«Self-assembly and dynamics in metastable states. From molecular and supramolecular to mesoscopic systems» (META-ASSEMBLY)

13:00-13:45 G. Floudas (UoI.)
- Financial issues related to THALIS
- Publicity/Evaluation
- Description of the program
- Description of systems - systems of interest
- Progress report for the UoI experimental team

13:45-14:00 G. Fytas / D. Vlassopoulos (UoC)
- Progress report for the UoC team

14:00-14:15 U. Jonas / M. Vamvakaki (FORTH)
- Progress report for the FORTH - synthesis team

14:15-14:30 D. Theodorou (N.T.U.A.)
- Progress report for the NTUA team

14:30-14:40 V. Harmandaris (UoC)
- Progress report for the computational sub-team of the UoC

14:40-15:00 M. Kosmas (UoI)
- Progress report for the computational sub-team of the UoI

15:00-16:00 Discussions

«ΘΑΛΗΣ» – Εντάξεις Πράξεων «ΘΑΛΗΣ» – ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ

14.06.2012 | ΑΕΙ, Αποφάσεις Ένταξης, Έρευνα, Ερευνητές, Προγράμματα ΑΕΙ

26/06/2012) Ένταξη της Πράξης **«ΘΑΛΗΣ – ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ – ΑΥΤΟ-ΟΡΓΑΝΩΣΗ ΚΑΙ ΔΥΝΑΜΙΚΗ ΣΕ ΜΕΤΑΣΤΑΘΕΙΣ ΚΑΤΑΣΤΑΣΕΙΣ. ΑΠΟ ΜΟΡΙΑΚΑ ΣΕ ΥΠΕΡΜΟΡΙΑΚΑ ΚΑΙ ΜΕΣΟΣΚΟΠΙΚΑ ΣΥΣΤΗΜΑΤΑ»,** με MIS: 379436 στο Επιχειρησιακό Πρόγραμμα «ΕΚΠΑΙΔΕΥΣΗ ΚΑΙ ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗ» 2007-2013. - ΑΠ10 (PDF|2,6 MB)

ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ
ΥΠΟΥΡΓΕΙΟ ΠΑΙΔΕΙΑΣ ΚΑΙ ΘΡΗΣΚΕΥΜΑΤΩΝ ΠΟΛΙΤΙΣΜΟΥ ΚΑΙ ΑΘΛΗΤΙΣΜΟΥ

ΕΝΙΑΙΟΣ ΔΙΟΙΚΗΤΙΚΟΣ ΤΟΜΕΑΣ ΕΥΡΩΠΑΪΚΩΝ ΠΟΡΩΝ

ΕΙΔΙΚΗ ΥΠΗΡΕΣΙΑ ΔΙΑΧΕΙΡΙΣΗΣ Ε.Π. ΕΚΠΑΙΔΕΥΣΗ ΚΑΙ ΔΙΑ ΒΙΟΥ ΜΑΘΗΣΗ ΜΟΝΑΔΑ Β3

Διεύθυνση: **Κωνσταντινουπόλεως 45-49,**
Τ.Κ. 11855, Αθήνα
Διεύθυνση ιστοσελίδας: **www.edulll.gr**

Πληροφορίες: **Ν. Φατσέας**
Τηλ.: **210 327 8104**
Φαξ: **210 327 8061**
e-mail: **nfatseas@epeaek.gr**

Αθήνα, 01/10/2012
Αρ. Πρωτ.: 15441

ΠΡΟΣ: **Πανεπιστήμιο Ιωαννίνων**
- Πρύτανη καθηγητή κ. Τρ. Αλμπάνη
- Πρόεδρο Ε.Ε. καθηγητή κ Ισ. Λαγαρή
- Υπεύθ. Πράξης καθηγητή κ Γ.Φλούδα
- Γραμμ. Ε.Ε. κ. Γ. Ντέτσικα

ΘΕΜΑ: Προέγκριση Σχεδίου για την Απόφαση Εκτέλεσης με ίδια μέσα του υποέργου με τίτλο «**Αυτό-οργάνωση & δυναμική σε μεταστατικές καταστάσεις.Από μοριακά σε υπερμοριακά & μεσοσκοπικά συστήματα**» και α/α «01» της πράξης με τίτλο «**ΘΑΛΗΣ – ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ – Αυτό-οργάνωση & δυναμική σε μεταστατικές καταστάσεις.Από μοριακά σε υπερμοριακά & μεσοσκοπικά συστήματα**» του ΕΠΕΔΒΜ με κωδικό MIS 379436.

Ημ/νία : 1.11.2012

16/11/2012.

Πρόσκληση Εκδήλωσης Ενδιαφέροντος

για υποβολή πρότασης προς σύναψη σύμβασης μίσθωσης έργου ιδιωτικού δικαίου για την παροχή έργου στο πλαίσιο υλοποίησης της Πράξης

« ΘΑΛΗΣ – ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ – Αυτό-οργάνωση και δυναμική σε μετασταθείς καταστάσεις. Από μοριακά σε υπερμοριακά και μεσοσκοπικά συστήματα»

ΥΔ 1	**«Μελέτη Δισκόμορφων Υγρών Κρυστάλλων με ηλεκτρικά δίπολα με χρήση σκέδασης ακτίνων Χ, διηλεκτρικής φασματοσκοπίας συναρτήσει της θερμοκρασίας και της πίεσης, και ρεολογίας, καθώς και η μελέτη της δομής και της δυναμικής των νανοσωματιδίων SiO_2, χρυσού και αργύρου»**
ΥΔ 3	**«Λεπτομερή μοριακό χαρακτηρισμό και προσδιορισμό της δομής και δυναμικής συμπεριφοράς αυτο-οργανούμενων συστημάτων με χρήση εξειδικευμένων τεχνικών σκέδασης ακτίνων -Laser και –Χ, και ρεολογίας»**
ΥΔ 4	**«Ατομιστικές προσομοιώσεις δισκόμορφων υγρών κρυστάλλων: δομή και δυναμική»**
ΜΔ 1	**«Θεωρητική μελέτη Δισκόμορφων Υγρών Κρυστάλλων».**

10. ΚΑΤΑΝΟΜΗ ΔΗΜΟΣΙΑΣ ΔΑΠΑΝΗΣ ΑΝΑ ΚΑΤΗΓΟΡΙΑ ΔΑΠΑΝΗΣ			
ΚΩΔΙΚΟΣ ΚΑΤΗΓΟΡΙΩΝ ΔΑΠΑΝΩΝ		ΣΥΝΟΛΙΚΗ ΔΗΜΟΣΙΑ ΔΑΠΑΝΗ	ΕΠΙΛΕΞΙΜΗ ΔΗΜΟΣΙΑ ΔΑΠΑΝΗ ΑΠΟ Ε.Π.
Άμεσες Δαπάνες			
Βάση Παραστατικων	i.χωρίς ΦΠΑ	434,593.65	512,820.51
	ii.ΦΠΑ	78,226.86	
Σύνολο (1)		512,820.51	512,820.51
Έμμεσες Δαπάνες			
Βάση Παραστατικων	i.χωρίς ΦΠΑ	87,179.49	87,179.49
	ii.ΦΠΑ	0.00	
Σύνολο (2)		87,179.49	87,179.49
ΣΥΝΟΛΑ		600,000.00	600,000.00

