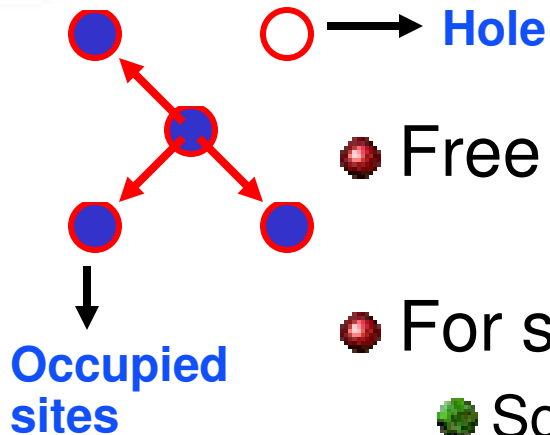
- For s-mer:
  - Scaling parameters:
    $P* = qz\,\varepsilon*/sv*; \; V* = v*/M_o; \; T* = qz\varepsilon*/cR \rightarrow$
    $$(P*V*/T*)M_o = Rc/s$$
  - $v*$: segmental repulsion volume
  - $\varepsilon*$: segmental attraction energy
  - *3c/s*: number of external modes (volume-dependent degrees of freedom) per segment:
    - Ideal flexible linear chain: *3c/s* → 1
    - Rigid chain: *3c/s* → 0

- The S-S theory describes the thermodynamic properties of liquids, explicitly providing information how the hole fraction ($h = 1 - y$) changes with independent variables.

- From the Helmholtz free energy, F, using standard definition of P and thermodynamic equilibrium condition a coupled equation of states (eos) was derived:

$$\tilde{P} \equiv -\left(\partial \tilde{F}/\partial \tilde{V}\right)_{T} \Rightarrow \tilde{P}\tilde{V}/\tilde{T} = (1-\eta)^{-1} + 2yG^{2}\left(AQ^{2} - B\right)/\tilde{T}$$

$$\left(\partial \tilde{F}/\partial y\right)_{\tilde{V},\tilde{T}} = 0 \Rightarrow 3c\left[(\eta - 1/3)/(1-\eta) - yQ^{2}\left(3AQ^{2} - 2B\right)/6\tilde{T}\right]$$

$$+ (1-s) - s\,ln\left[(1-y)/y\right] = 0$$

$$where: \quad A = 1.011; B = 1.2045; \quad \eta = 2^{-1/6}yQ^{1/3}; \quad Q = \left(y\tilde{V}\right)^{-1}$$

Binary mixtures

- Assuming random mixing in binary mixtures, Jain & Simha (1979) expressed the Helmholtz free energy in terms of averages, <>:

$$F_m / RT = x_1 \ln x_1 + x_2 \ln x_2 + (<s>/y)(1-y)\ln(1-y) - (<s>-1)\ln[(z-1)/e]$$

$$- <c>\{\ln[<v^*>(1-\eta)^3/Q] - (yQ^2/2\tilde{T})(AQ^2 - 2B)\}$$

$$- (3/2)\{x_1 c_1 \ln[2\pi<M_{o1}>RT(N_A h)^{-2}] + x_2 c_2 \ln[2\pi<M_{o2}>RT(N_A h)^{-2}]\}$$

- With definitions:

$$<s> = x_1 s_1 + x_2 s_2 ; \quad <c> = x_1 c_1 + x_2 c_2 ; \quad <M_o> = (x_1 s_1 M_{o1} + x_2 s_2 M_{o2})/<s>$$

$$<\varepsilon^*><v^*>^k = X_1^2 \varepsilon_{11}^* v_{11}^{*k} + X_2^2 \varepsilon_{22}^* v_{22}^{*k} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*k} ; \quad k = 2,4$$

$$\text{where} \quad X_1 = 1 - X_2 = x_1[s_1(z-2)+2]/<qz>$$

- The two cross-interaction parameters are expressed as:

$$\text{Interaction energy}: \varepsilon_{12}^* = \delta_\varepsilon \sqrt{\varepsilon_{11}^* \varepsilon_{22}^*} ; \quad \delta_\varepsilon \cong \delta_v \cong 1$$

$$\text{Repulsion volume}: v_{12}^* = \delta_v \left(v_{11}^{*1/3} + v_{22}^{*1/3}\right)^3 / 8$$

- In binary mixtures the interaction parameters are <u>molar averages</u>.

- Polymeric Nano-Composites (PNC) are mixtures of two components: flexible PA-6 and rigid "particles" of clay.

- The idealized clay particle is 100 nm in diameter and 1 nm in thickness, hence its "molecular mass" and "molecular volume" is:

$$M = N_A \, \rho \pi d^2 h / 4 = 10{,}443 \ (\text{kg/mol}), \text{ and}$$
$$V_{plat} = \pi (d/2)^2 h = 4.73 \times 10^6 \ (\text{mL/mol}).$$

- The lattice-hole theory assumes that the hard core volumes of the constituents do not differ too much, usually equal.

- For the inherent to the theory 6-12 potential the factor $2^{1/2}$ relates the positions of potential minimum and onset of repulsion, thus for PA-6: $v^*_{hard} = M_s V^* / 2^{1/2} = 17.60 \ (\text{mL/mol})$ also adopted for the clay "segment".

Ref.: R. Simha, L. A. Utracki and A. Garcia-Rejon, "Pressure-Volume-Temperature Relations of a Poly-ε-caprolactam and its Nanocomposite", *Composite Interfaces*, 8, 345-353 (2001); L. A. Utracki, R. Simha, and A. Garcia-Rejon, "*Pressure-Volume-Temperature Relations in Nanocomposite*", *Macromolecules*, **36**, 2114-21 (2003).

To directly compare the specific volume and the hole fraction variations with T and P for PA and PNC, the ratios *V(PA)/V(PNC)* and *h(PA)/h(PNC)* at identical T and P for each point are shown.
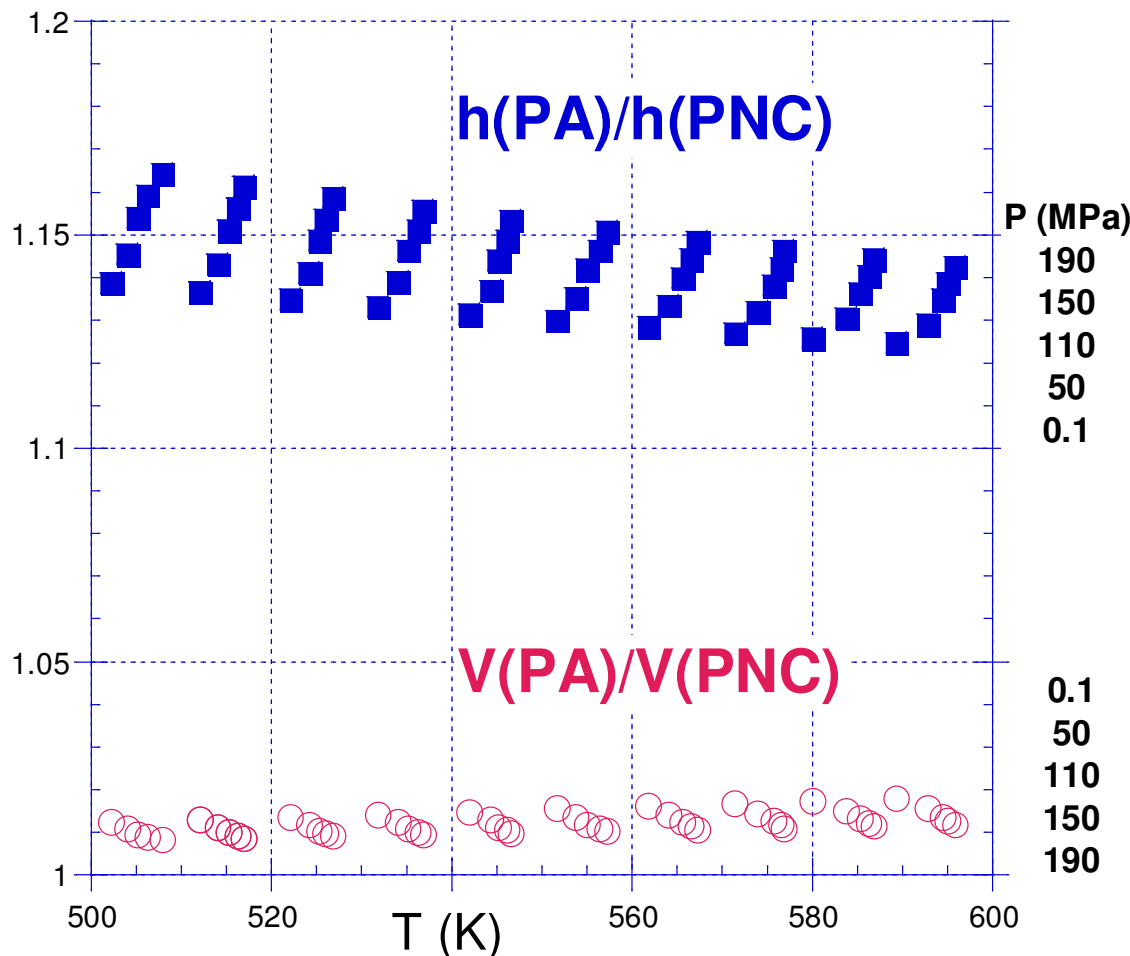
Theoretical V-ratio for PNC with 0.64 vol% clay is:
V(PA)/V(PNC) = 1.0088.

The experimental ratio:
V(PA)/V(PNC) = 1.008 to 1.018.

The holes ratio:
h(PA)/h(PNC) = 1.125 to 1.159.

h(PA)/h(PNC)

V(PA)/V(PNC)

P (MPa)
190
150
110
50
0.1

0.1
50
110
150
190

T (K)

Computed S-S eos parameters for PP and PP-PNC

#	Code	Sci#	C15A	M_o	P* (bar)	10000V*	T* (K)	r^2	σ
	IPP Zoller	ppz	0	40.853	6043 ± 79	1,1827 ± 24	10535 ± 56	0.999997	0.002045
0	PP	2845	0	50.459	4973 ± 113	1,1932 ± 42	10804 ± 117	0.999998	0.001706
A	PP256	256	0	43.115	5727 ± 68	1,1728 ± 22	10449 ± 57	0.999998	0.001647
1	E0-2100	2867	2	48.364	5169 ± 103	1,1874 ± 37	10712 ± 98	0.999998	0.001916
B	PP256	pnc	3	46.720	5457 ± 55	1,1712 ± 18	10775 ± 49	0.999998	0.001845
2	E1-2-E43	3578	2	49.432	5230 ± 117	1,2060 ± 42	11251 ± 120	0.999996	0.002505
3	E1-2-3150	3045	2	51.585	4923 ± 99	1,1971 ± 37	10970 ± 101	0.999996	0.002482
4	E2-2GMA	2923	2	47.774	5247 ± 95	1,1993 ± 34	10848 ± 90	0.999997	0.002261
5	E0-3200	2989	4	50,748	5028 ± 93	1,1857 ± 34	10917 ± 92	0.999997	0.002274
6a	E1-E43	3069	0	49.194	5111 ± 95	1,1926 ± 34	10820 ± 91	0.999997	0.002350
6b	E1-4-E43	367	4	45.611	5625 ± 146	1,1731 ± 48	10860 ± 132	0.999996	0.002421
7	E1-4-3150	3450	4	48.490	5266 ± 93	1,1931 ± 33	10993 ± 91	0.999996	0.002554
8	E2-4GMA	3151	4	49.412	5203 ± 96	1,1807 ± 34	10952 ± 94	0.999997	0.002272
9	M1	3167	2	52.238	4924 ± 90	1,2000 ± 34	11138 ± 95	0.999997	0.002256
10	M2	3224	2	46.893	5483 ± 105	1,1784 ± 36	10933 ± 100	0.999997	0.002251

- Computed values of the characteristic reducing parameters, as well as assessment of the goodness of fit are presented above.

- For the sake of comparison the data published by Zoller are also shown.

- To develop a model, first only the samples: A, B, 1, and 5 were used.

Ref.: L. A. Utracki, and R. Simha, "*Pressure-Volume-Temperature Dependence of Polypropylene/ Organoclay Nanocomposite*", *Macromolecules*, **37**, XXX (2004).

- Basics:
  - The "molecular mass" of clay platelet 100 nm diameter and 1 nm thick: $M = N_A \rho \pi d^2 h/4 = 10{,}878$ (kg/mol).
  - The "molecular volume" of clay platelet:
    $$V_{plat} = M/\rho = N_A \pi (d/2)^2 h = 4.73 \ 10^6 \ (\text{mL/mol}).$$
  - The lattice is built of cells of constant volume, accommodating one hard core statistical segment of clay or one hard core statistical segment of PP with the molecular volume of:
    $$v^*_{hard} = 28.9/2^{1/2} = 20.4 \ (\text{mL/mol}).$$
  - Thus, the number of segments for PP (s_1) and clay (s_2) are:
    $s_1(PP) = 4871$, and
    $$s_2 = V_{plat}/v^*_{hard}, = 2.6873 \ 10^5$$
  - The site fractions are defined as:
    $$X_1 = 1 = X_2 = x_1 z q_1/(x_1 z q_1 + x_2 z q_2)$$
    where $x_1 + x_2 = 1$ are molar fractions, e.g.:
    $x_1 = (m_1/M_{s1})/(m_1/M_{s1} + m_2/M_{s2})$
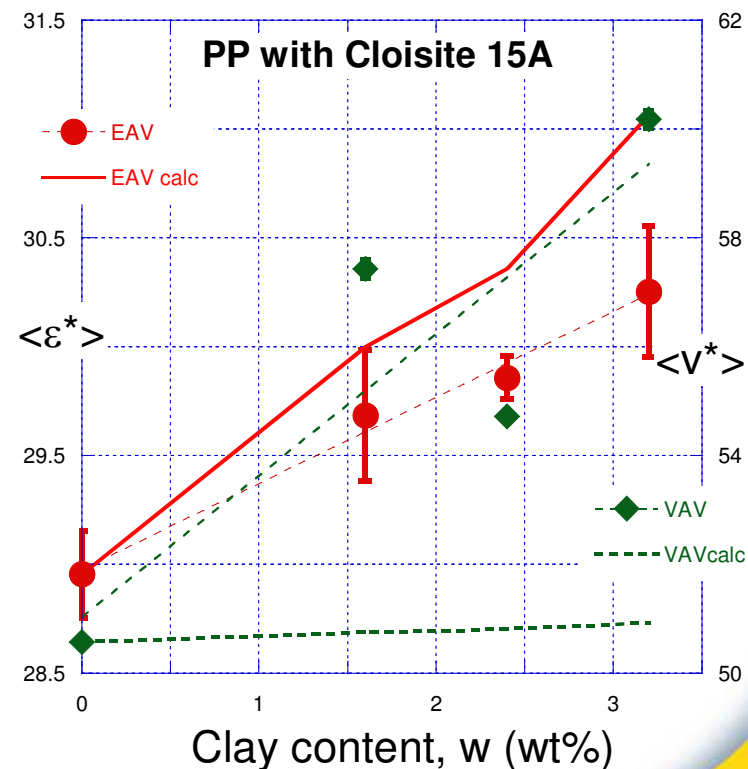
PVT of PNC – Model 1

- The input data are:
  PP + C15A

Organoclay	Clay	$\langle \varepsilon^* \rangle$	$\langle v^* \rangle$
(wt)%	w (wt%)	EAV (kJ/mol)	VAV (mL/mol)
0	0.0000	28.954	50.565
2	1.6000	29.683	57.427
3	2.1429	29.858	54.718
4	3.2000	30.251	60.172

- There are two possibilities of interpretation:
  - Assume that organoclay platelets are dispersed in PP matrix as <u>short stacks</u> – no good (see Figure ⇒).
  - Assume inorganic platelets are <u>coated with 6 nm thick solidified PP</u> and dispersed in PP matrix with properties changing with the distance from the clay platelet.

- Depending on the assumption the side fractions, X_i, will vary.
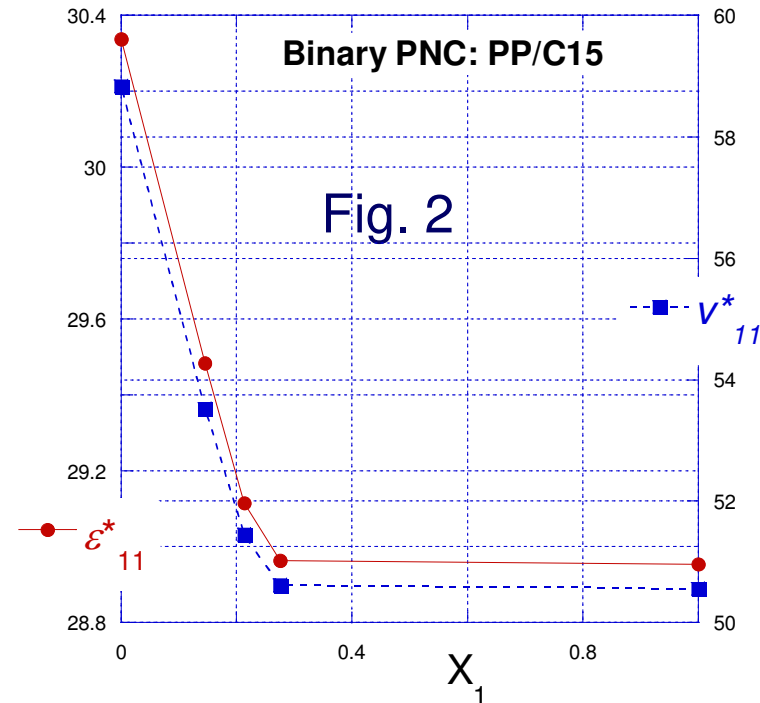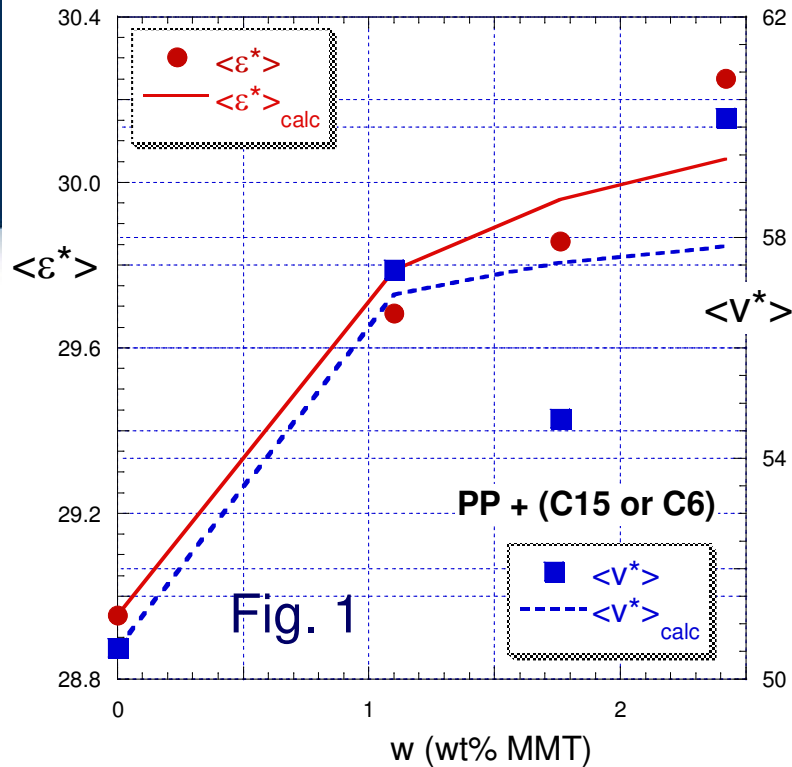