7. Δείκτες Εκροών			
Κωδικός	**Ονομασία Δείκτη (ή περιγραφή)**	**Μονάδα Μέτρησης**	**Τιμή Στόχος**
6442	Αριθμός δημοσιεύσεων / ανακοινώσεων /μονογραφιών	Αριθμός	20.00
6911	Αριθμός ενισχυόμενων προγραμμάτων διδακτορικής και μεταδιδακτορικής έρευνας.Η ΤΙΜΗ ΣΤΟΧΟΣ ΑΝΑΦΕΡΕΤΑΙ ΣΤΟ ΣΥΝΟΛΟ ΤΗΣ ΧΩΡΑΣ	Αριθμός	1.00
6912	Αριθμός ενισχυόμενων ερευνητικών προγραμμάτων.Η ΤΙΜΗ ΣΤΟΧΟΣ ΑΝΑΦΕΡΕΤΑΙ ΣΤΟ ΣΥΝΟΛΟ ΤΗΣ ΧΩΡΑΣ	Αριθμός	1.00
6913	Αριθμός ερευνητών που συμμετέχουν σε ενισχυόμενα ερευνητικά προγράμματα	Αριθμός	24.00
6914	Αριθμός μετακαλούμενων ερευνητών από το εξωτερικό	Αριθμός	2.00

Κανόνες Δημοσιότητας Ι

ΚΕΙΜΕΝΟ ΔΗΜΟΣΙΕΥΣΕΩΝ ΘΑΛΗ

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS. Investing in knowledge society through the European Social Fund.

Η παρούσα έρευνα έχει συγχρηματοδοτηθεί από την Ευρωπαϊκή Ένωση (Ευρωπαϊκό Κοινωνικό Ταμείο - ΕΚΤ) και από εθνικούς πόρους μέσω του Επιχειρησιακού Προγράμματος «Εκπαίδευση και Δια Βίου Μάθηση» του Εθνικού Στρατηγικού Πλαισίου Αναφοράς (ΕΣΠΑ) – Ερευνητικό Χρηματοδοτούμενο Έργο: ΘΑΛΗΣ. Επένδυση στην κοινωνία της γνώσης μέσω του Ευρωπαϊκού Κοινωνικού Ταμείου.

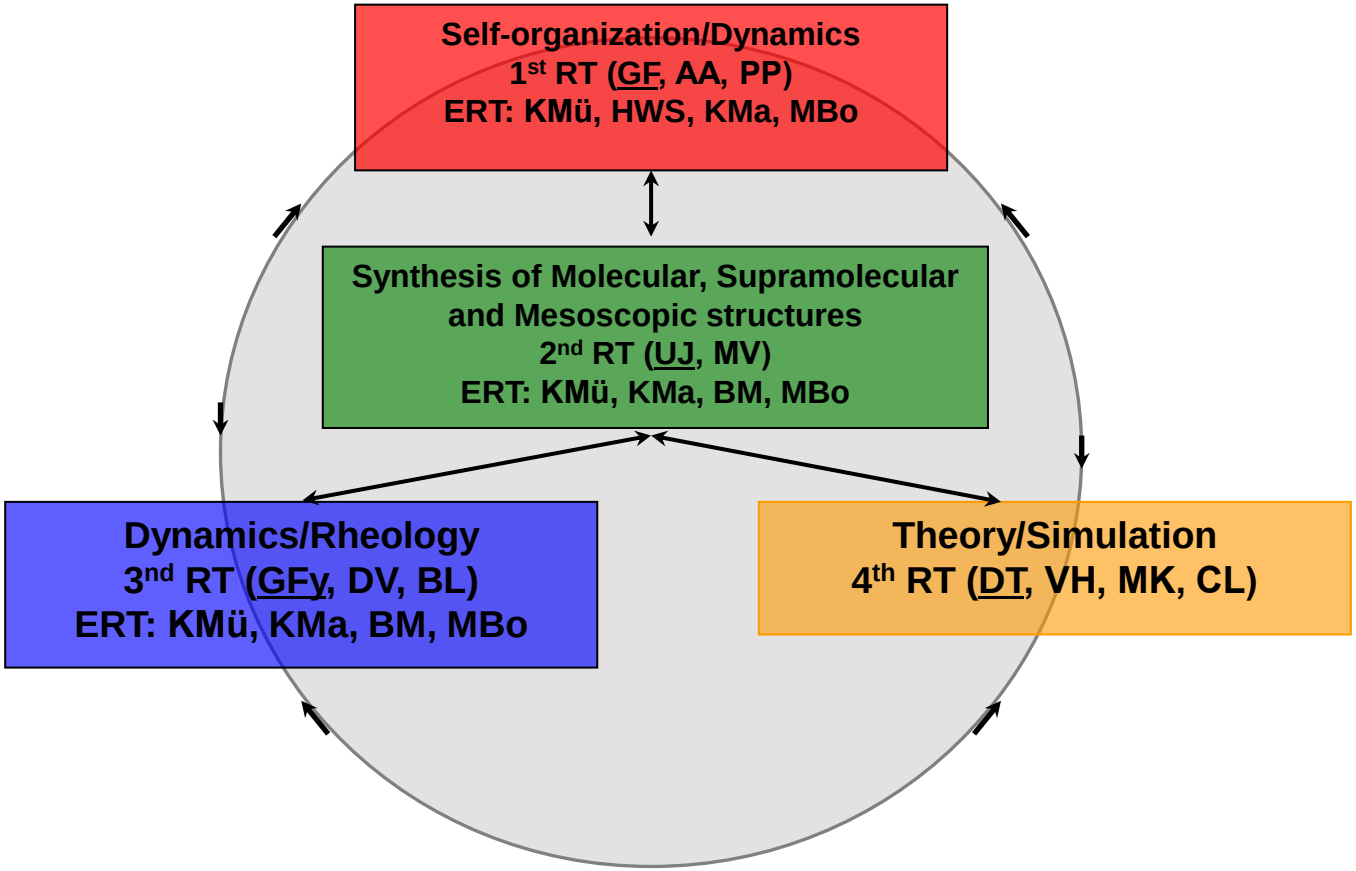
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

Κανόνες Δημοσιότητας ΙΙ

ΑΑ	Τύπος Παραδοτέου	Τίτλος Παραδοτέου	Κωδικός Πακέτου Εργασίας	Πρώτη Ημερομηνία Παράδοσης	Περ.
26	Άλλο Επιστημονικό Παραδοτέο	Δημοσιεύσεις σε έγκριτα επιστημονικά περιοδικά και ανακοινώσεις σε διεθνή συνέδρια με κριτές (20)	Δ26	30/9/2015	0
27	Περιοδικός Επιστημονικός Απολογισμός	Τεχνικές αναφορές και ετήσιες απολογιστικές εκθέσεις	Δ26	31/12/2012	12
28	Άλλο Επιστημονικό Παραδοτέο	Συγγραφή 5 διδακτορικών διατριβών ΥΔ	Δ26	30/9/2015	0
29	Άλλο Επιστημονικό Παραδοτέο	Έκθεση εσωτερικής αξιολόγησης	Δ27	30/9/2015	0
30	Άλλο Επιστημονικό Παραδοτέο	Έκθεση εξωτερικής αξιολόγησης	Δ27	30/9/2015	0
31	Εξαμηνιαίο Δελτίο	Εξαμηνιαίο Δελτίο		30/6/2012	6
32	Τελικός Επιστημονικός Απολογισμός	Έκθεση ολοκλήρωσης πράξης		30/9/2015	0
33	Μηνιαίο Δελτίο	Μηνιαίο Δελτίο		31/1/2012	1

RT1 University of Ioannina (UoI): **1PhD student**

RT2 FORTH: **1 PhD student**



RT3 University of Crete**: 1 PhD student**

RT4: NTUA, UoC, UoI, UoV
3 PhD students / 1 post-doc

PhD / Post-doc positions

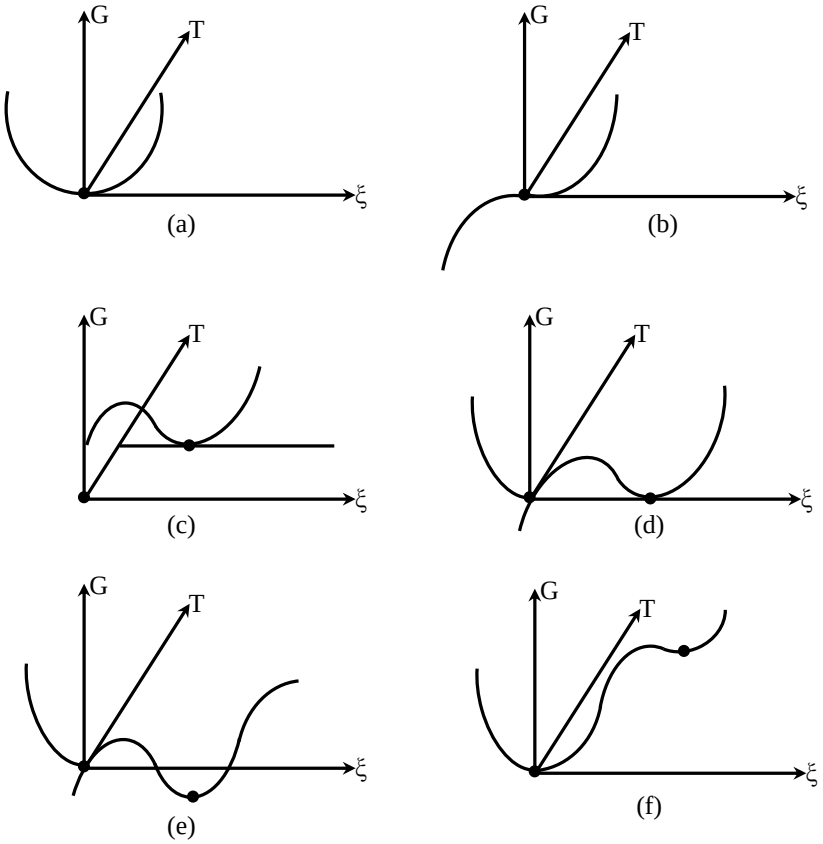
√ PhD 1 : UoI (RT1) (G. Floudas)
PhD 2 : FORTH (RT2) (U. Jonas/M. Vamvakaki)
√ PhD 3 : UoC (RT3) (G. Fytas/D. Vlassopoulos)
√ PhD 4 : NTUA (RT4) (D. Theodorou)
PhD 5 : NTUA (RT4) (D. Theodorou)
PhD 6 : UoC (RT4) (V. Harmandaris)
√ Post-doc 1 : UoI (RT4) (M. Kosmas)

The advertisements for the positions (PROSKLHSEIS) will appear in ext 1-2 weeks.

The “candidates” should correspond directly with Mrs. Skolariki (tel 26510-07940, chskolar@cc.uoi.gr) for more information.

Self-assembly and Metastability in molecular, supramolecular and mesoscopic systems (META-ASSEMBLY)

$\partial G/\partial \xi = 0,\ \xi = 0$ $\qquad$ $\xi = 0,\ \partial G/\partial \xi = 0,\ \partial^2 G/\partial \xi^2 = 0,\ \ \partial^3 G/\partial \xi^3 = 0$



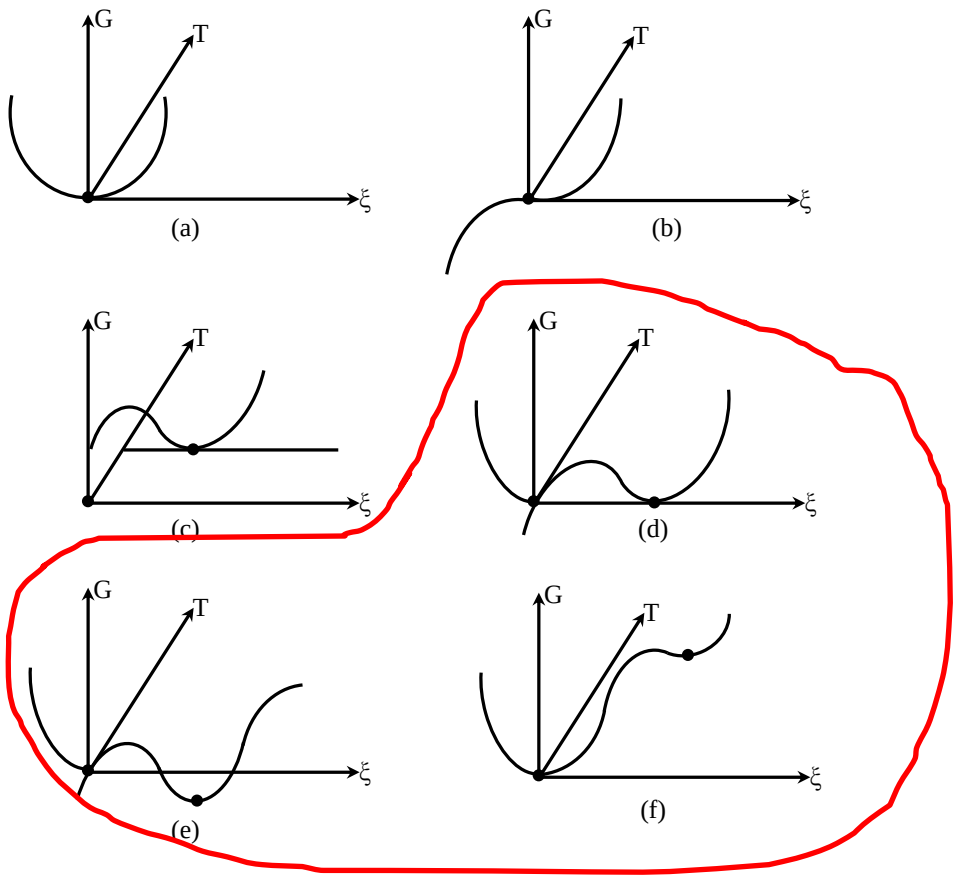
Landau: $G = G(T, P, \xi)$

$$G = G_0 + \alpha\xi + \beta\xi^2 + \frac{1}{3}\gamma\xi^3 + 0\left(\xi^4\right)$$

Free energy as a function of T and the order parameter ξ for some order-disorder Transitions.