PP with Cloisite 15A

- EAV
- EAV calc
- VAV
- VAVcalc

$\langle \varepsilon^* \rangle$ $\langle v^* \rangle$

Clay content, w (wt%)

- The second assumption implies that the solid components are 13 nm thick, and only ≥100 nm away from the clay surface bulk PP properties are to be found.
- In Fig. 1 the average thickness of molten PP above clay platelet is shown as a function of clay concentration.
- In Fig. 2 assumed profile of property vs. distance from clay platelet surface, Δh, is shown. The curves were computed from:

$$y(z) = \frac{y_0 y_\infty}{y_0 - (y_0 - y_\infty) exp\{n[(z - z_0)/(z - z_\infty)]\}}; \quad z_o \leq z < z_\infty$$

Fig. 1

Condition for absence of concentration-independent molten polymer: $x_1 = X_1 = 0$

Thickness of adsorbed polymer, Δh (nm) vs. Clay content, w (wt%)

Fig. 2

Matrix interaction parameters, ε_{11}^* or v_{11}^* vs. z (nm)

n: 5, 4, 3, 2, 1.5

Fig. 1

PP + (C15 or C6)

Binary PNC: PP/C15

Fig. 2
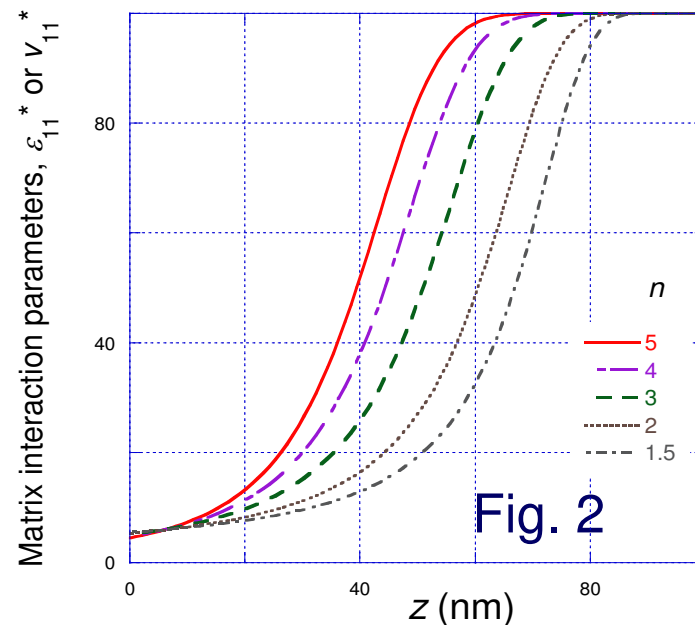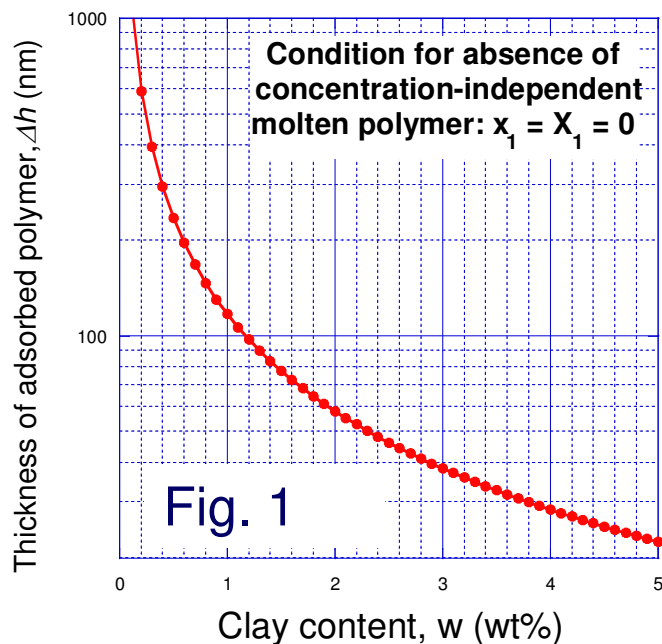
- The more rigorous approach involved three steps:
  - Calculate Δh as a function of clay content
  - Calculate ε_{11}^* and v_{11}^* in terms of Δh
  - Optimize the fit to Simha-Jain binary interactions Eqs.
- The approach provides the best fit to data (see Fig. 1), and acceptable parameter values:

$$\varepsilon_{22}^* = 30.3 \pm 1.0; \quad \varepsilon_{22}^* / \varepsilon_{10}^* = 1.047; \quad v_{22}^* = 58.6 \pm 1.0; \quad v_{22}^* / v_{10}^* = 1.158$$

- Figure 2 illustrates the predicted variation of matrix properties.

Next, the variation of hole fraction with composition was examined by computing the relative rations of the specific volume and the hole fraction:

- $V_r \equiv V(PNC)/V(PP)$
- $h_r \equiv h(PNC)/h(PP)$.

The Figure for PP/C15A series shows that addition of organoclay (no compatibilizer) has very little effect on sample density, but it reduces the free volume (at $P = 10$ MPa):
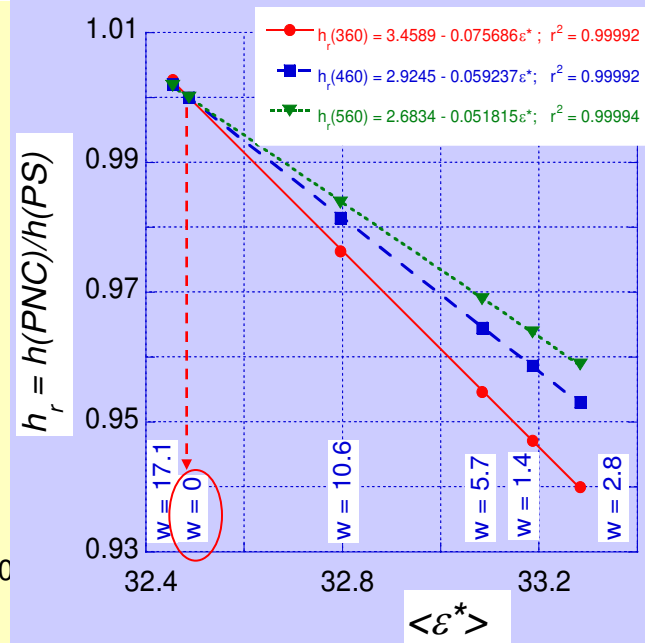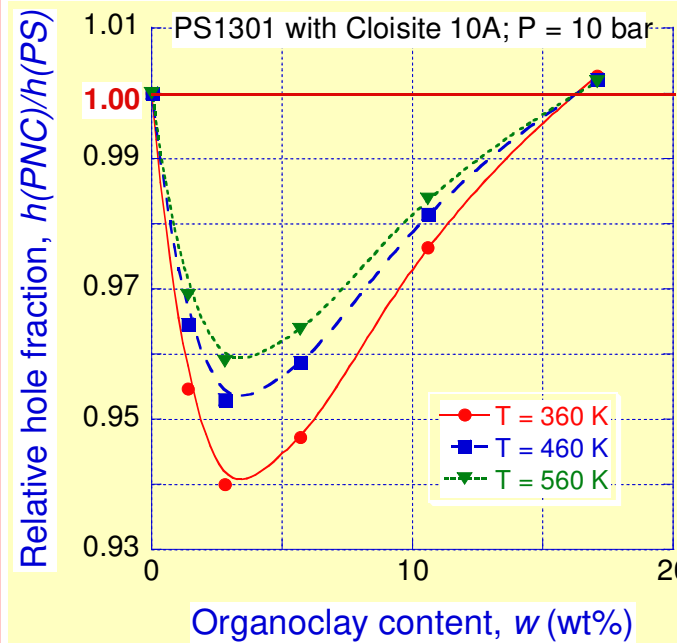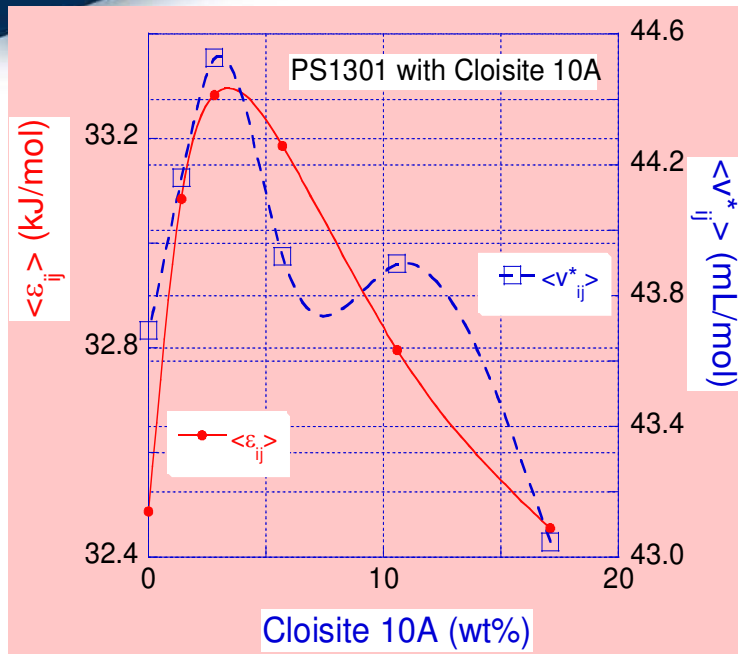
- At 2 wt% C15A by ca. 4.7%
- At 4 wt% C15A by ca. 8.0%

$V_r = V(PNC)/V(PP)$

$h_r = h(PNC)/h(PP);$

PP with 2 or 4 wt% C15A at P = 10 MPa

- V_r (2%)
- V_r (4%)
- h_r (2%)
- h_r (4%)

T (K)
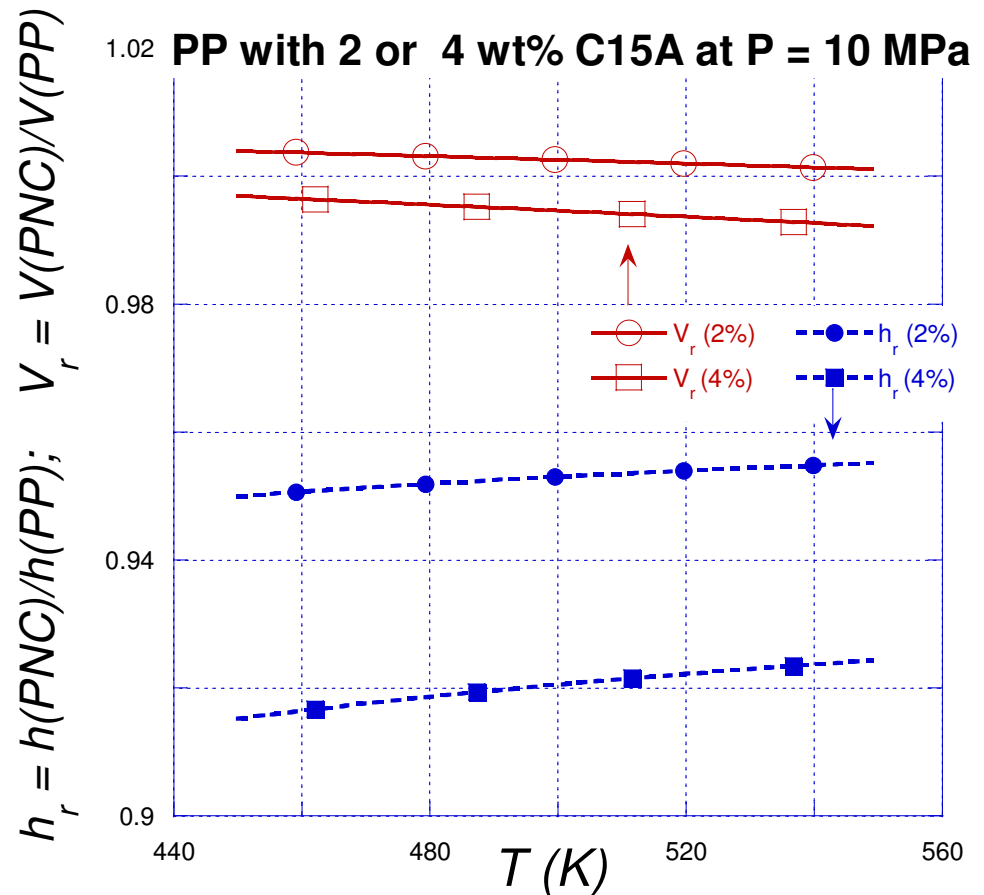
Owing to lower compressibility of PNC than that of a polymer the magnitude of h_r increases with P.

PVT of PS-based PNC

- From the PVT fit the reducing parameters and then the average values of the interaction parameters were calculated:

$$P^* = zq\langle\varepsilon^*\rangle/(s\langle v^*\rangle); \qquad T^* = zq\langle\varepsilon^*\rangle/Rc; \quad V^* = \langle v^*\rangle/M_s$$

- The minimum in the hole fraction (at ca. 2 wt% C10A) corresponds to maximum clay platelets dispersion.
- There is a simple relation between the free volume and the average interaction parameter, $\langle\varepsilon^*\rangle$.
- The two average interactions parameters are proportional to each other.

- The Figure shows interlayer spacing, d_{001}, for PNC samples containing 2-wt% organoclay.

- Several compositions were measured using different specimens – the standard deviation of the data was established as ± 0.15 nm.

- The Figure illustrates the correlation between d_{001}, and computed from the PVT data reduction of h (at 100 MPa; 500 K).

Correlation for 2 wt% organoclay

$\Delta h\ (\%) = 100[1 - h(PNC)/h(poly)]$

$d_{001}\ (nm)$

PA-6

PP

PS

PNC without compatibilizer:
$\Delta h = 2.50 + 0.833d_{011}$; r = 1

PP-PNC with compatibilizer:
$\Delta h = -21.73 + 9.38d_{001}$; r = 0.927

- Two dependencies are seen:
  - For a two component PNC (polymer/organoclay)
  - For three component: PP/organoclay/compatibilizer systems.

- The compatibilizers (PP grafted with MAH or GMA) dramatically reduced h with only a small effect on d_{001} (immiscibility).

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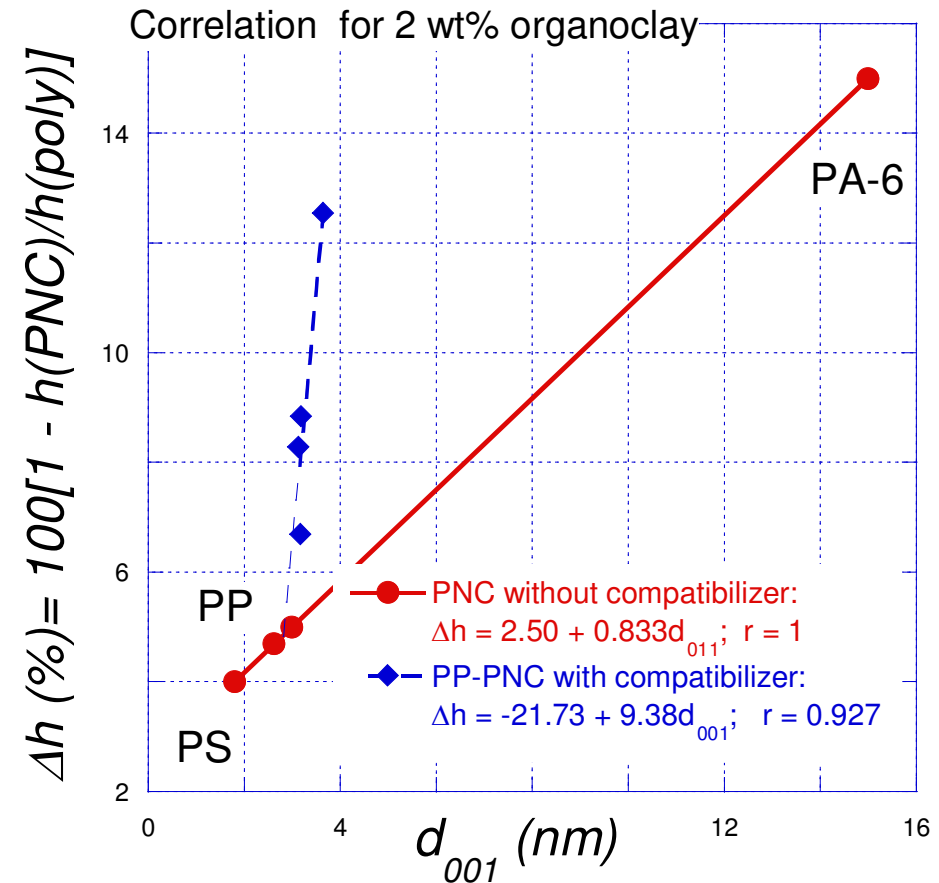
Summary of Part #1: Thermodynamics

- Clay platelets, with 40% atoms on the surface, have high surface energy, and are poly-ionic (hydrophilic).
  - Molecular adsorption causes formation of two layers:
    - 6 nm thick solidified inner layer
    - From 6 to ca. 100 nm outer layer with increasing molecular mobility

  - The Simha-Somcynsky eos well describes the *PVT*, yielding:
    - The bulk-averaged (Lennard-Jones type) interaction parameters
    - The free volume parameter, $h = h(V, T)$.

  - To extract meaningful binary parameters from the bulk-averaged ones, a "hairy-clay platelet" (HCP) model was postulated:
    - The model assumes presence of:
      - Solid particles of clay enrobed with 6 nm thick layer of organic solids
      - A matrix composed of non-solidified melt (intercalant, polymer, and compatibilizer) – at a distance of 6 to 100 nm the matrix properties vary.
    - The loss of the matrix free volume linearly depends on d_{001}: $\Delta h = \Delta h(d_{001})$.
    - The loss of free volume is expected from the reduction of mobility.

Rheology of PNC

- **Thermodynamics suggest the hairy-clay platelet (HCP) model for PNC.**

- **PA-6 and PA-6-based PNC from Ube** were dried and then compounded in a TSE with: 0; 25; 50; 75; and 100% of PNC.