Self-assembly and Metastability in molecular, supramolecular and mesoscopic systems (META-ASSEMBLY)

$\partial G/\partial \xi = 0,\ \xi = 0$ $\qquad$ $\xi = 0,\ \partial G/\partial \xi = 0,\ \partial^2 G/\partial \xi^2 = 0,\ \ \partial^3 G/\partial \xi^3 = 0$

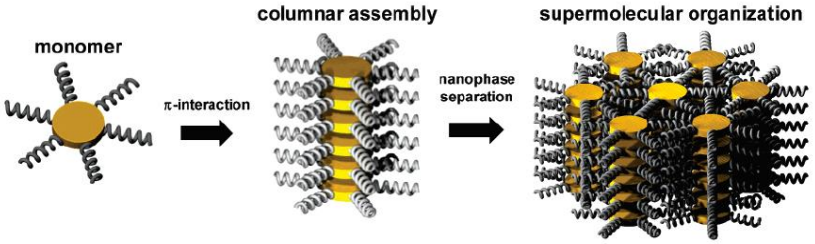


Landau: $G = G(T, P, \xi)$

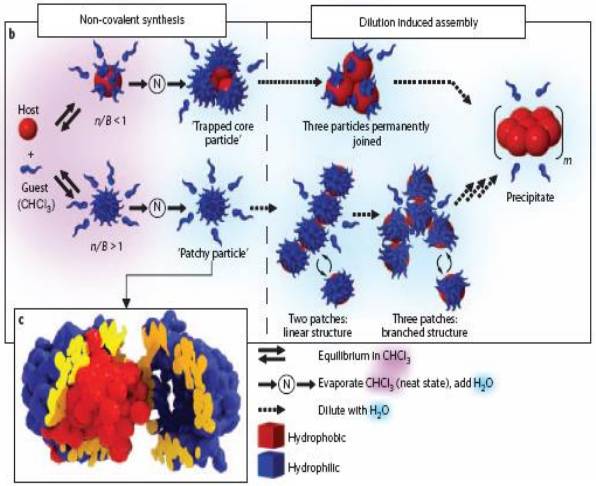
$$G = G_0 + \alpha\xi + \beta\xi^2 + \frac{1}{3}\gamma\xi^3 + 0\left(\xi^4\right)$$

Free energy as a function of T and the order parameter ξ for some order-disorder Transitions.

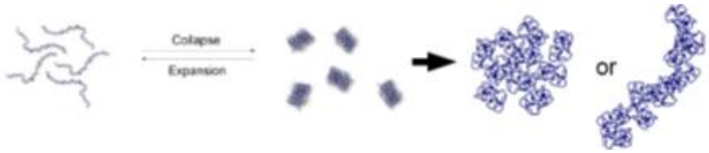
Self-assembly and Metastability in molecular, supramolecular and mesoscopic systems (META-ASSEMBLY)



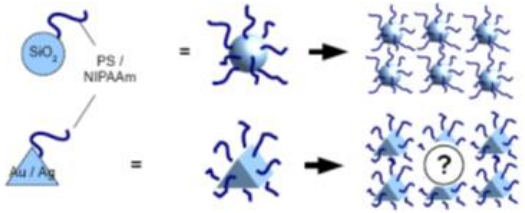
- **Molecular systems: Discotic Liquid Crystals of nano-graphenes with enthalpic/entropic interactions**

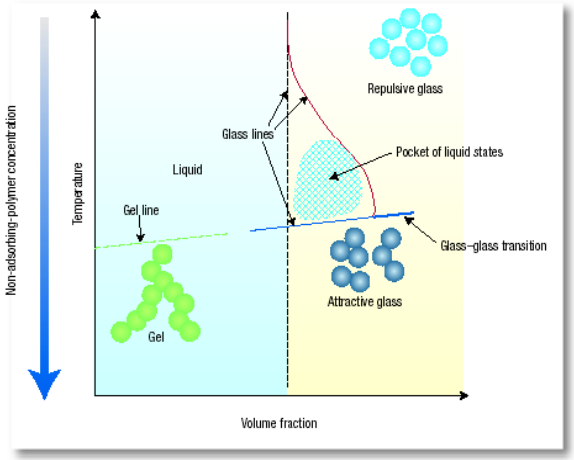


- **Self-assembly and dynamics of supramolecular systems: tailoring directional interactions**
  - Janus particles
  - Patchy particles (hydrophobic/hydrophilic)
  - Supramolecular assemblies (polynorbornene derivatives)



- **Mesoscopic Colloidal systems: tunable osmotic interactions and kinetic arrest**
  - Inorganic/organic core/shell nanoparticles
  - Core: SiO2, shell: PS, PNIPAAm
  - Rod/Plate: Au, Ag; surface: PS, PNIPAAm





Progress Report: UoI experimental team

WP1: **Project coordination** *Duration*: 48 m

Deliverable: Coordination of research.

WP2: Synthesis and characterization of new dipole-substituted discotic liquid crystals *Duration*: 6 m

√ *Deliverables:* New discotic liquid crystals of the hexabenzocoronene and coronene type substituted with different electric dipoles (H- OMe-, I-, F-, Br-, Cl-, CF_3-, $COOCH_3$-, CN-) and side chains.

Synthesis of DLCs with hydrophilic/hydrophobic side chains.

√ **WP3:Effects of core size, dipole substitution and packing on the stability of DLC phases** *Duration:*12 m

Deliverables: DLC phases with emphasis on the self-assembly within the crystalline phase.

√ **WP 4: Disk dynamics – defects in columnar phases of DLCs** *Duration:* 12 m

Deliverables: Relaxation times of disk dynamics as a function of temperature for the different phases. Glass temperature as a function of dipole substitution, core size and type of side chains. Identification of structural defects and of their dynamics.

√ **WP 5: Thermodynamic phase diagram of DLCs** *Duration:* 12 m

Deliverables: Detailed phase diagrams for dipole- and alkyl-substituted Coronene and HBC-type DLCs with emphasis to the location of the crystalline phase pertinent to electronic applications.

√ **WP 6: Kinetics of structure formation** *Duration:* 12 m

Deliverables: Identification of possible intermediate and metastable states and their characteristic half-time.

WP 7: Effects of external non-linear fields to the self-assembly and dynamics of DLCs *Duration:* 12 m

Deliverables: Identification of possible metastable states and their characteristics in the presence of strong external (electric, magnetic, mechanical) fields.

WP 8: Self-assembly and dynamics of core-shell nanoparticles *Duration:* 12 m

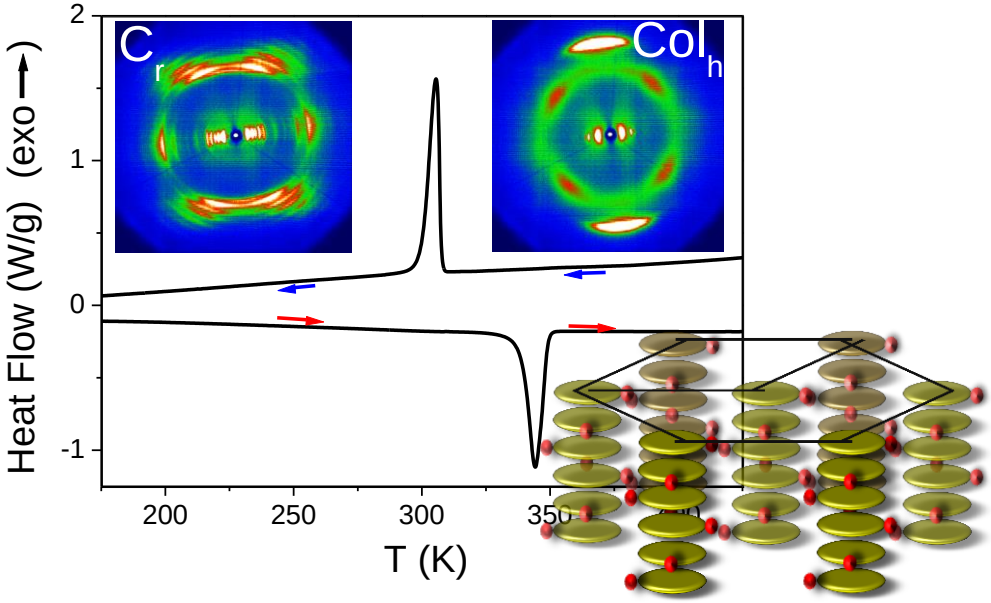
Deliverables: Phase diagrams of nanoparticles based on SiO_2, Au, Ag with various polymeric shells and as a function of the (different) polymer chain fractions, densities and lengths. Collective dynamics within the different phases.