- The rheological tests were carried out at 240°C under blanket of dry N_2 [Utracki & Lyngaae-Jørgensen, *Rheologica Acta,* **41,** 394 (2002)].

- During the time sweep the storage (G') and loss (G'') shear moduli increased with time, due to polycondensation & exfoliation.

- The rates of these two processes differently depended on the intercalated clay content.

- All raw data were corrected for the polycondensation effects by extrapolating the measured signal to $t = 0$.

Time-sweep of PA-6 with 2-wt% Cloisite® 15A
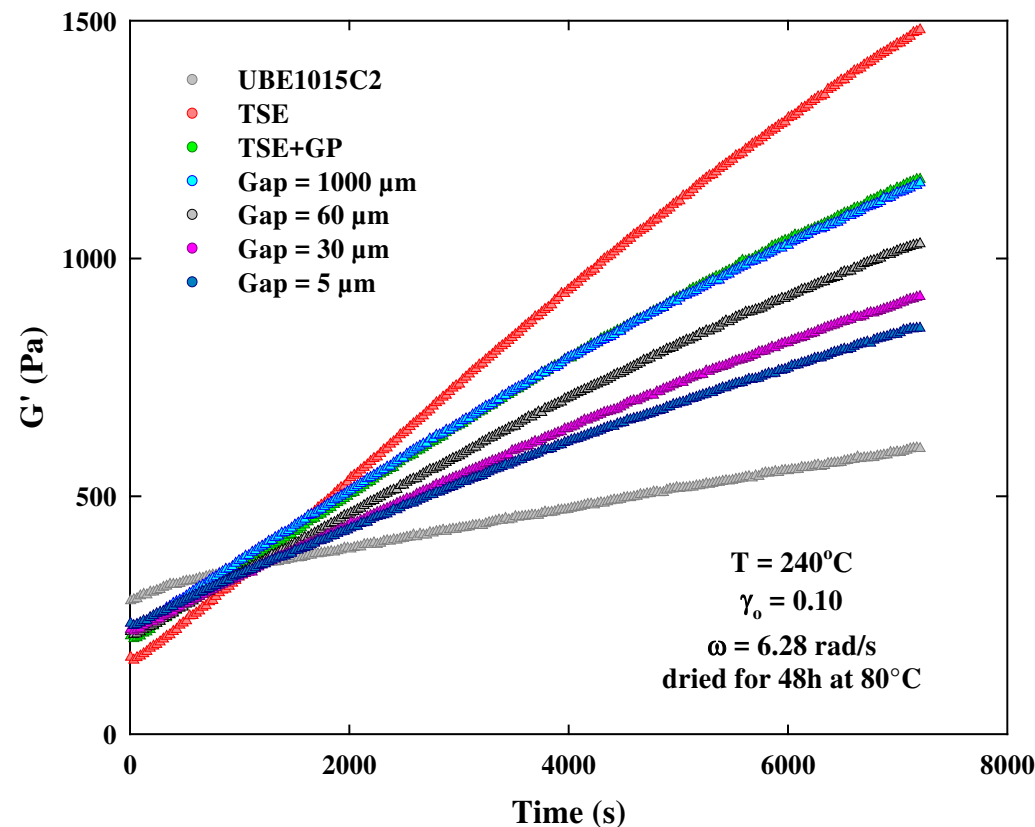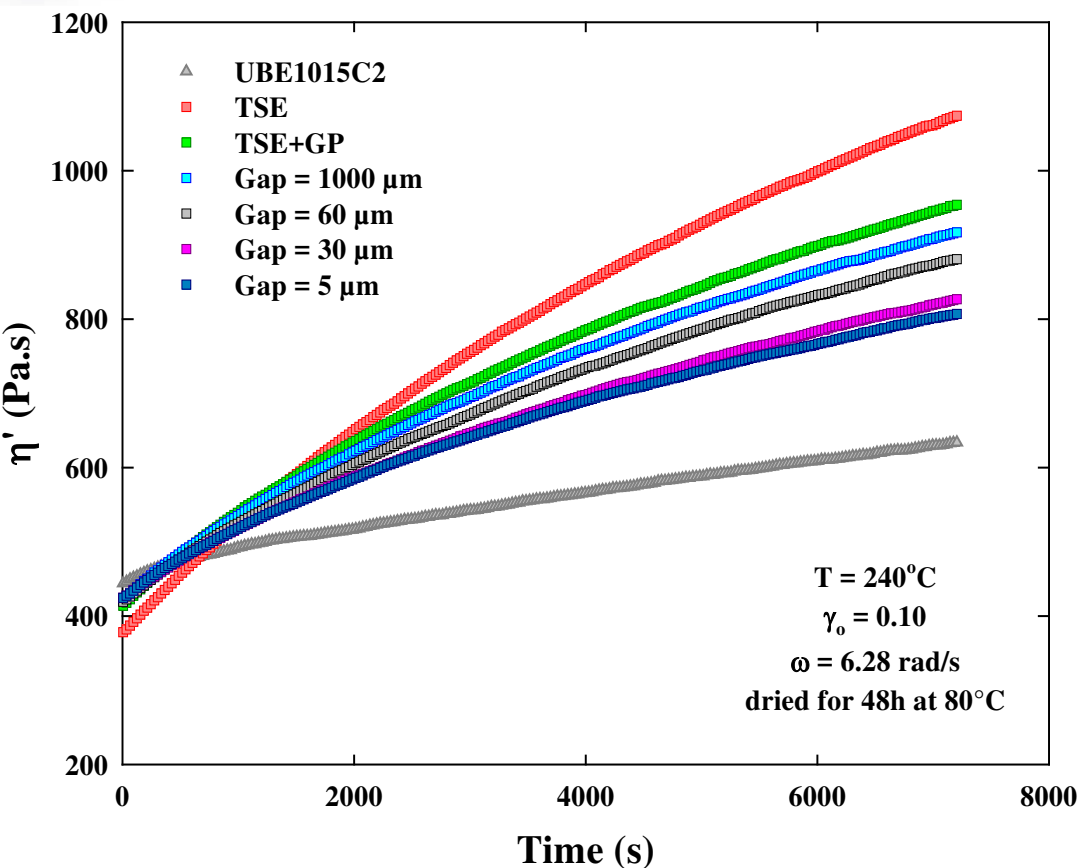
- The dynamic viscosity (left Figure) and the storage modulus (right Figure) are presented [M. Sepehr, 2004].
- The polycondensation rate decreases with the increasing degree of clay dispersion.

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- The data were fitted to the relation, where:
  η_0 = zero-shear viscosity,
  τ = the prime relaxation time,
  n = the power-law exponent.

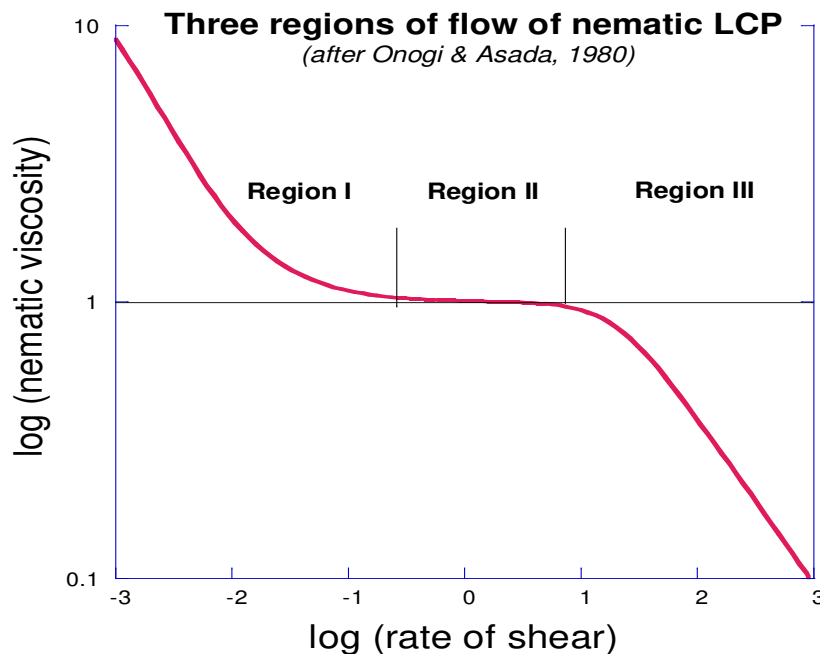$$G''/\omega = \eta_o \left[1 + (\omega\tau)^{m_1} \right]^{-m_2}$$

$$n = 1 - m_1 m_2$$

Summary of dynamic viscosity data

- PA
- 25% PNC
- 50% PNC
- 75% PNC
- 100% PNC

$T = 240°C; \gamma = 40\%$
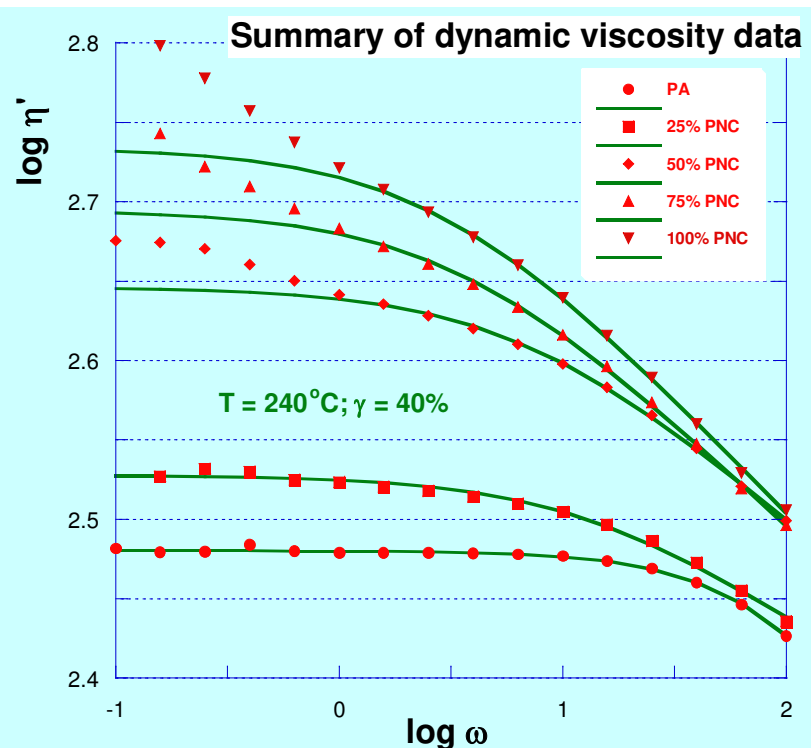
- Next, from η_0 the relative viscosity vs. clay volume fraction was calculated:

$$\eta_r \equiv \eta_o' / \eta_{o,PA}' = 1 + [\eta]\phi + k\left([\eta]\phi\right)^2$$

- The intrinsic viscosity, $[\eta]$, is related to the aspect ratio, p: $[\eta] = 2.5 - a(1-p^b)$.

- The calculated value $p = 287 \pm 9$ agrees well with $p = 286$ determined from the oxygen permeability data.

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LCP model

Flow of PA-6/PNC follows the LCP behavior

Three regions of flow of nematic LCP
(after Onogi & Asada, 1980)

log (nematic viscosity) vs log (rate of shear)

Region I   Region II   Region III

Steady-state shearing of PNC with Δt (s) between data points (T = 240°C)

Shear viscosity, η (Pas) vs Rate of shear (1/s)

Δt (s)
- 540
- 360
- 180
- 90
- 0
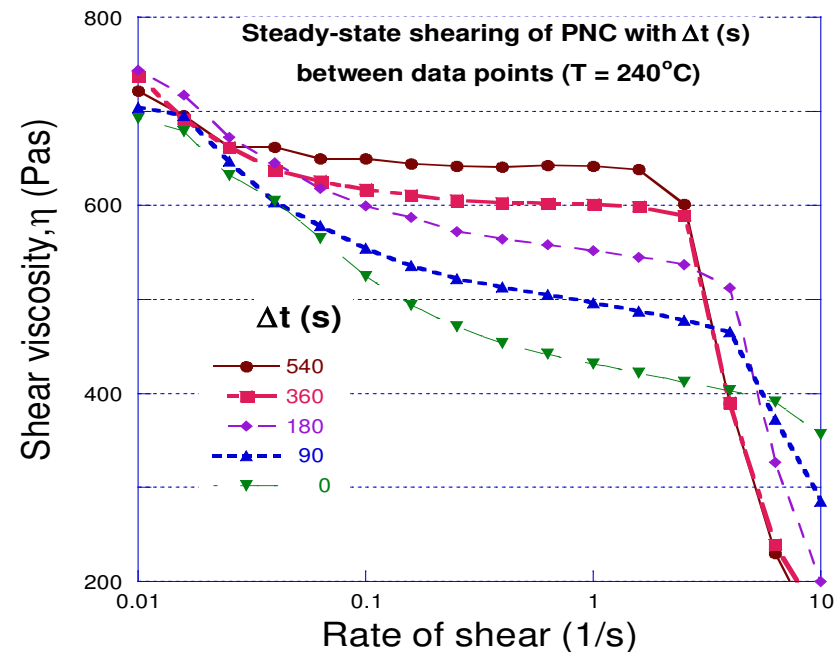
The flow of liquid crystal polymers (LCP) is characterized by the presence of three regions [Onogi & Asada, 1980]:

- I – The poly-domain structure is gradually destroyed by shear.
- II – The nematic domains rotate in a mono-domain continuous matrix.
- III – The tumbling flow of II is gradually replaced by flow alignment.

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Flow reversal for PNC at T = 240 °C

Rest time = 500 s
Rest time = 2000 s
Rest time = 4000 s

A

Base line (polycondensation)

Viscosity, η (Pas)

Time, t(s)

$\Delta\eta = a \exp\{-b/t\}$

a = 212.6 ± 7.4
b = 290.4 ± 28.9
r^2 = 0.9967

B

experimental

computed

$\Delta\eta$ (Pas)
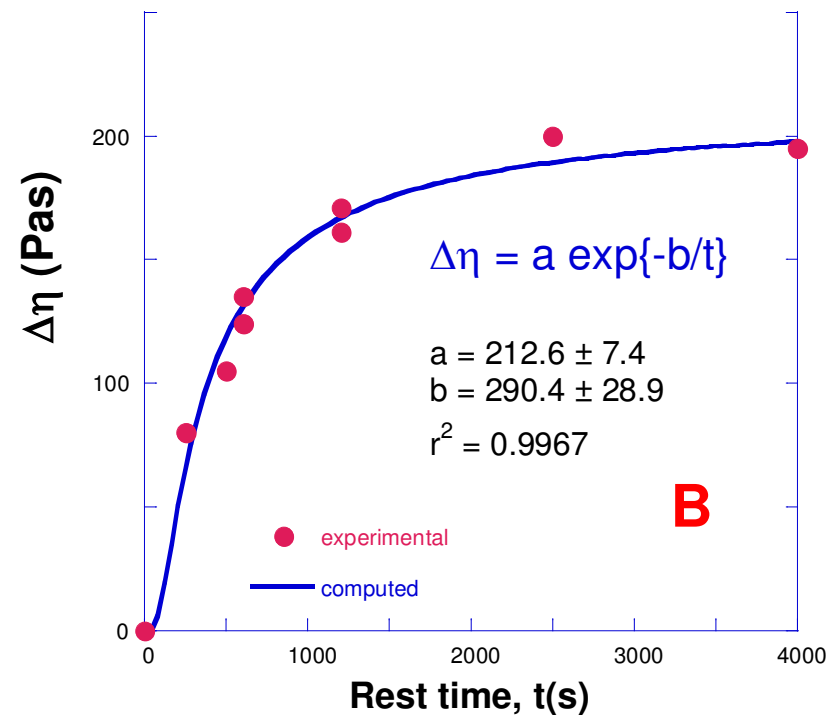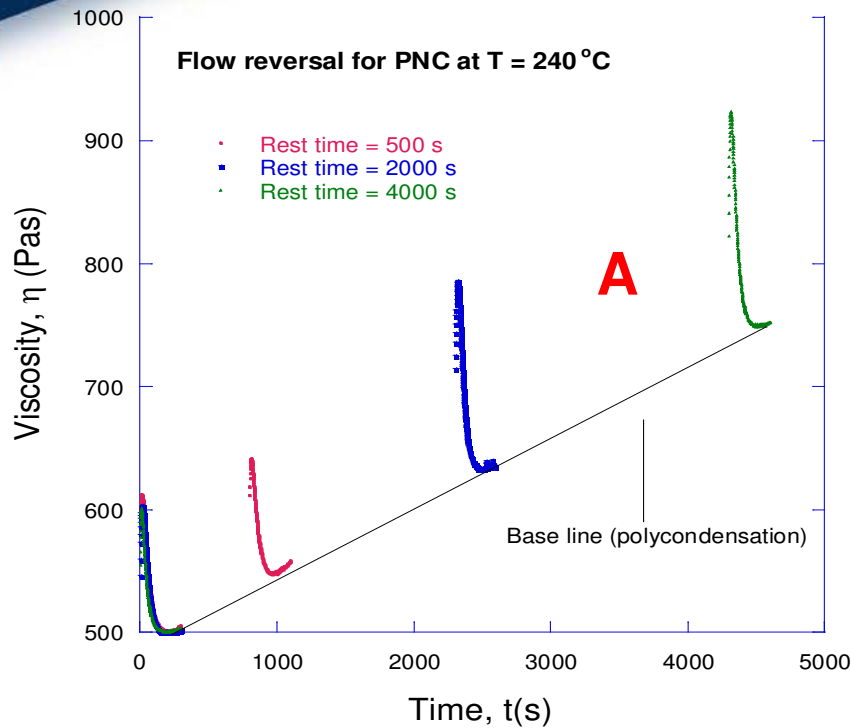
Rest time, t(s)

- Orientation of clay platelets leads to a strong stress overshoot effect when the direction of shearing is reversed (see Fig. A).

- The magnitude of the stress overshoot depends on the rest time at 240°C (see Fig. B).

- It takes about 1 hr for the platelets to return to the pre-shear random orientation.