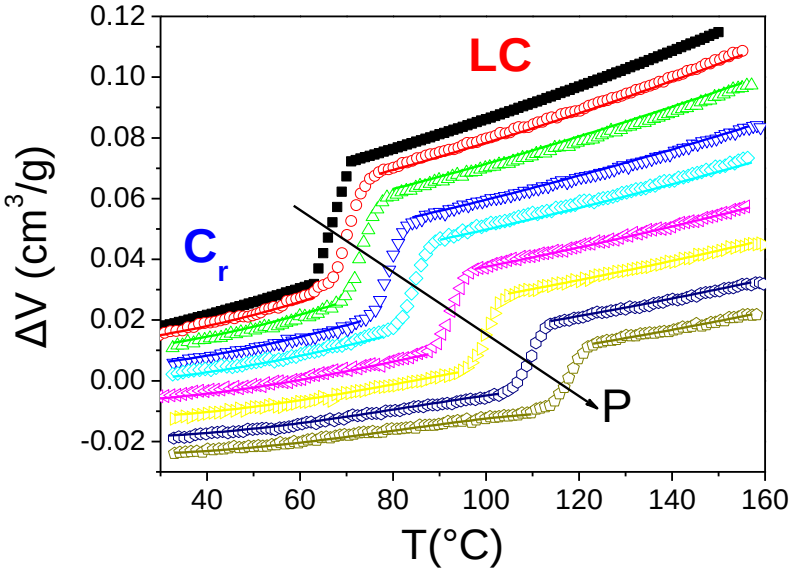
WP 9: Self-assembly in the presence or absence of surfaces with advanced microscopy *Duration* 12m

Deliverables: Study of the structure with or without the presence of surfaces as well as the structure-properties relations in the proposed systems.

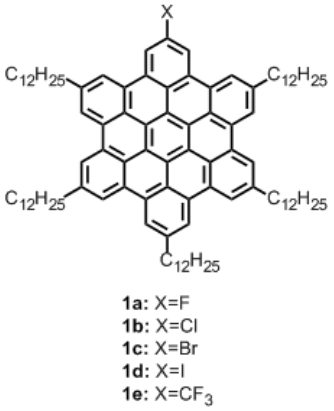
Progress Report: UoI experimental team

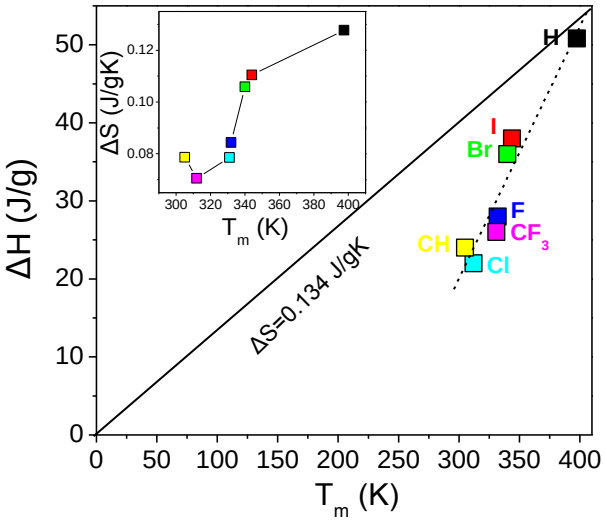
WP3:Effects of core size, dipole substitution and packing on the stability of DLCs





PVT data are used to construct the equilibrium phase diagrams



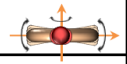
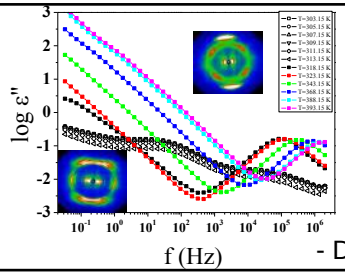
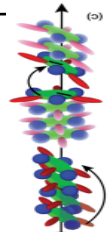
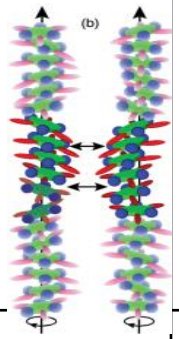
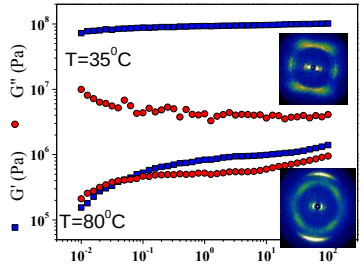
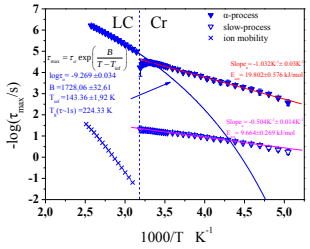


J. Phys. Chem. B 115, 5807 (2011)

WP 4: Disk dynamics – defects in columnar phases of DLCs

Relaxation over 16 decades

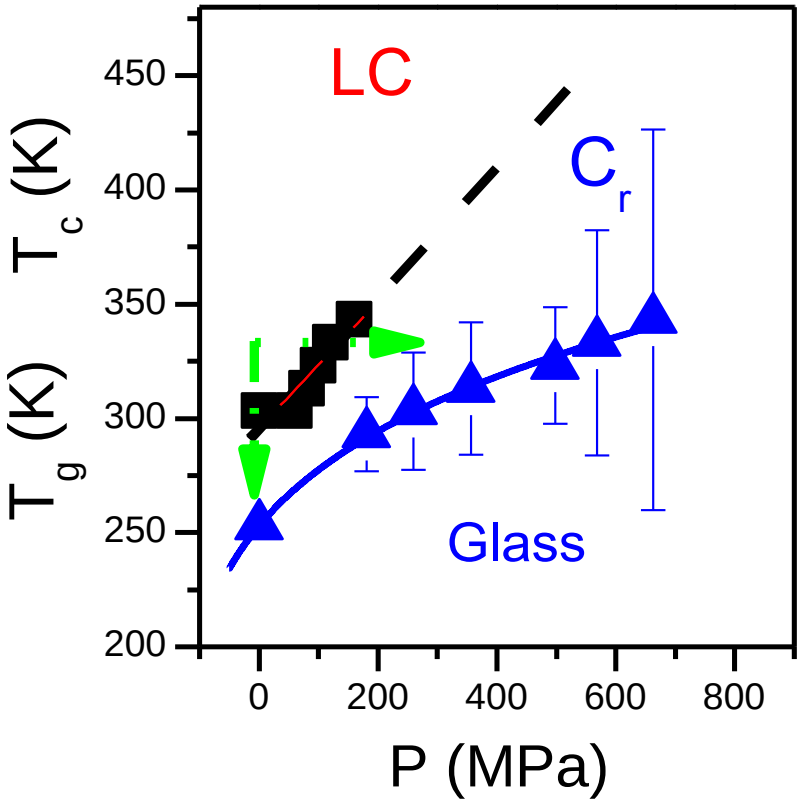
Small molecules with polymer-like dynamics

Geometry of motion	Time scale	Experiment
1. Vibrations 	~10^{-14} s	- IR
2. Re-orientation 	10^{-9} to 10^{-12} s	- DS solution exp.
3. Collective α-process in LC phase • non – Debye • non - Arrhenius S~0.42 	10^{-8} to 10^{-4} s	 - DS
4. Intra-Columnar dynamics within the LC phase 	~10^{-6} s	- NMR - DS - WAXS
5. Inter-Columnar ultra-slow dynamics within the LC phase 	>100 s	 - Rheology
6. Collective slow process within the Cr phase S~0.9-1 	10^{-3} to 100 s	 - DS, NMR

JACS 130, 5311 (2008)
PRL100, 107801 (2008)
PRL 107, 257801 (2011)

Progress Report: UoI experimental team

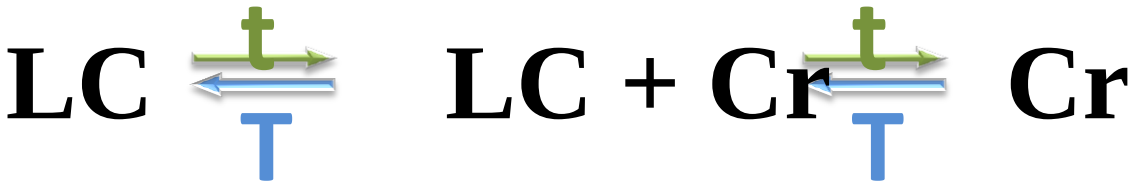
WP 5: Thermodynamic phase diagram of DLCs

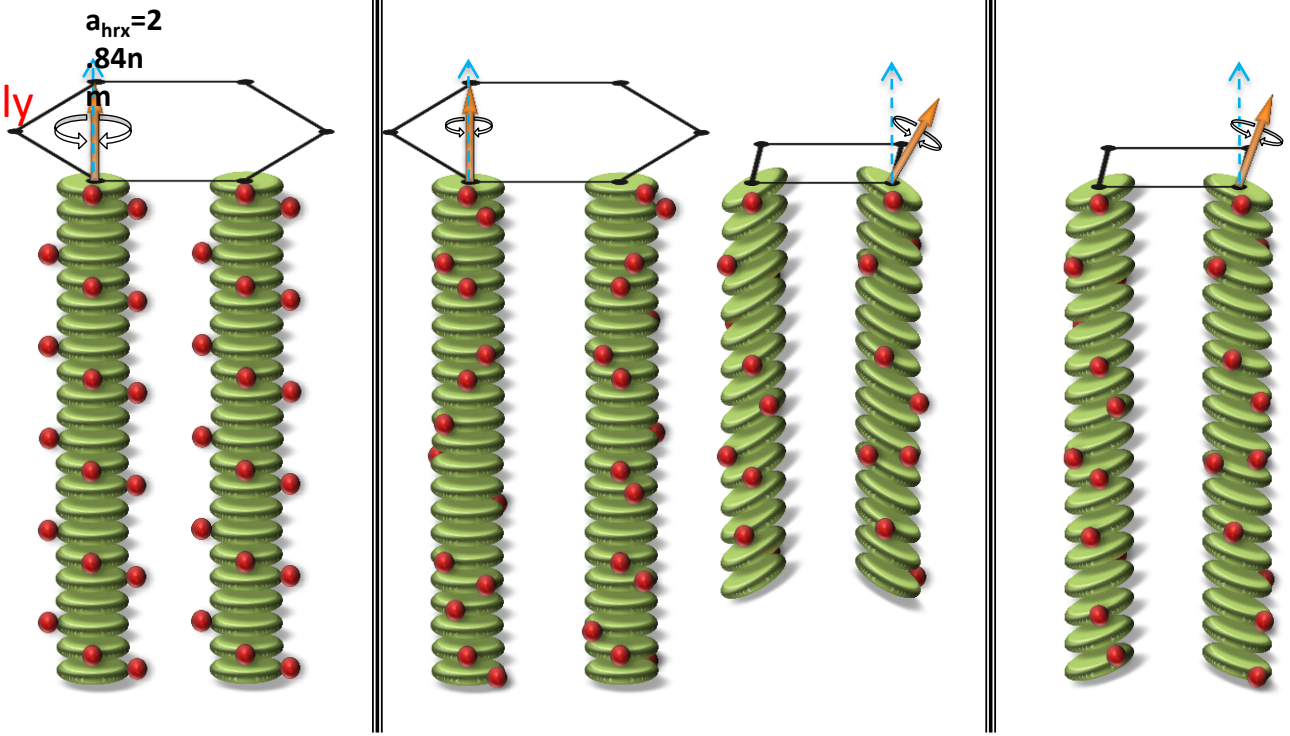


JACS 130, 5311 (2008)

Progress Report: UoI experimental team

WP6: Kinetics of structure formation





LC: Electrically ordered phase

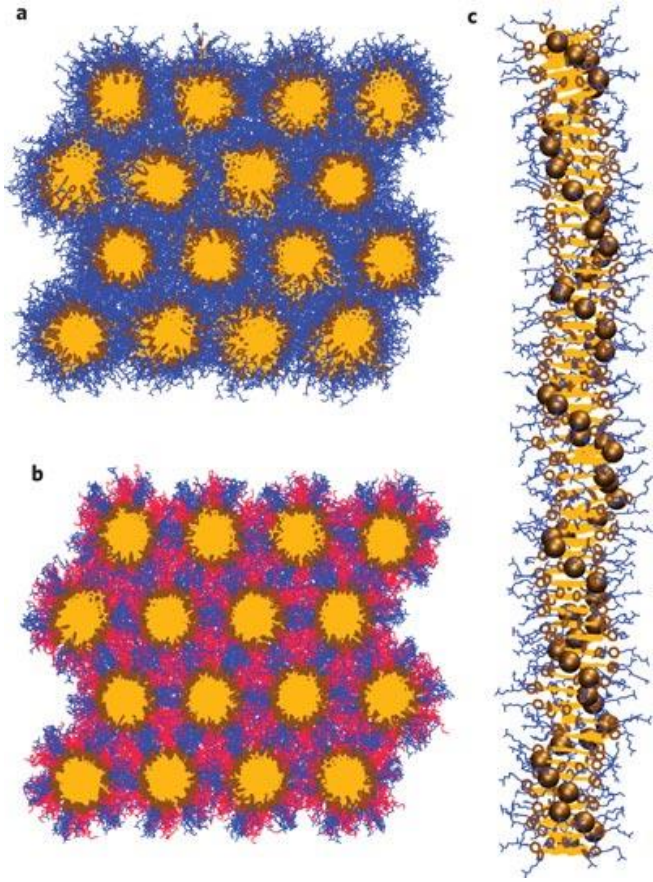
Cr: Structurally ordered but electrically disordered