FTR of PA-6 PNC

PNC: time sweep at T = 240°C, ν = 10 Hz

Fourier transform rheology for PNC

ν = 10 Hz

ν = 1 Hz

Legend:
- ν = 1 Hz; γ = 20%
- ν = 1 Hz; γ = 30%
- ν = 1 Hz; γ = 60%
- ν = 1 Hz; γ = 70%
- ν = 10 Hz; γ = 70%

Intensity — Frequency (Hz)

Relative intensity, $R_3 = 100(I_3/I_1)$ — Shearing time, t(s)
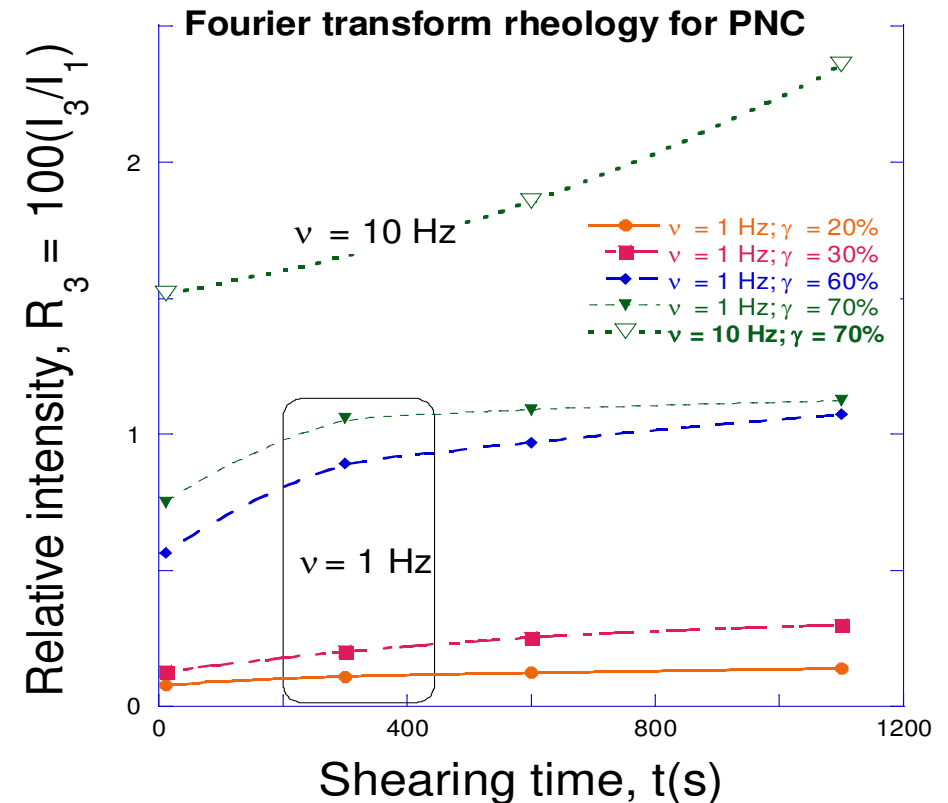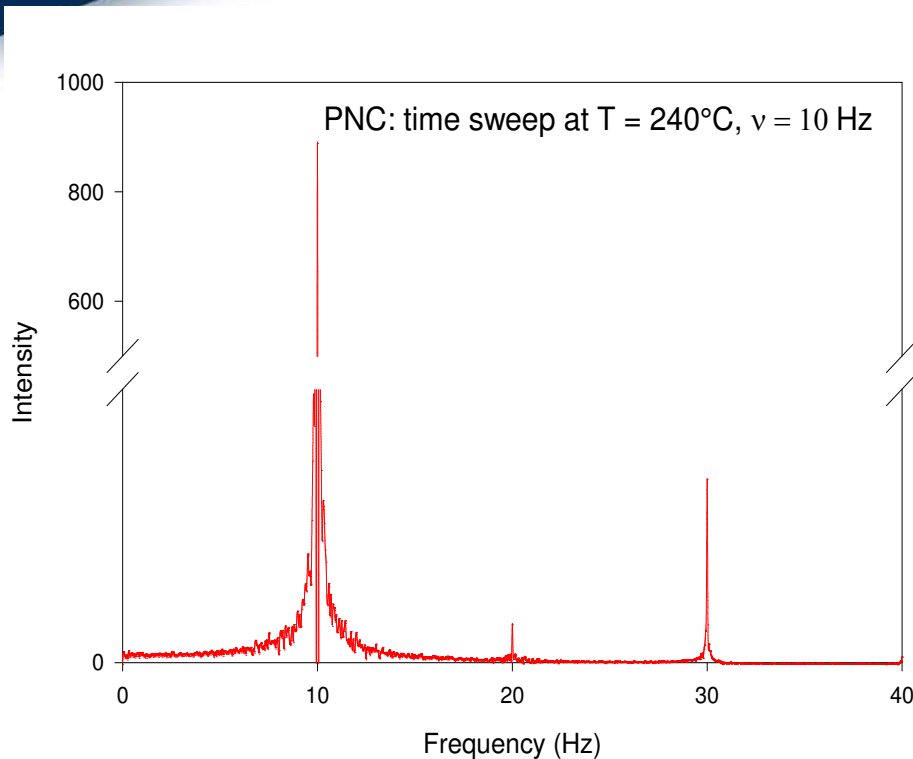
- **The Fourier-transform rheology (FTR) is a new method for quantifying the non-linear viscoelastic behavior of matter.**
  - Left Figure shows the raw data: input peak and 3rd harmonic.
  - Right Figure show the relative intensity of the 3rd harmonic – a measure of non-linearity as a function of frequency, strain and shearing time.

Rheology of PS PNC

- PS-based PNC were prepared in solution and by melt compounding PS with 0 to 10-wt% Cloisite® 10A (C10A) in a CORI.

- C10A = MMT pre-intercalated with di-methyl benzyl hydrogenated tallow ammonium chloride.

- Owing to thermo-oxidative degradation of C10A the degree of dispersion was poor, viz. the aspect ratio: $p = 16$ – to be compared with $p = 269$ determined for the solution-prepared PNC.

- Flow properties were determined in dynamic and steady state shear as well as under extensional flow conditions.

- The Fourier-transform rheology (FTR) indicated strong dependence on strain but weak on time.

- The time-temperature superposition held in the full range of variables.

- Strain hardening in extensional flow of the PNC (with 0 to 10 wt% C10A) was virtually concentration-independent.

FTR of PS/C10A PNC
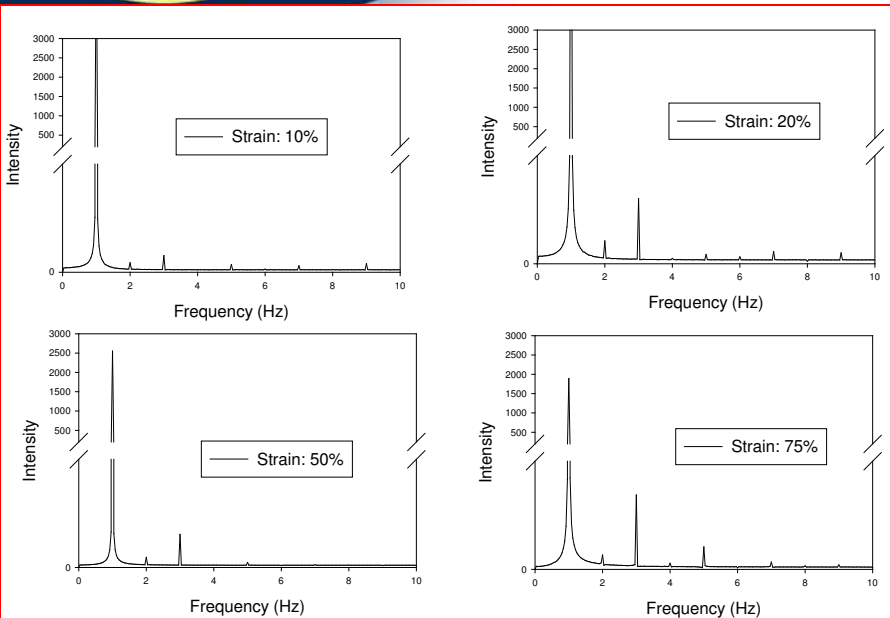
- PS (M_w = 310 kg/mol) with 2-10 wt% of C10A tested *at T = 200ºC* and γ = 10, 20, 50 & 75%

- The <u>melt compounded</u> PNC with 2 wt% organoclay behaves similar to PS

- Solution prepared PNC with 2 wt% C10A shows stronger non-linearity than the melt compounded one containing 10 wt% C10A.

- Top Figure shows raw data at n = 1 Hz and at strains: γ = 10, 20, 50 and 75%.

- Fig. **B** shows R_3 = 1000I_3/I_1 vs. γ. Solid points are experimental, open symbols are calculated from:

$$R_3(\omega) = R_{max}\left[1 - \exp\left\{-(\gamma - \gamma_L)/k\right\}\right]; \quad \gamma > \gamma_L$$

$$or \quad R_3(\omega) = a\left\{1 - 1/[1 + (b\gamma)^c]\right\}$$

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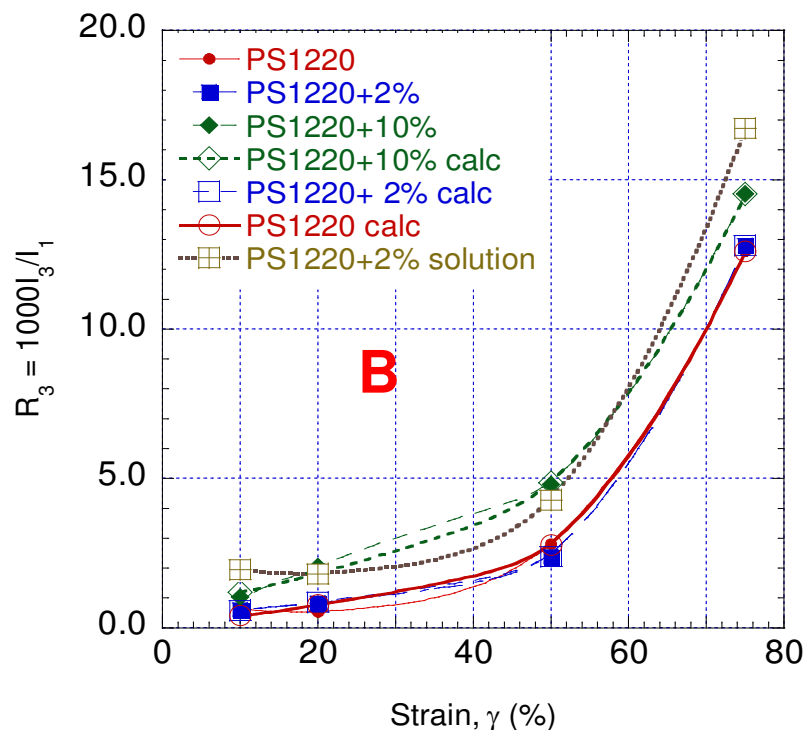
Summary of Part #2:
Rheology of PNC

- The characteristic feature of the PNC flow is the presence an yield-like behavior at low deformation rates, i.e., the viscoelastic non-linearity (VNL).

- The better dispersed is the system, the higher is the VNL.

- The flow of exfoliated PNC resembles that of lamellar LCP with very large mesogens (relaxation time of ca. 60 min).

- Fourier-transform rheology (FTR) is a useful tool for characterization of VNL hence the degree of dispersion.

- To interpret the PNC flow behavior the hairy-clay platelet (HCP) model was used:

  - The clay are enrobed in solidified organic phase, from which emanate long, able to entangle macromolecules

  - Consequently, for well dispersed PNC the VNL behavior is observed at concentration below that calculated from the encompassed volume principle.

  - Owing to large aspect ratio ($p \leq 300$) there is a strong orientational effect

Grafted clay platelets

Stretched brush

blob

σ $\quad$ 1 $\quad$ $N^{1/2}$ $N^{2/3}$ N $\quad$ **P**

1

S>0

λ_2 Immiscible

A

$N^{-1/2}$ $\qquad$ B

ISB $\qquad$ **NSB**

N^{-1} SSB

$N^{-6/5}$

SM $\qquad$ IM

D

L
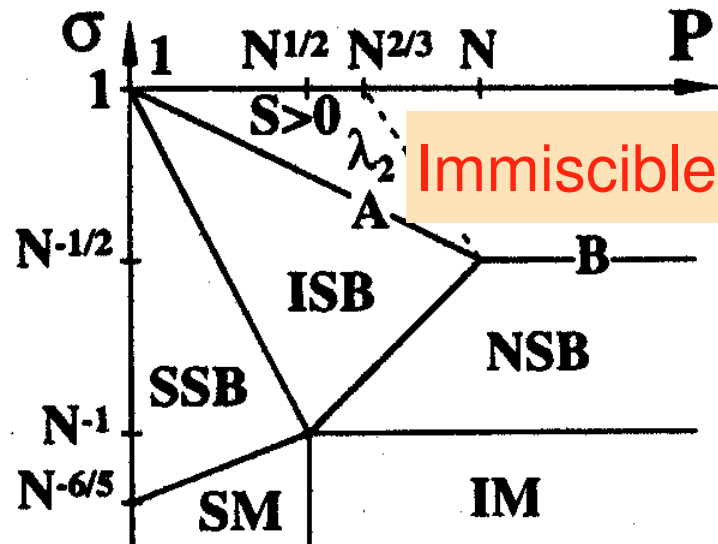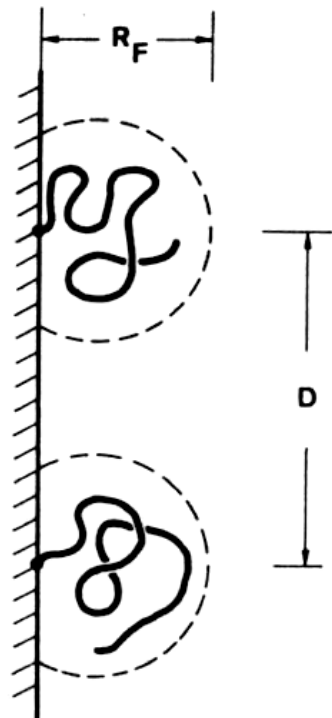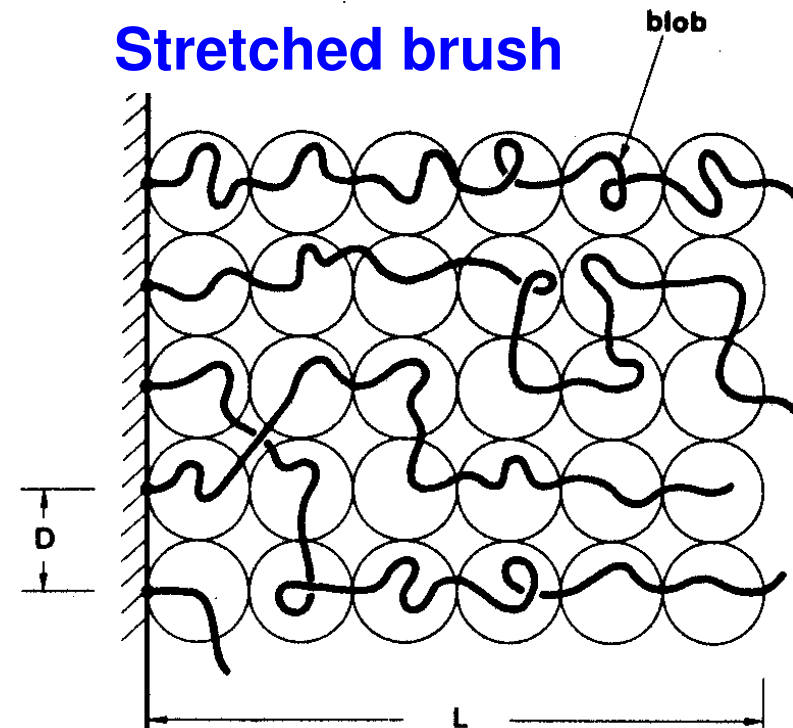
- Properties of end-grafted polymers on solid surface have been studied for **nearly 30 years.**

- In melt of polymer P <u>clay grafted with chemically identical, end-terminated polymer</u> N is dispersed; $N \le P$.

- For low σ, the phase diagram show swollen (S) and ideal (I) **mushrooms** (M), at higher S-, and I-**stretched brush**, as well as non-stretched brush (NSB); for high $\sigma > N^{-1/2}$, and high P > N the brush is non-penetrating – <u>the grafted clay phase separates from the melt</u> [Gay, 1997].

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Aggregation of grafted clay

- Consider two clay platelets grafted at the grafting density σ with chains of length L.

- The energy of interaction free energy between such two platelets at a separation H is $F = F(H)$.

- Computations [Ferreira *et al.*, 1998; Wang *et al.*, 2003] indicate repulsion for low σ and L, but aggregation at higher values of these variables.
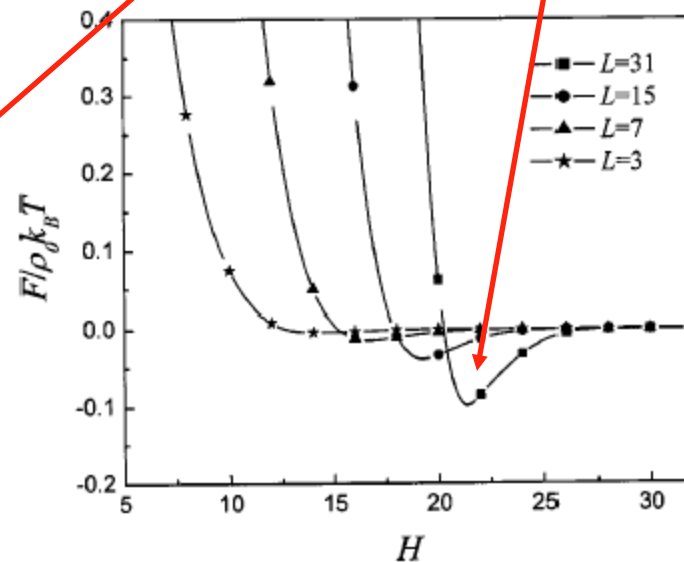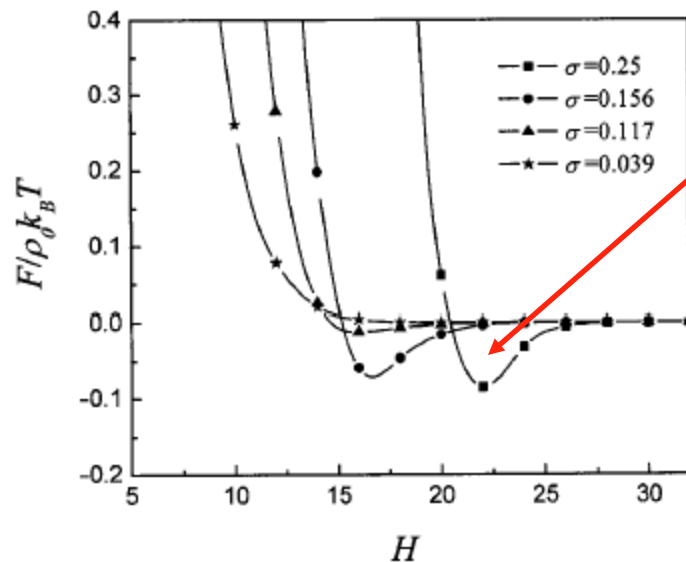
Numerical model for CPNC macromolecules