Soft Matter 7, 4680 (2011)
J. Phys. Chem. B 115, 14919 (2011)

DLCs: open questions I – Simulations/Theory

- Earlier pertinent work (Andrienko and co-workers) explored:

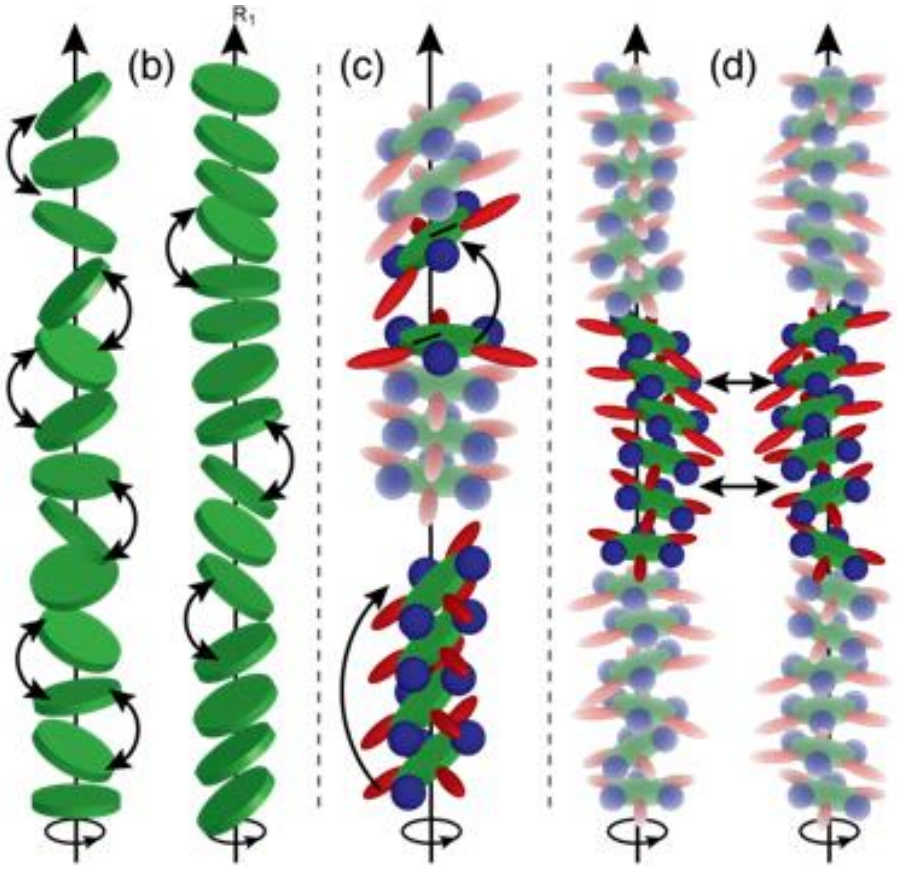
(i) the effects of the length and number of side chains on the columnar self-assembly
(ii) The effect of disk size and shape on optimizing the intra-columnar charge transport



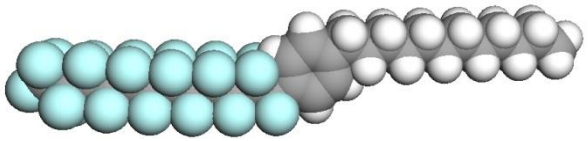
X. Feng et al.
Nature Materials 2009

DLCs: open questions II

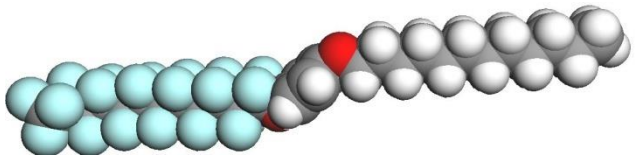
- Time-scales of motion as a function of the core size/alkyl side chains
- Nature of Lc to Cr transformation
- Nature of defects and their dynamics
- Effect of hydrophilic/hydrophobic side chains on the self-assembly and dynamics



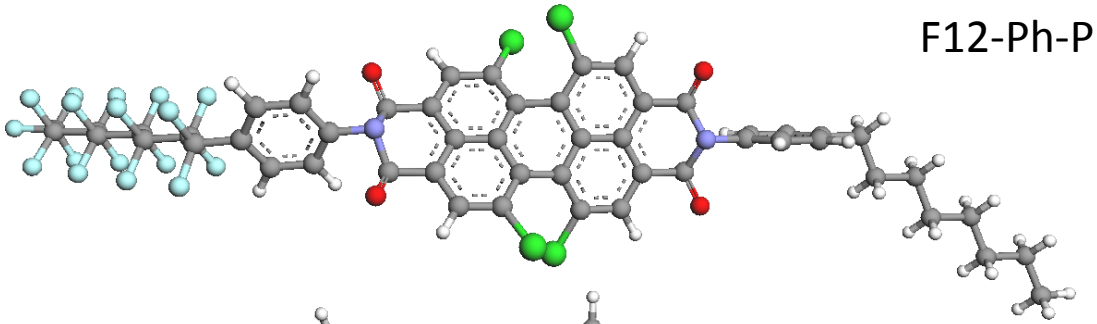
- DLCs with hydrophilic/hydrophobic side chains (R. Stangenberg/K. Muellen)



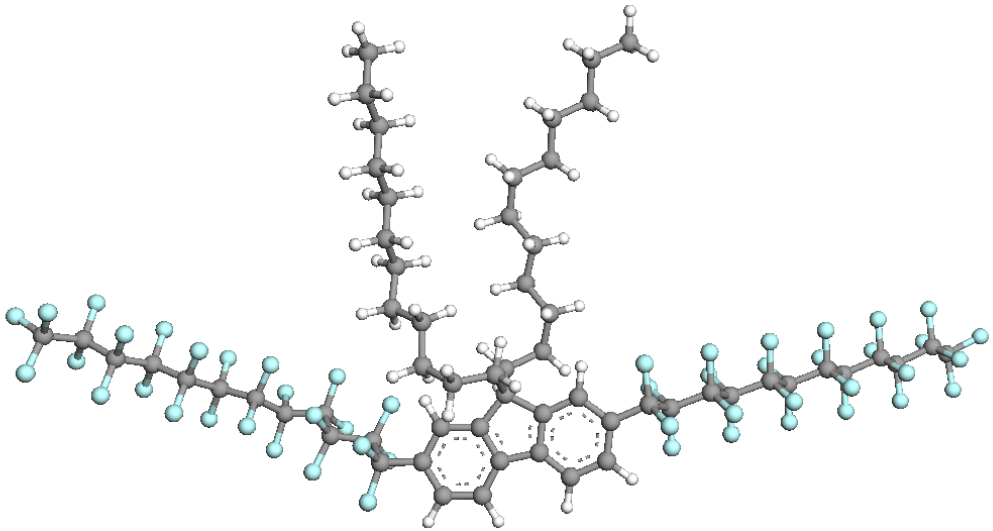
F12-Ph-C12



F12-O-Ph-O-C12



F12-Ph-PDI-Ph-C12



Self-assembly and dynamics in metastable states: From molecular and supramolecular to mesoscopic systems
(META-ASSEMBLY)

Maria Vamvakaki and Uli Jonas
Research Team 2

Foundation for Research and Technology – Hellas
Institute of Electronic Structure and Laser, Heraklion Crete, Greece

FORTH Contribution I

WP 10: Synthesis of inorganic/organic core-shell NPs (Duration 36 months)

***Researchers*:** U. Jonas, M. Vamvakaki (FORTH), K. Matyjaszewski (CMU)

Growth of polymer chains from appropriately modified inorganic nanoparticles (SiO_2, Au, Ag) using surface-initiated ATRP

Steps: (1) synthesis of appropriately functionalized ATRP initiator,

(2) Immobilization of the initiator on the nanoparticle surface, and

(3) growth of the polymer chains from the nanoparticle surface by ATRP.