Kuhn Segment
$MW \cong 260$

Strong bonding of s with o & g
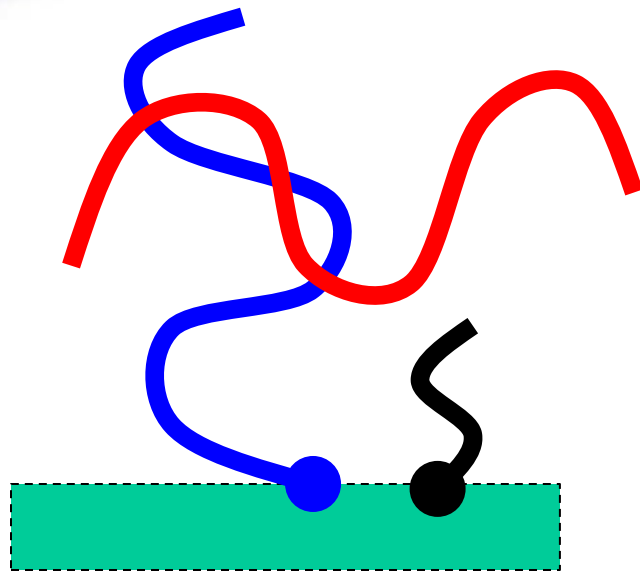
Physical Chain model
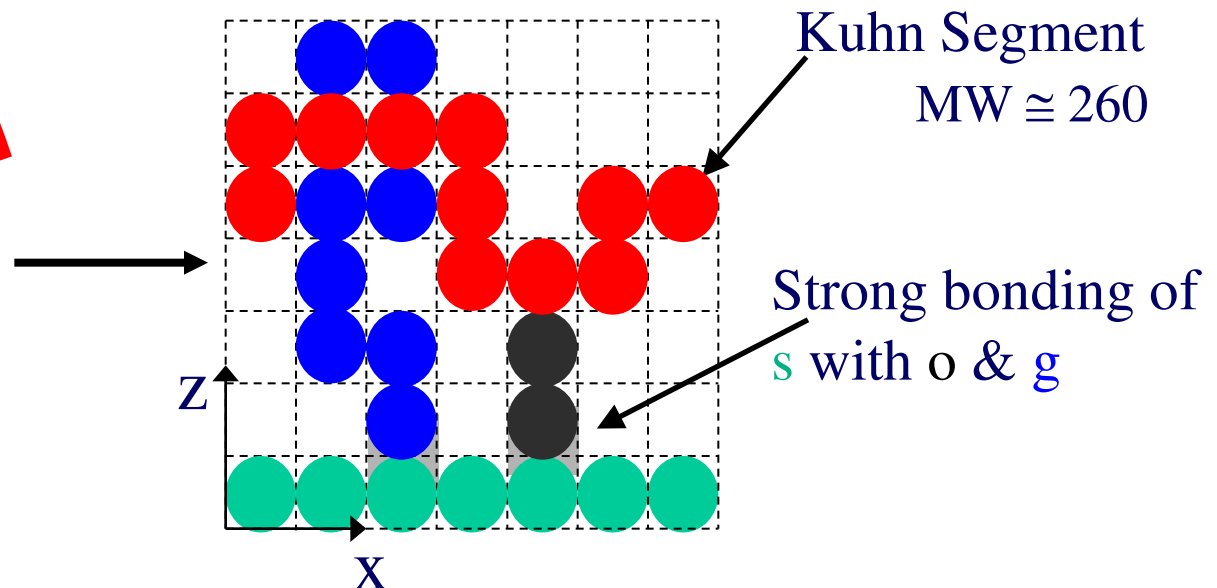
Statistical Representation

- Clay platelet (s): No conformational energy
- Host polymer (h): Conformational and mixing energy
- Compatibilizer (g): Strong bonding to the surface
- Organic modifier (o): Strong bonding to clay surface

Vaia's thesis of 1995 provided the first thermodynamic description of PNC as a function of distance (h) between platelets (r_i is radius of interacting segment).

- Intercalant entropy gain only up to full stretch (Dolan-Edward).
- Macromolecule entropy loss within the sandwich (Huggins-Flory).
- Enthalpy taken from van Opstal *et al.* (1991); $\varepsilon_{ho} \approx 0$:

$$\Delta e_v = \hat{\varphi}_1 \hat{\varphi}_2 \Delta \varepsilon = \frac{2\hat{\varphi}_1 \hat{\varphi}_2 \left(\varepsilon_{sh,so} / h_o + \varepsilon_{ho} / r_2 \right)}{1 - \hat{\varphi}_2 \left[1 - (r_1 / r_2) - (r_1 / h_o) \right]}$$

$$\Delta G = \Delta H - T \Delta S$$

Left plot: $\Delta S_A / R$ ($10^6 / m^2$) vs $h - h_o$ (nm), showing curves labeled Intercalant, Total, Polymer.

Right plot: ΔF_A (mJ/m^2) vs $h - h_o$ (nm), curves labeled $\varepsilon_{sh,so} = 0$, $\varepsilon_{sh,so} = -4$, $\varepsilon_{sh,so} = -8$, $\varepsilon_{sh,so} = -10$.

Only intercalation

●The 1D **SCF** lattice model [Balazs *et al.*, 1998] considers two, parallel, infinitely large clay platelets in molten polymer bath. The properties change with the short range interactions, ε, and the distance from clay surface, $h_o < z < h$:

$$F(z) = \sum_i \phi_i(z) \ln G_i(z) + (1/2) \sum_{ij} \chi_{ij} \int \varepsilon(z - z')\phi_i(z)\phi_j(z')dz'$$
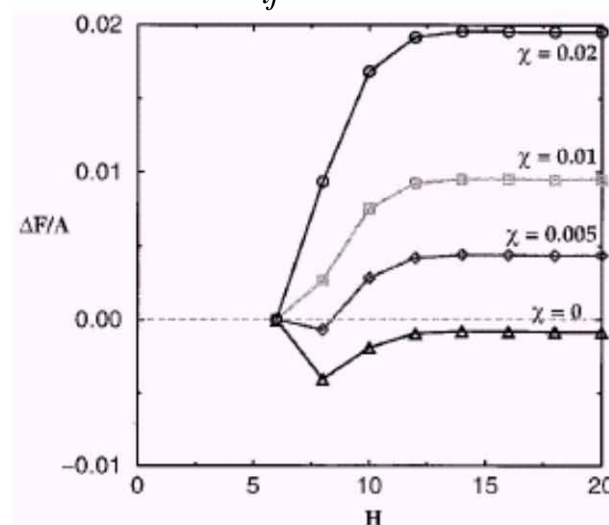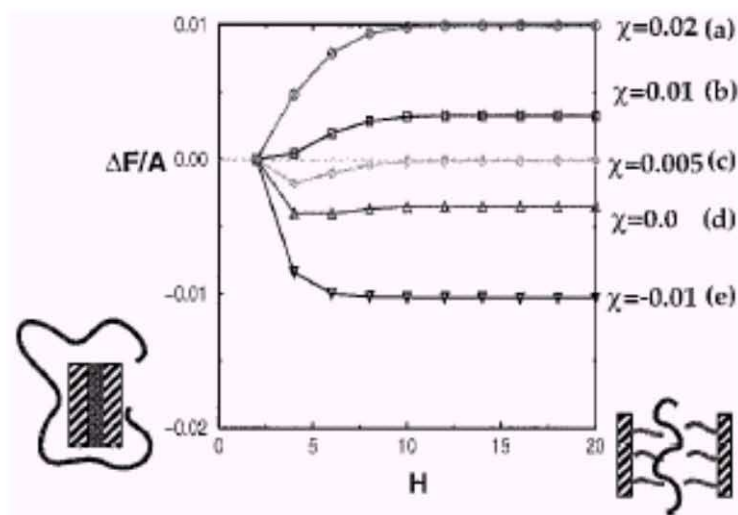
Free energy per unit area as a function of surface separation for five different values of the polymer-intercalant interaction parameter, χ_{ho}. Other parameters are: N = 100; N_i = 25 and $\chi_{sh} = \chi_{so} = 0$. **In the LHS and the RHS Figures the grafting density: ρ = 0.04 and 0.12, respectively.** The cartoons, left and center, show the initial and final state, respectively, where the surfaces are separated by macromolecules.

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Balazs *et al. contribution 2*

after: Balazs *et al.*, 1998
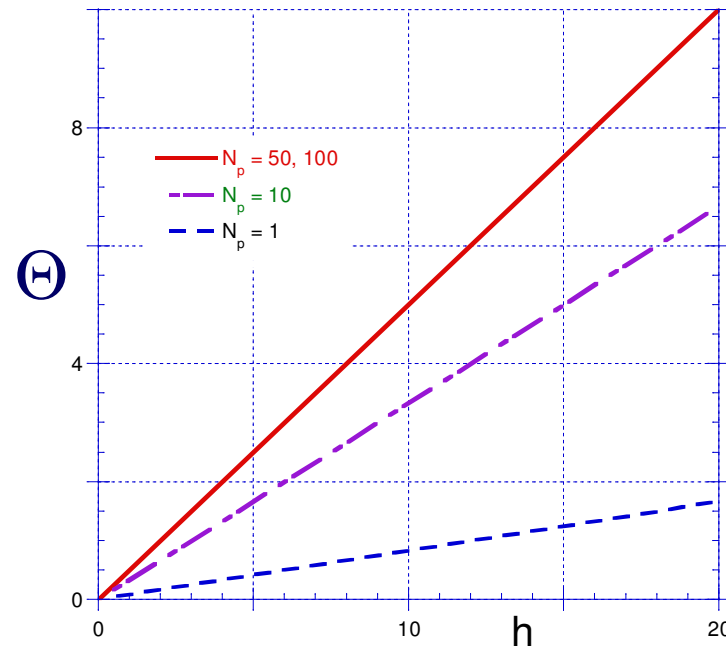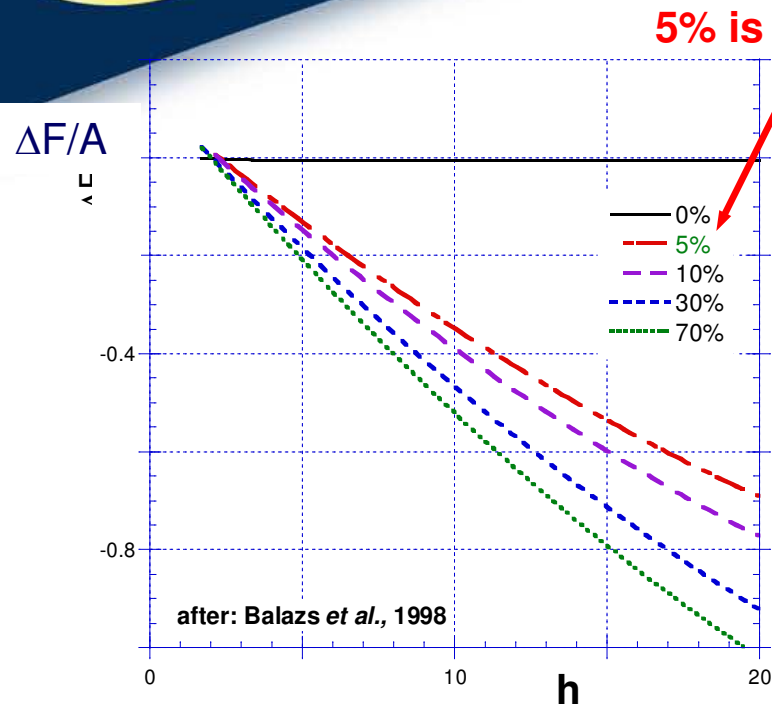
- Free energy vs. gallery height for clay-polymer-"sticker" system (its content is indicated). Thus, 5 wt% of "sticker" is sufficient for exfoliation.

- The amount of adsorbed "sticker" polymer with $N_{gr} = 75$ and concentration $\phi = 0.05$ for four chain lengths of the non-functionalized polymer, $N = 1, 10, 50$ and 100 [Balazs *et al.*, 1998].

Phase structures for CPNC:
(a) isotropic, (b) nematic, (c) smectic, (d) columnar, (e) plastic solid (house of cards), and (f) crystal. The nematic director is in the Z direction, platelets in X-Y [Ginzburg *et al.*, 2000].
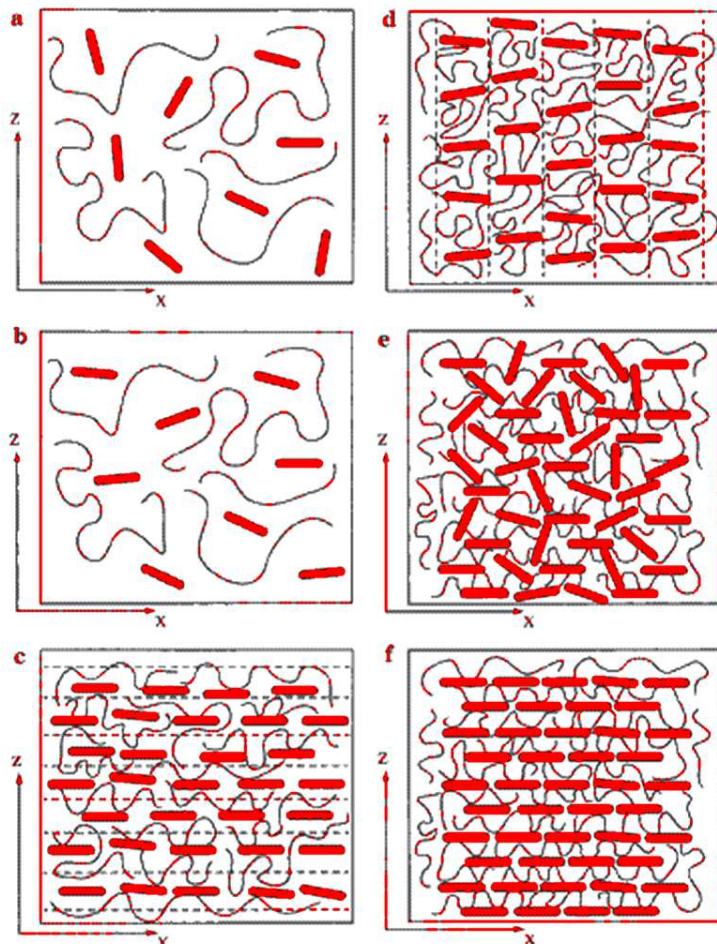
Computed phase diagrams of polymer-clay mixtures: (a) $\rho = 0.04$, $N_i = 50$, and (b) $\rho = 0.02$, $N_i = 100$.
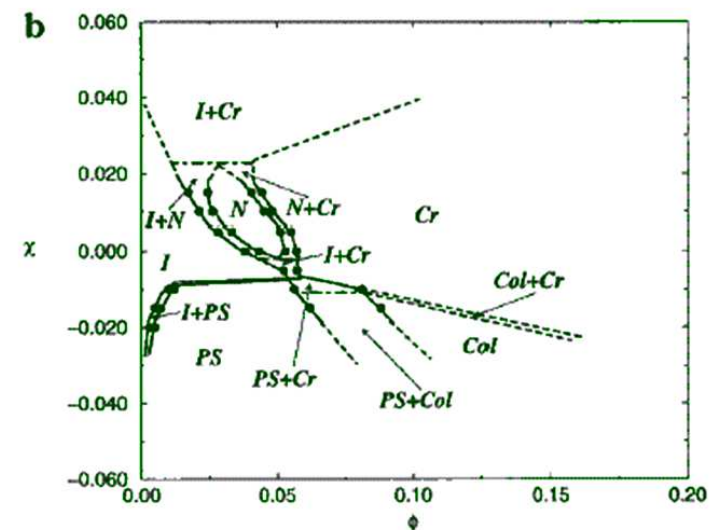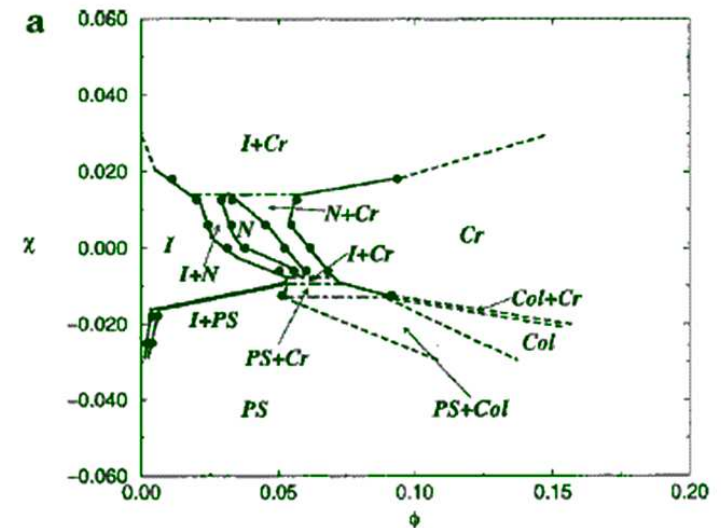
Excess free energy

Conformational Entropy:

Number of ways to occupy free lattice site
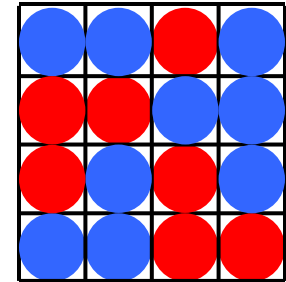
Mixing Enthalpy:

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

Huggins-Flory short-range parameters

solid-liquid : χ_{hs}, χ_{hs}, χ_{os}
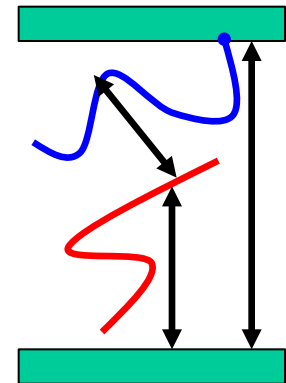
Long-range interactions for solid-solid :

Van der Waals force between clay plates with Hamaker constant, A:
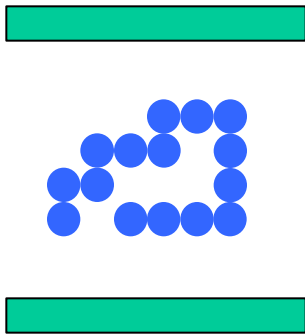
$$F = \frac{-As}{12\pi d^2}$$
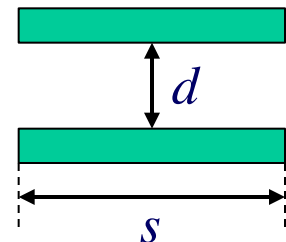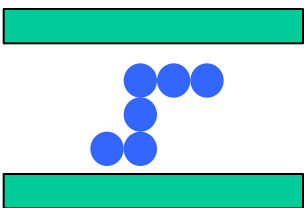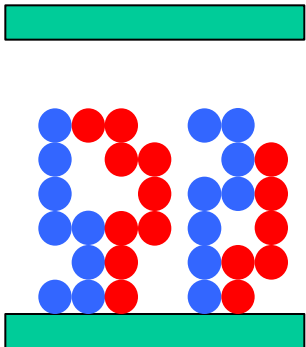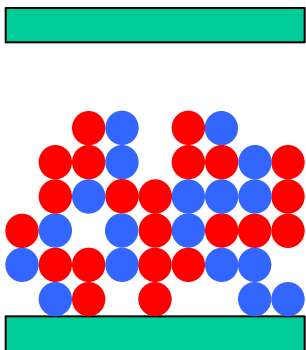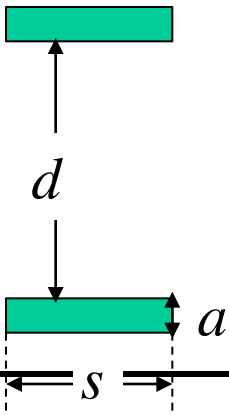
Fundamentals 2

- Equilibrium Thermodynamics.

Immiscible ($\Delta F > 0$)

Intercalated (minimum on ΔF)

Exfoliated [ΔF ($h \to \infty$) < 0]

|	
	Solid inorganic clay
	Macromolecules
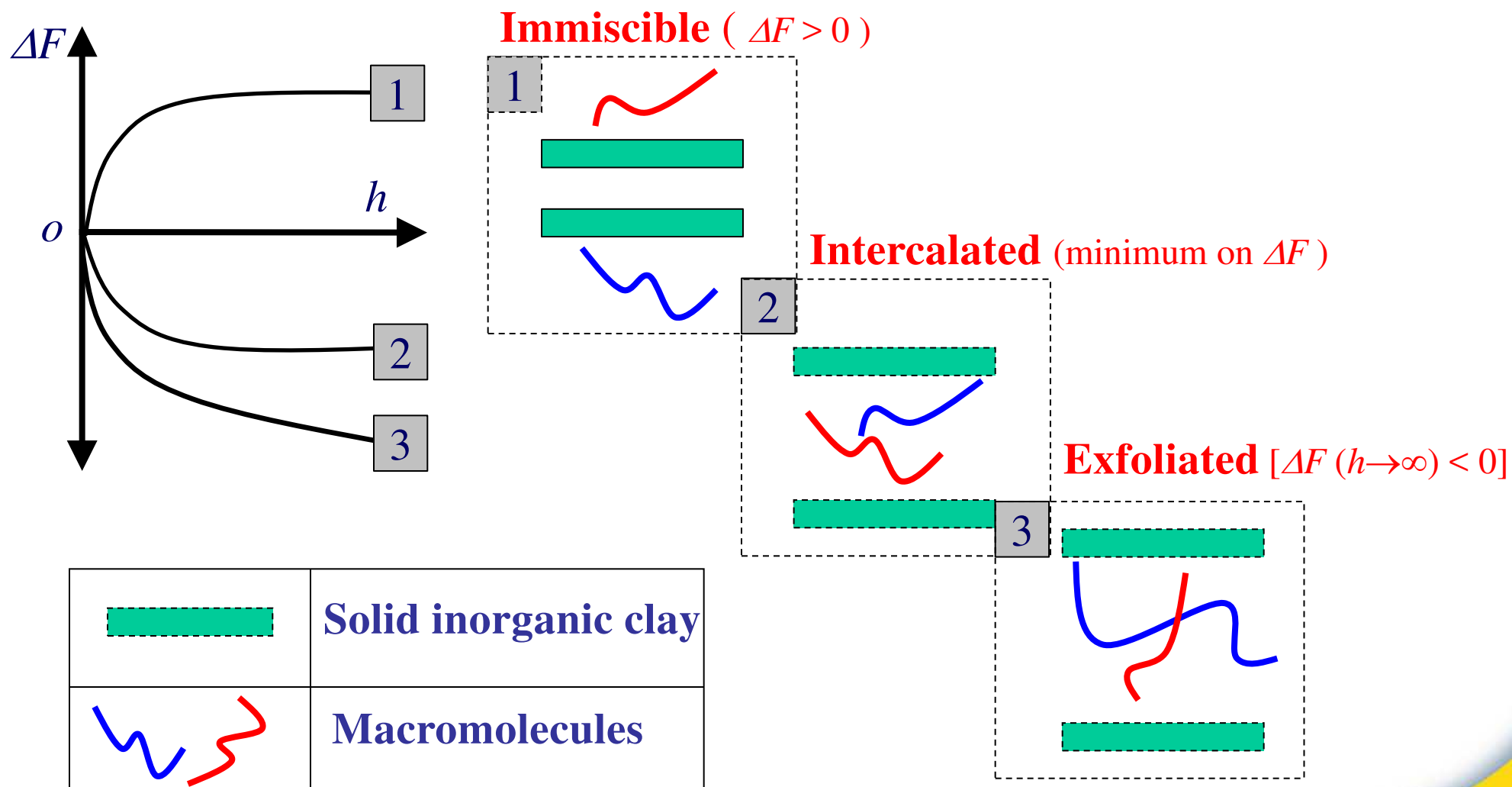
Entropy	Enthalpy	Solid energy

Short chain
Thin gap

Poor solubility

High area-lattice ratio

Unfavorable
$\Delta F \rightarrow (+)$

Long chain
Thick gap

Good solubility

Low area-lattice ratio

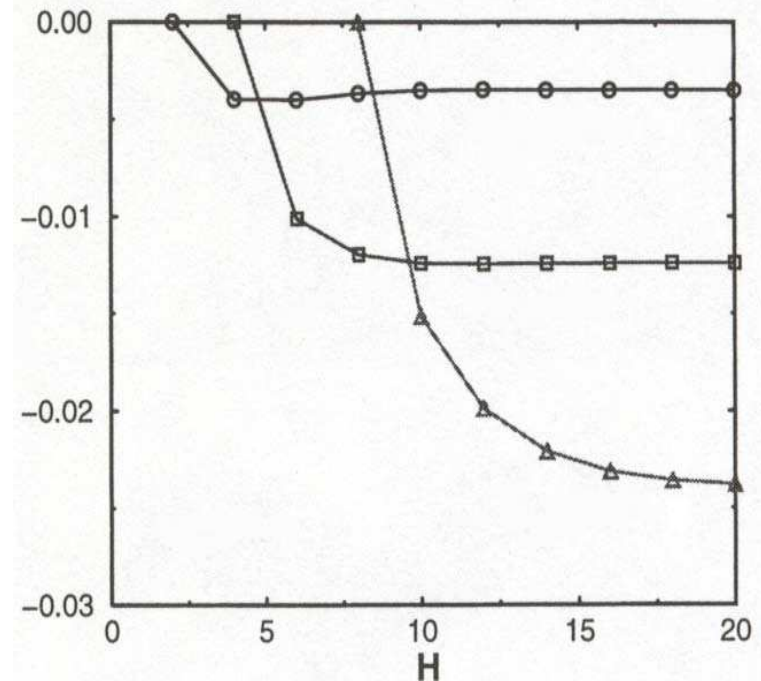Favorable
$\Delta F \rightarrow (-)$

d

a

s

* Area-lattice ratio of solid (bare) surface: $\varepsilon = s / a$

- For 1D the influence of statistical chain length on the excess free energy $(N_h = 100, N_g \in [25,100], \rho_g = 0.04, \chi_{gh} = 0)$
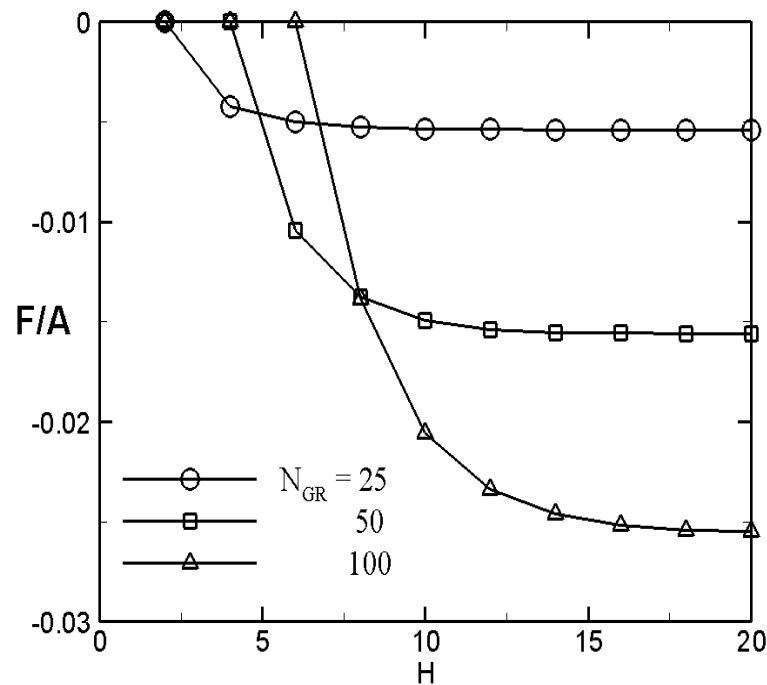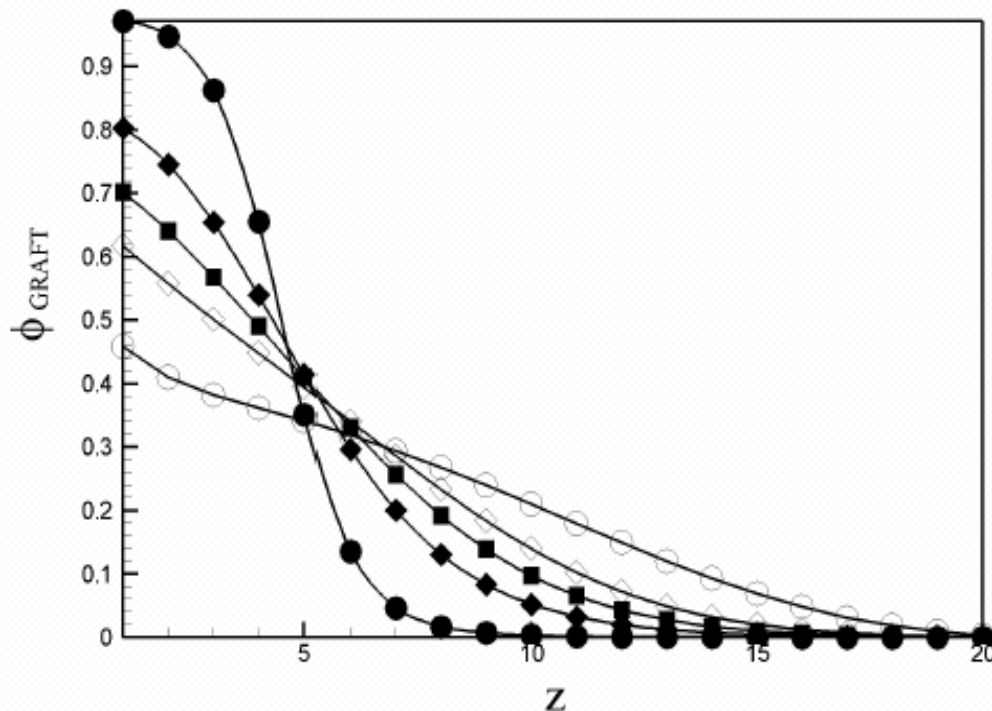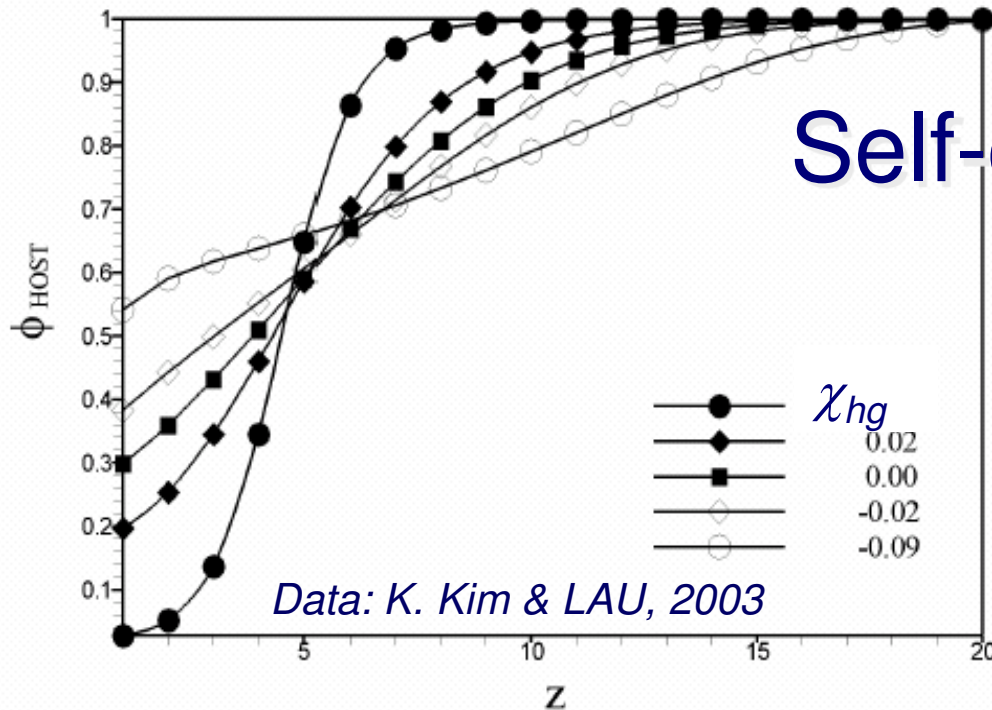
(a) Kim *et al.* (2004)   (b) Balazs *et al.* (1998)

Self-consistent field (SCF) 2

Data: K. Kim & LAU, 2003

- The system: clay + compatibilizer, $N_g = 100$, + polymer $N_h = 100$; grafting density: $\rho_g = 0.04$
- 1D computational model
- Computed effects of the binary intercalation parameter on the chemical composition of the lattice layers, $z = 1 - 20$.
- Results:
  - For $\chi_{hg} > 0$ compatibilizer is immiscible with h-polymer
  - For $\chi_{hg} = 0$ the system is miscible.
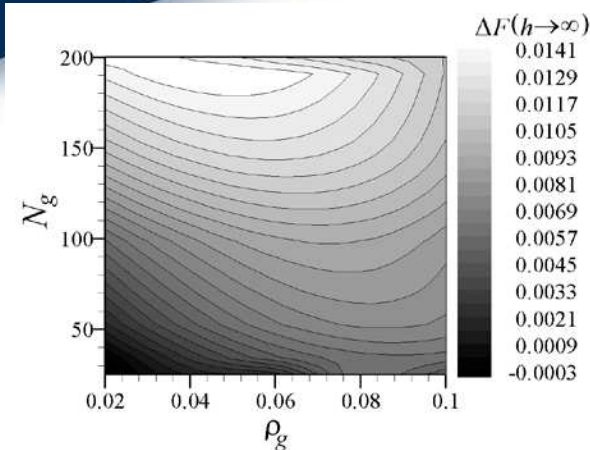 - The miscibility increases with χ_{hg} and N_{gr}.
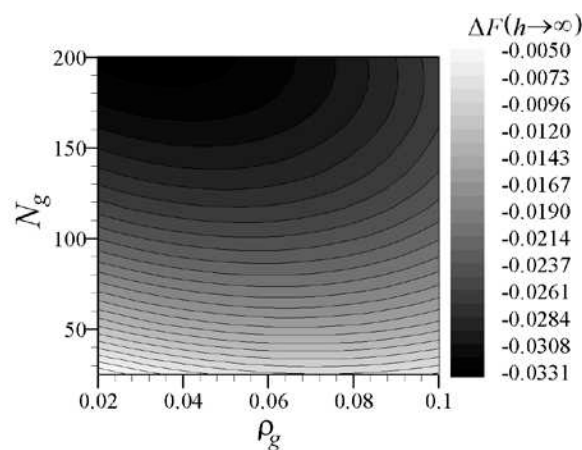
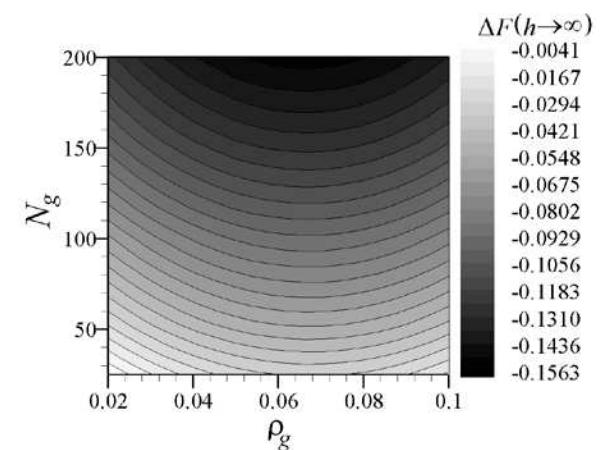Fig. 1; $\chi_{hg} = 0.02$ Fig. 2; $\chi_{hg} = 0.00$ Fig. 3; $\chi_{hg} = -0.02$

- Optimization of compatibilizer content
  - The 1D free energy $(h \rightarrow \infty)$ for homopolymer with $N_h = 200$ depends on:
    - Compatibilizer $N_g \in [25, 200]$, $\rho_g \in [0.02, 1]$,
    - Binary interaction parameter: $\chi_{hg} \in [-0.02, 0.02]$.
  - Following Balazs *et al.* publications, the 1D model assumes clay platelet enrobed by intercalant.

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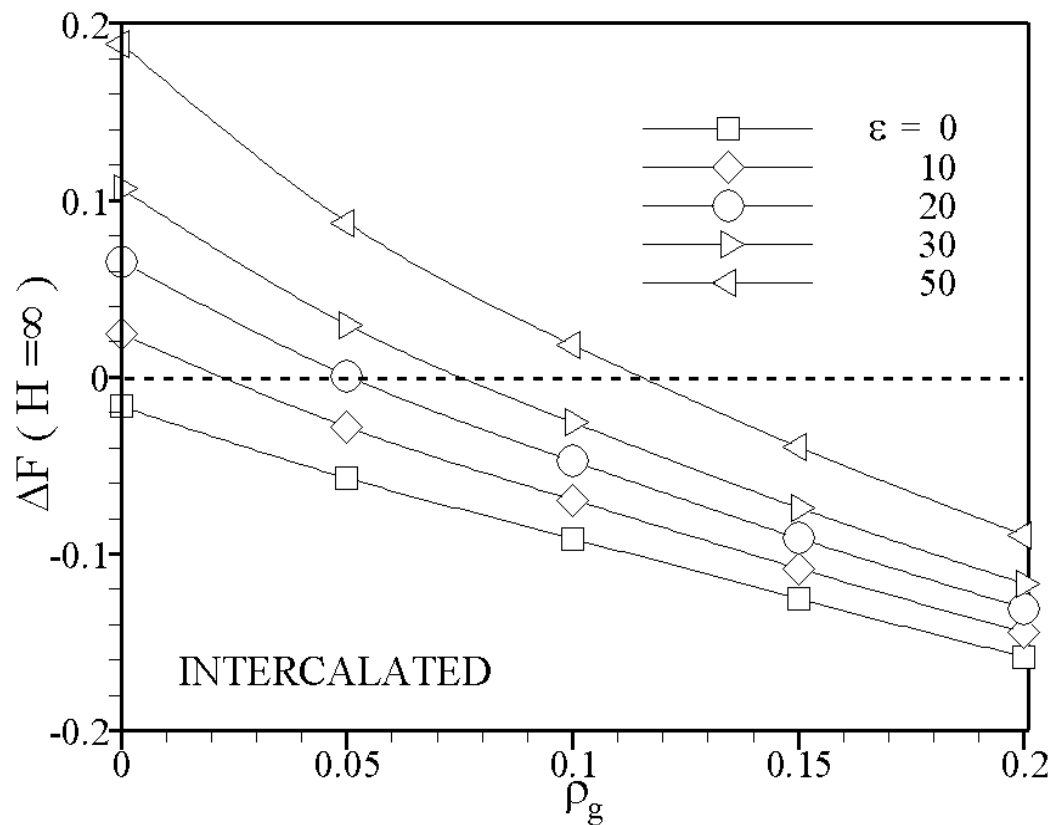
Statistical chain lengths:

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

Surface grafting density:

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

Solid-solid interactions:

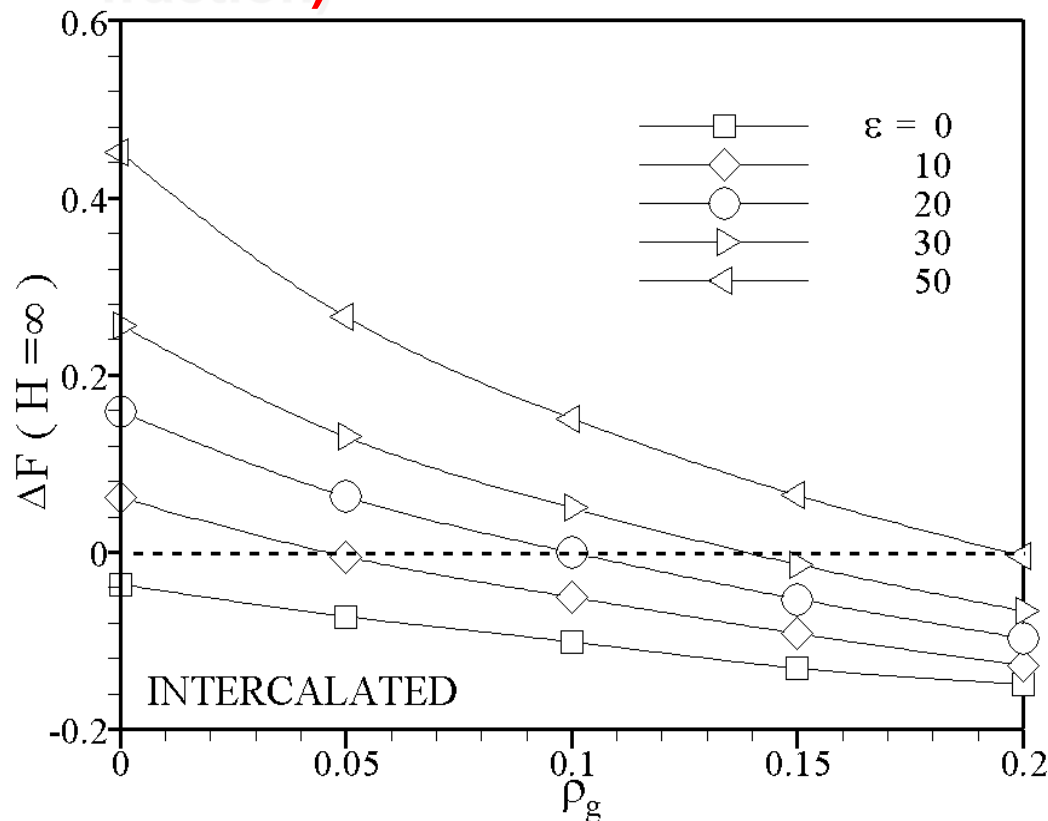$A = 20(k_B T)$, $\varepsilon \in [0,50]$

Binary interaction parameters:

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

The binary interactions are taken for the PNC with PP as the matrix, i.e., for PP/compatibilizer/intercalant/clay.

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

Statistical chain lengths:

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

Surface grafting density:

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

Solid-solid interactions:

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

Binary interaction parameters:

$\underline{\chi_{hg} = 0.0}$, $\chi_{ho} = 0$, $\chi_{go} = 0$,

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

Comparing with the preceding graph one may conclude that doubling the void fraction significantly improved miscibility ($\Delta F < 0$).

Statistical chain lengths:

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

Surface grafting density:

$\rho_g = 0 \sim 20\%$, $\rho_o = 70\%$, $\underline{\rho_v = 5 \sim 10\%}$
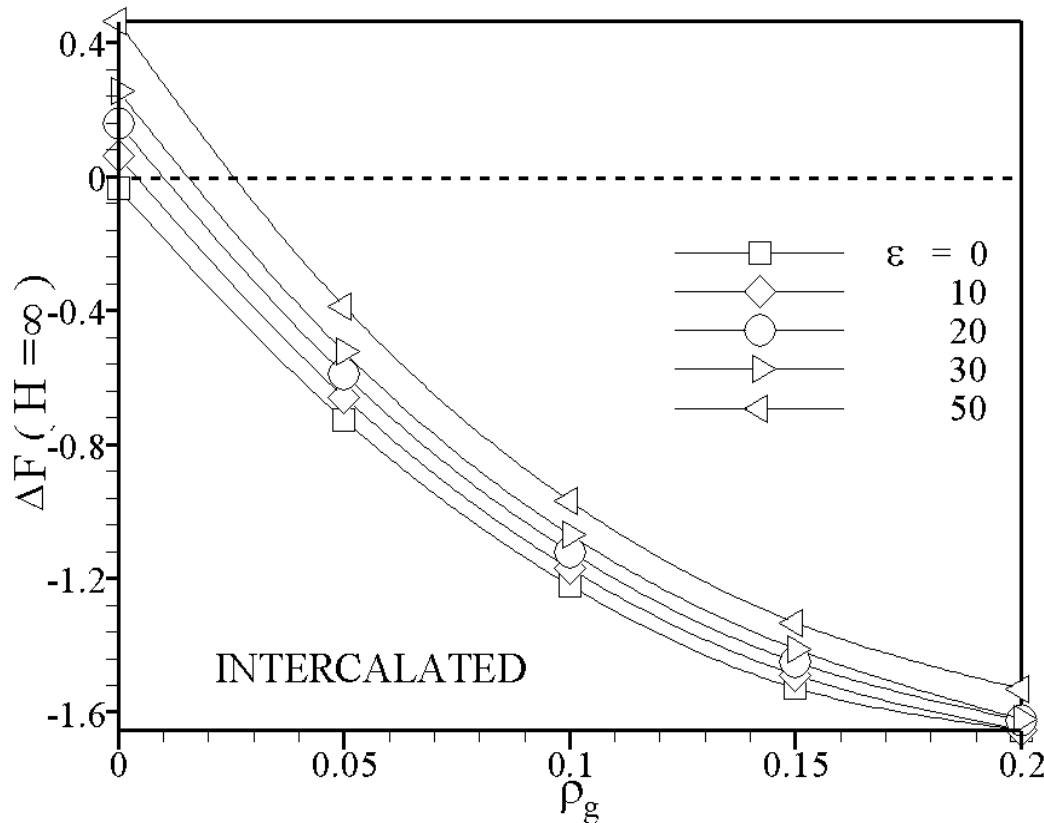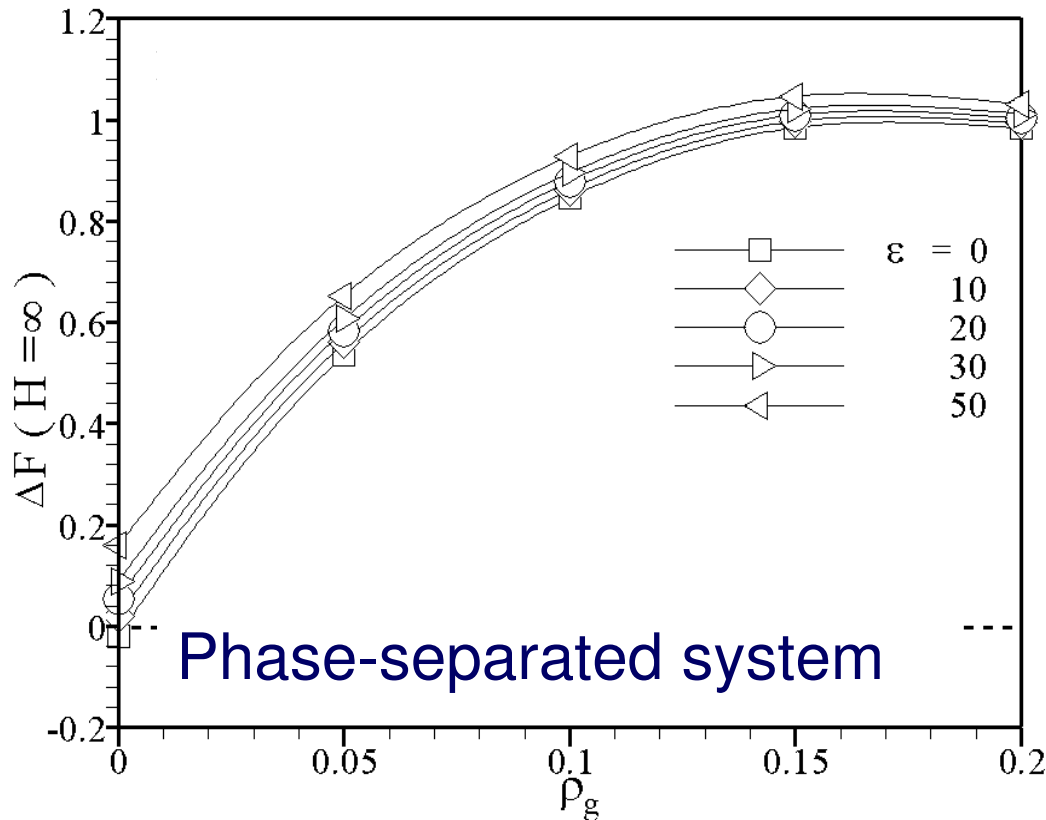
Solid-solid interactions:

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

Binary interaction parameters:

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

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

Favorable polymer/compatibilizer interactions, along with favorable solid grafting interactions and high vacancy fraction are expected to lead to easy exfoliation.

Statistical chain lengths:

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

Surface grafting density:

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

Solid-solid interactions:

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

Binary interaction parameters:

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

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

Phase-separated system

Unfavorable (repulsive) interactions between polymer and compatibilizer have a dramatic effect on system miscibility, in spite of favorable solid grafting interactions and high vacancy fraction.

- 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.

Lattice

Clay

  - 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 (center-edge) hence the configurational entropy and enthalpy (where pertinent).
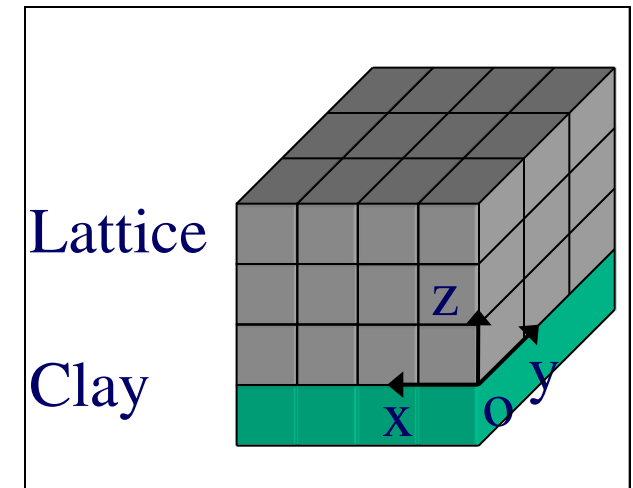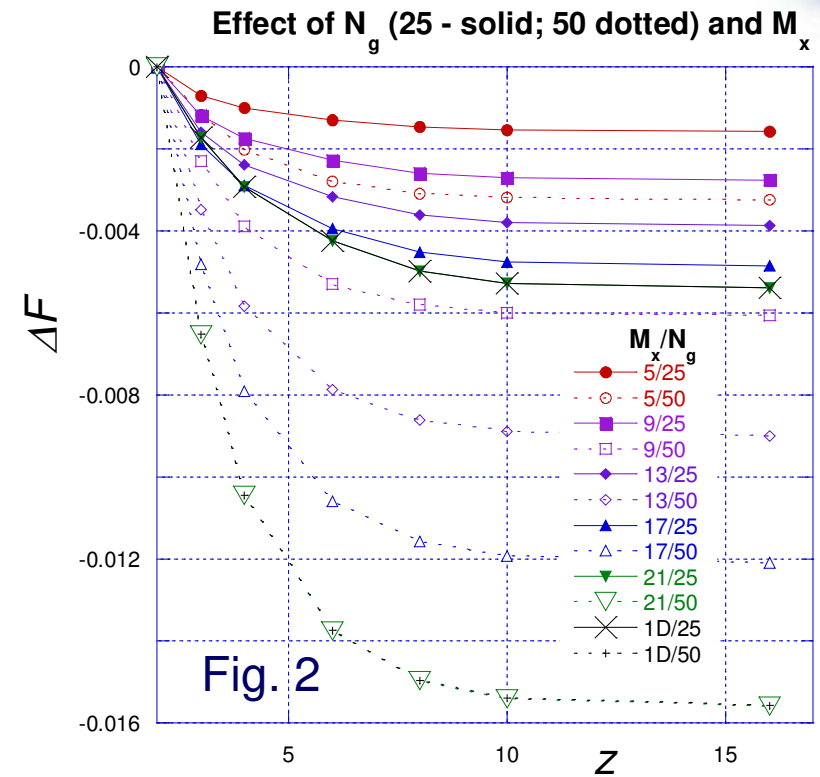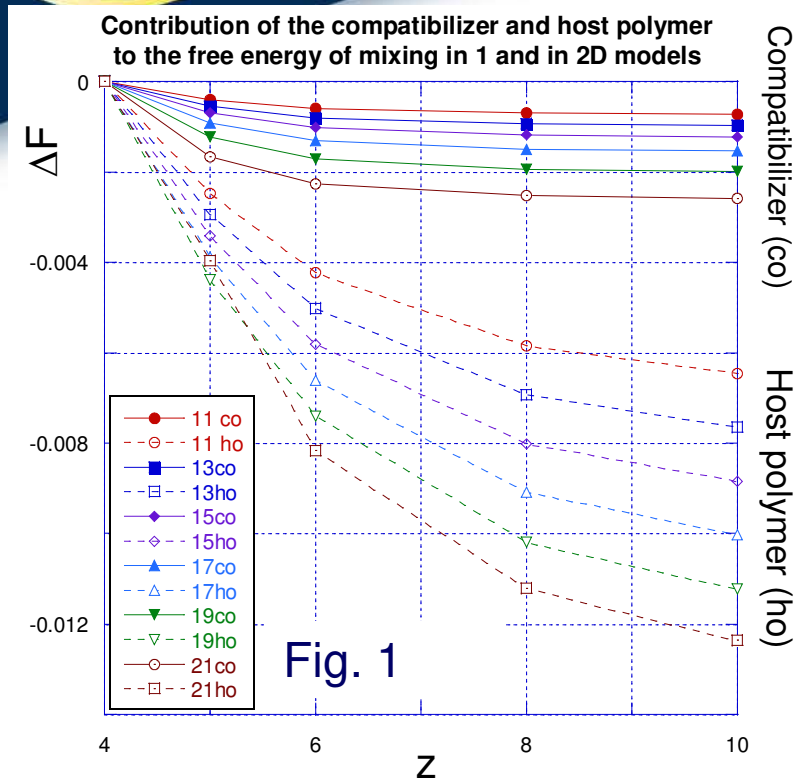
Results for 1D & 2D
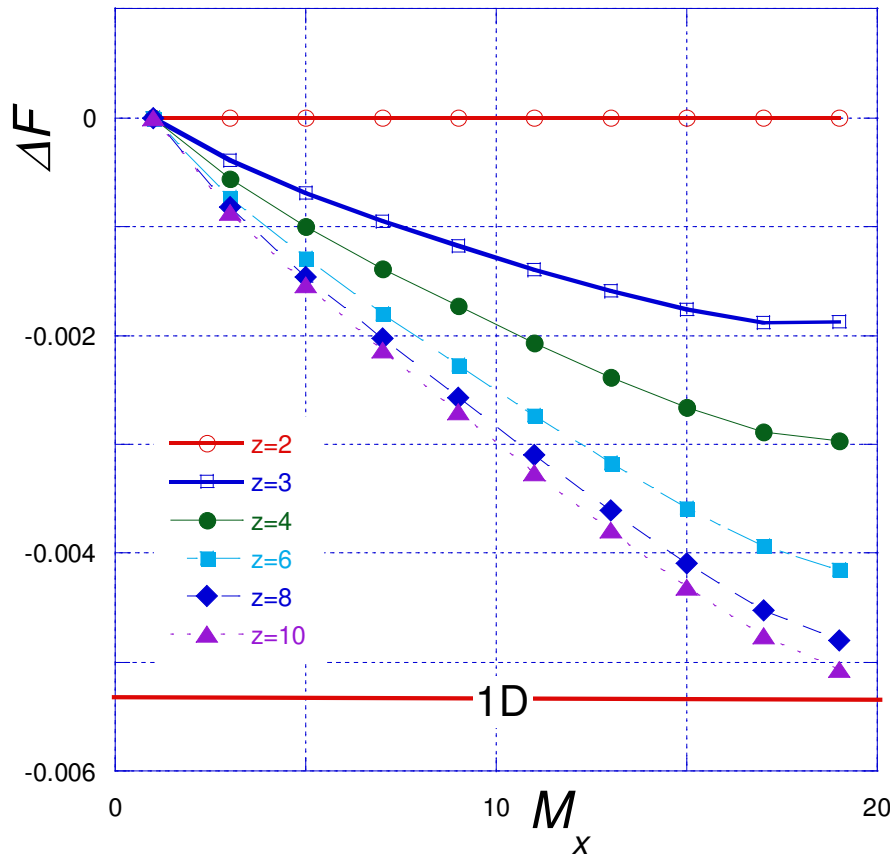
- The 1D model assumes presence of two parallel platelets immersed in a molten polymeric matrix.

- In this model the platelets are infinitely large, thus only in the vertical z-direction the properties may change.

- The 1D data of Kim *et al.* (2004) reproduced results by Balazs *et al.* (1998).

- The 2D model assumes finite size of clay platelets in the x-direction, and invariance in the y-direction; the variation with respect to the lateral dimension, y, is averaged,

- The Figure displays variation of the excess free energy with the number of cells in x-direction. The data are computed at different distance from the clay surface z = 2 to 10 for: $N_g = 25$, $N_h = 100$, $\rho_g = 0.04$, and $\chi_{hg} = 0$

- The 1D prediction is indicated by a horizontal red line.

Fig. 1 — Contribution of the compatibilizer and host polymer to the free energy of mixing in 1 and in 2D models

Fig. 2 — Effect of N_g (25 - solid; 50 dotted) and M_x

- Variation of ΔF with z and M_x were computed for: $N_g = 25$ or 50, $N_h = 100$, $\rho_g = 0.04$, and $\chi_{hg} = 0$.

- Fig. 1 illustrates contributions originating from the end-terminated compatibilizer (co), and that from the host polymer (ho).

- Fig. 2 shows total ΔF for number of cells $M_x = 3$ to 21 and for the 1D case; the 1D results are recovered for $M_x = 21$.

$$\chi_{hg} = 0.0, \; \chi_{hs} = 0.01, \; \chi_{gs} = -0.01, \chi_{os} = -0.02$$
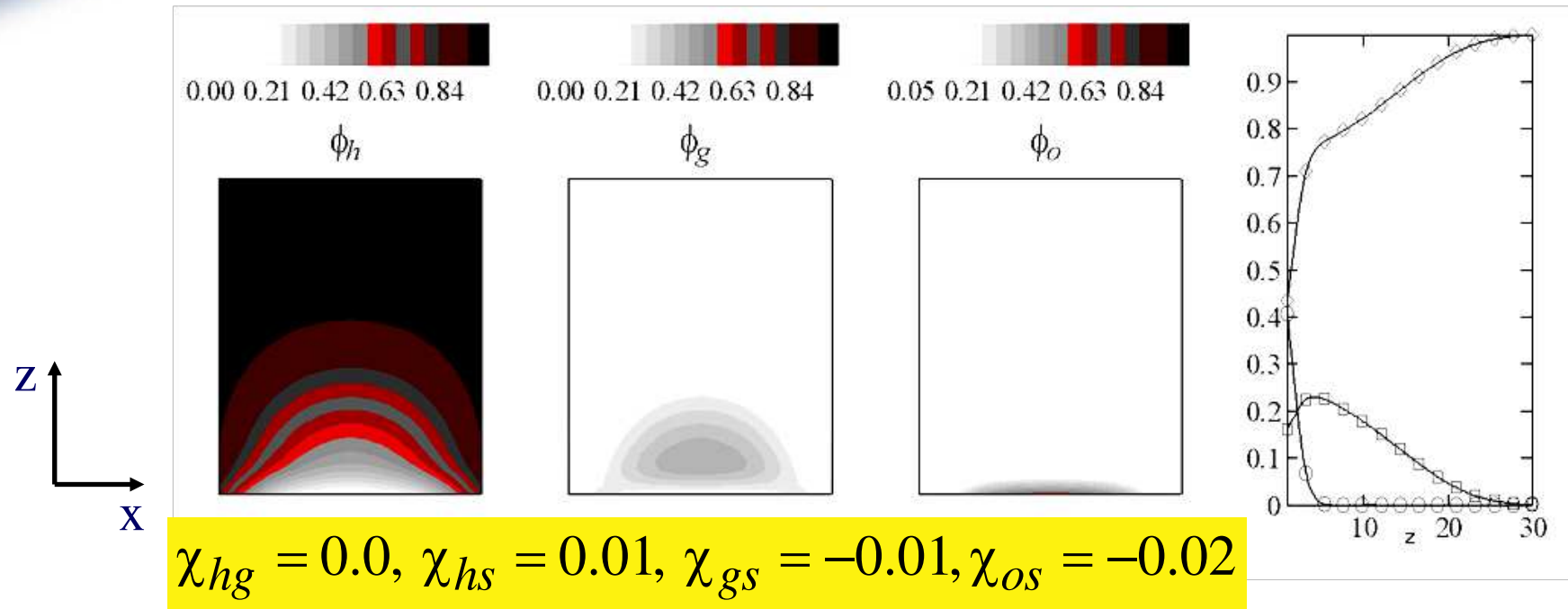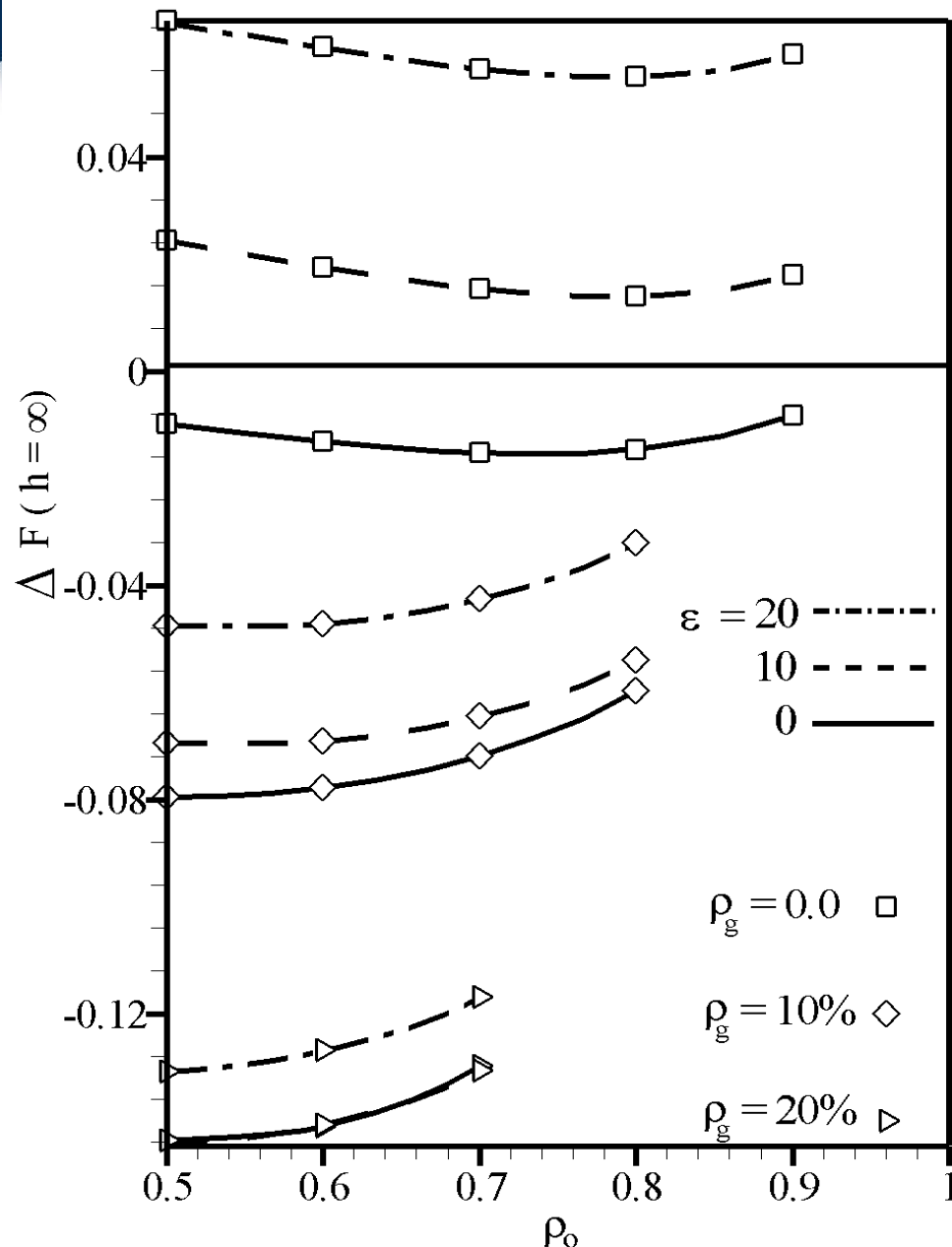
- Influence of the binary interaction parameters on the concentration profiles for:

  - $A = 20(k_B T), \; N_h = 400, \; N_g = 200, \; N_o = 100,$

  - $\rho_o = 0.7, \; \rho_g = 0.15, \; \rho_h = 0.05,$ and $\rho_v = 2 \sim 10\%,$.

- The influence of the bare-solid area-lattice ratio (ε) and grafting density (ρ_g, ρ_o) on the excess free energy ($h = z \to \infty$).

- **Statistical chain length**

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

- **Surface properties**

  $\rho_g \in [0, 0.2]$; $\rho_o \in [0.5, 0.9]$; and $\rho_v \in [0.02, 0.05]$

- **Influence of solid-solid interactions**

  $A = 20(k_B T)$, $\varepsilon \in [0, 20]$
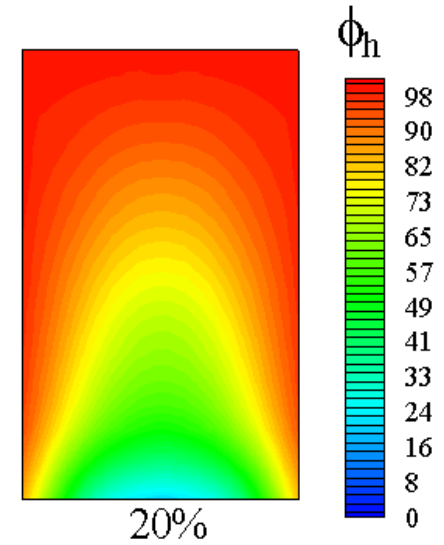
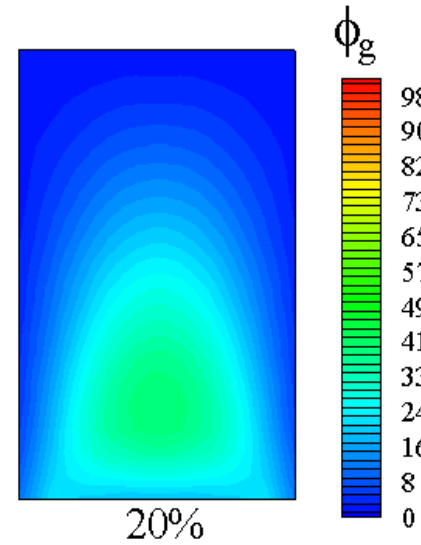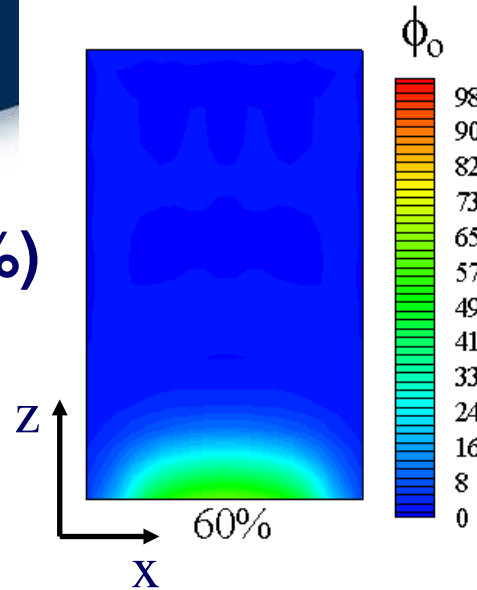- **Binary interaction parameters**

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

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

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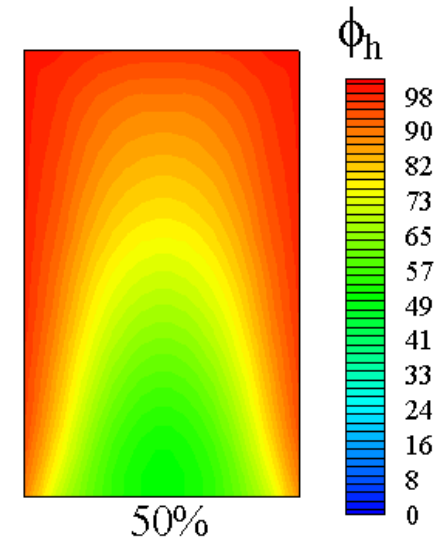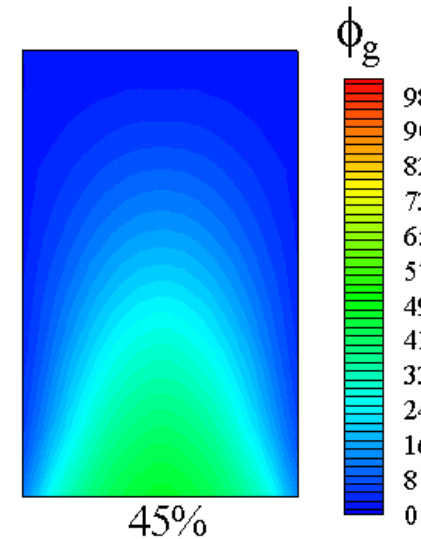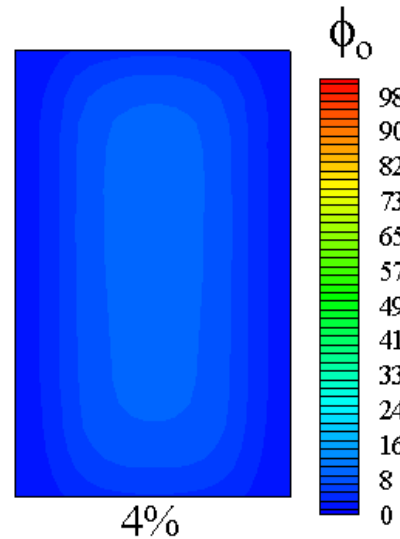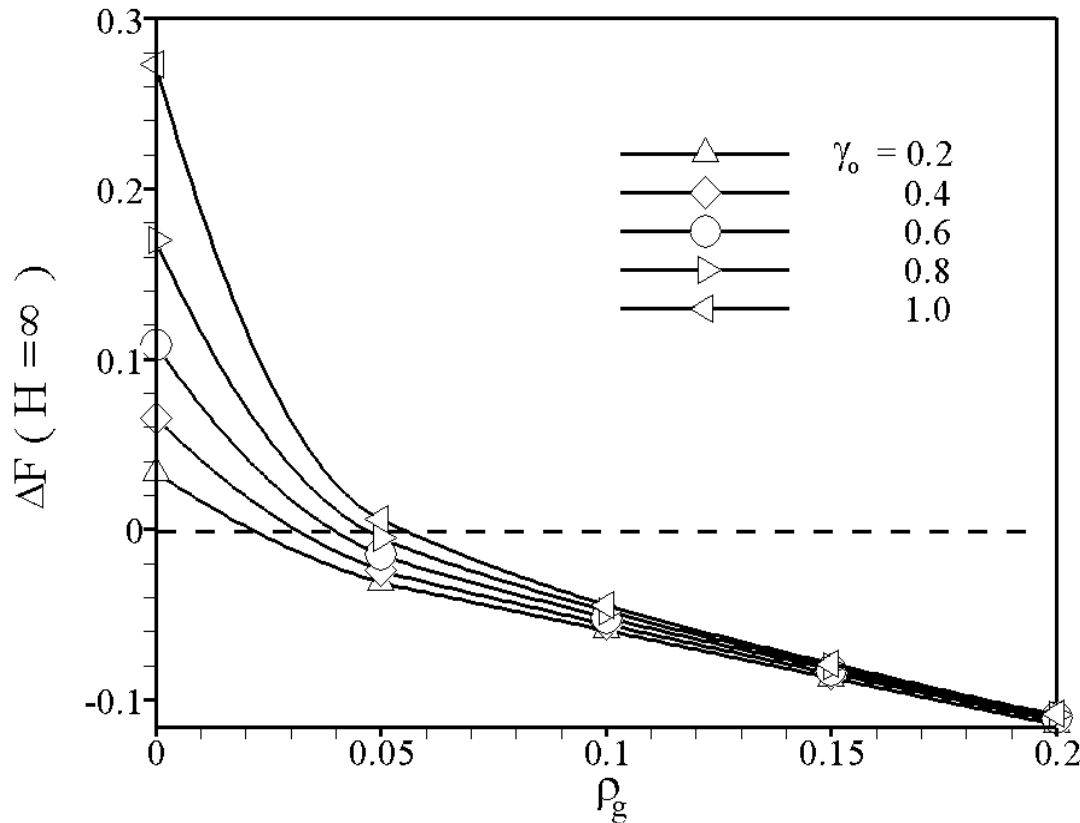# Degradation effect 1

Degradation (%)

$\gamma_g = 0.0\ \%$

$\gamma_g = 100\ \%$

Effect of **intercalant degradation** on the concentration profiles in 2D lattice with: $N_g = 200$, $N_h = 400$, $N_o = 100$, $\rho_g = 15\%$, $\rho_o = 80\%$, $\rho_v = 2{\sim}5\%$, $A = 20(k_B T)$, $\chi_{hg} = 0$, $\chi_{ho} = 0$, $\chi_{go} = 0$, $\chi_{hs} = 0.01$, $\chi_{gs} = -0.01$, $\chi_{os} = -0.02$.

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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

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

- Degradation of intercalant can readily be compensated by incorporation of compatibilizer, capable of forming stable bonds with clay surface.

- Grafting density of ca. 6% would compensate for the degradation.

Solutions of practical problems

Problem	Suggested solution
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 interactions)	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 as well as saturate the clay surface with compatibilizer and organic modifier, both miscible with polymer

Summary of Part #3:
Mathematical modeling

- To reduce surface energy crystalline solids adsorb molecules.

- For optimum dispersion of solid there is MW-dependent grafting density – above it the grafted particles aggregates (immiscibility).

- The Kim *et al.* SCF model reproduces previous 1D results.

- 2D computations predict <u>lower</u> miscibility than 1D.

- To achieve exfoliation in 4-component system:
  - Clay: Intercalated ($\phi_o \approx 70\text{-}80$ %), but with surface partially bare for interacting with a compatibilizer (functionalized polymer)
  - Stable intercalant – no thermal degradation or extraction by melt
  - Bare clay surface, caused by inadequate intercalation or degradation can be compensated by compatibilization
  - Compatibilizer ($\phi_g \approx 6$ vol%)
    - Strongly interacting with clay surface
    - High molecular weight ($N \leq P$)
    - With non-positive ΔF of mixing with host polymer
  - Host polymer – MW comparable to that of compatibilizer.

Global conclusions

The three sources of information: the thermodynamics, rheology, and modeling yield consistent information:

- The clay platelets have high surface energy that results in solidification of molecules – the effect is felt up to 100 nm away from the surface.

- In the pre-intercalated organoclay (with paraffin chain up to C_{18}) the intercalant is mostly solidified (stretched chain length is ca. 2.22 nm), and the system has reduced free volume.

- Exfoliated platelets are large, anisometric and sluggish.

- In the PP-based PNC, where the binary liquid-liquid type interactions are neutral ($\chi_{ij} = 0$) the successful exfoliation depends on the end-functionalized polymer, a compatibilizer:

  - The compatibilizer must strongly interact with clay, and have MW comparable to that of the host polymer.

  - For the compatibilizer to react with organoclay the intercalant grafting should be reduced.

  - **The intercalant and compatibilizer bonding must be thermo-mechanically stable (within the range of compounding & processing conditions).**