Parameters to be varied: the nature of the polymer chains (inert *vs.* responsive), the polymer grafting density and the polymer chain length.

Characterization by ATR-FTIR, TGA, DLS, SEM and TEM.

Particle dispersion will be determined both in solution and in polymer melt.

Deliverables: Fully characterized SiO_2, Au and Ag nanoparticles bearing various polymeric shells of different polymer chain densities and lengths.

FORTH Contribution II

WP 11: Synthesis of polynorbornene derivatives carrying protected 2-ureido-pyrimidone groups (Duration 24 months)

***Researchers*:** E.W. Mejier (Eindhoven)

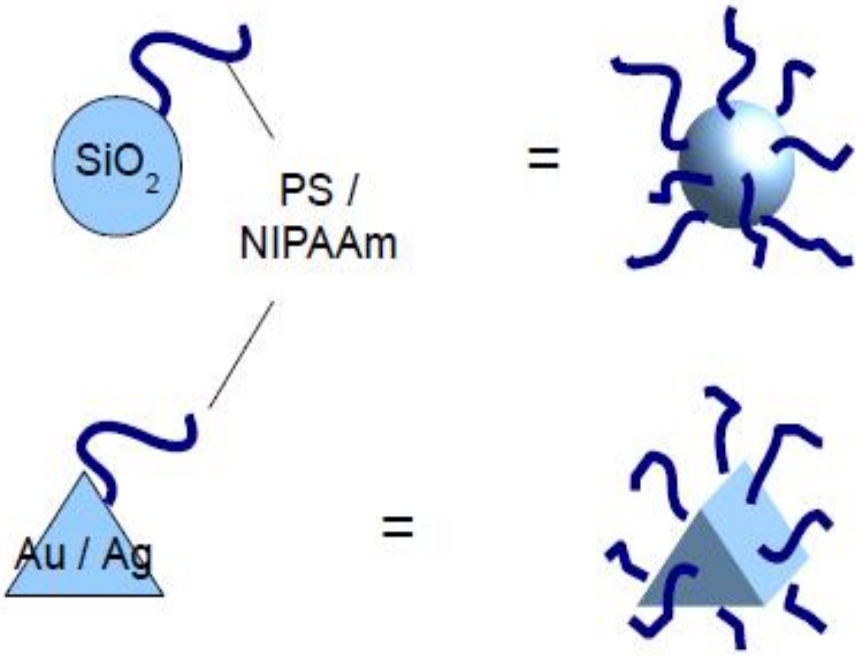
Polynorbornene copolymers prepared by ring opening metathesis polymerization. 10-20 mol% 2-ureido-pyrimidone groups (protected with o-nitrochloro-benzene) will be incorporated along the polymer chain via urea or urethane linkages.

The polymer molecular weight will be between 150 and 200 kDa with a molecular weight distribution of 1.5-2.0.

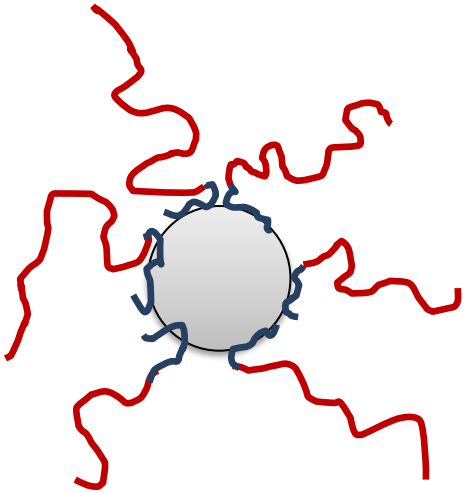
The nitro-benzene groups in the polymer will be cleaved by UV irradiation and the liberated 2-ureido-pyrimidone groups will form hydrogen bonds among the polymer chains leading to the formation of supramolecular assemblies.

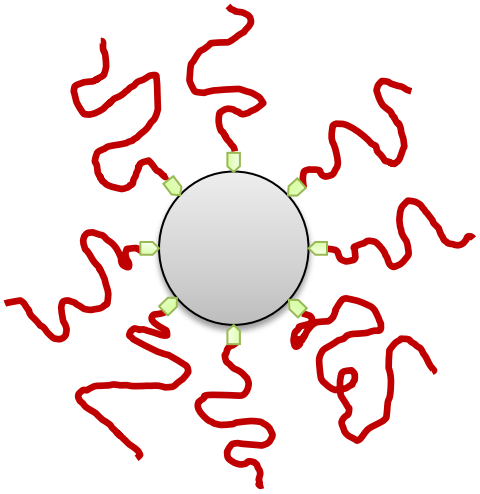
***Deliverables*:** Fully characterized polynorbornenes carrying protected 2-ureido-pyrimidone groups.

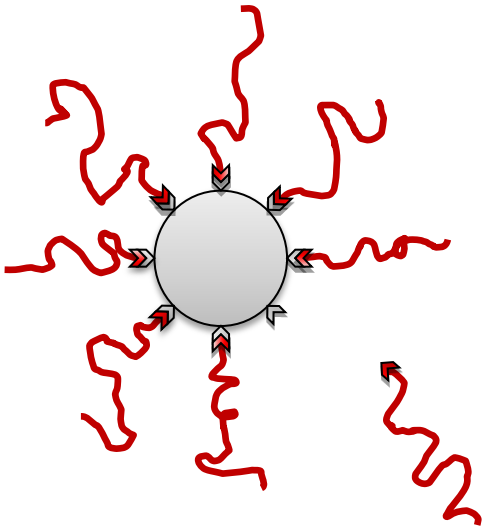
WP:10 Core-shell particles



Grafting Methods







"Grafting to"

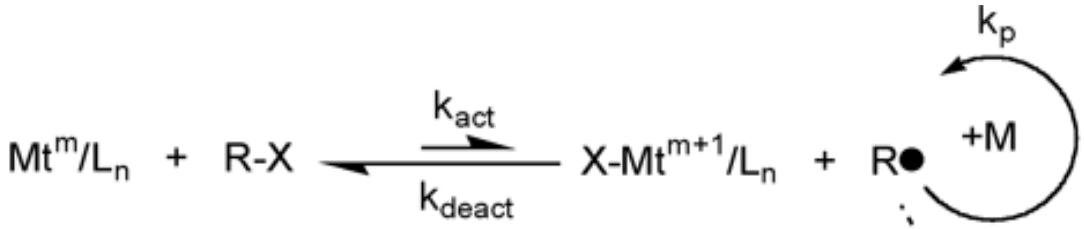
"Grafting from"

Our approach

Different grafting densities

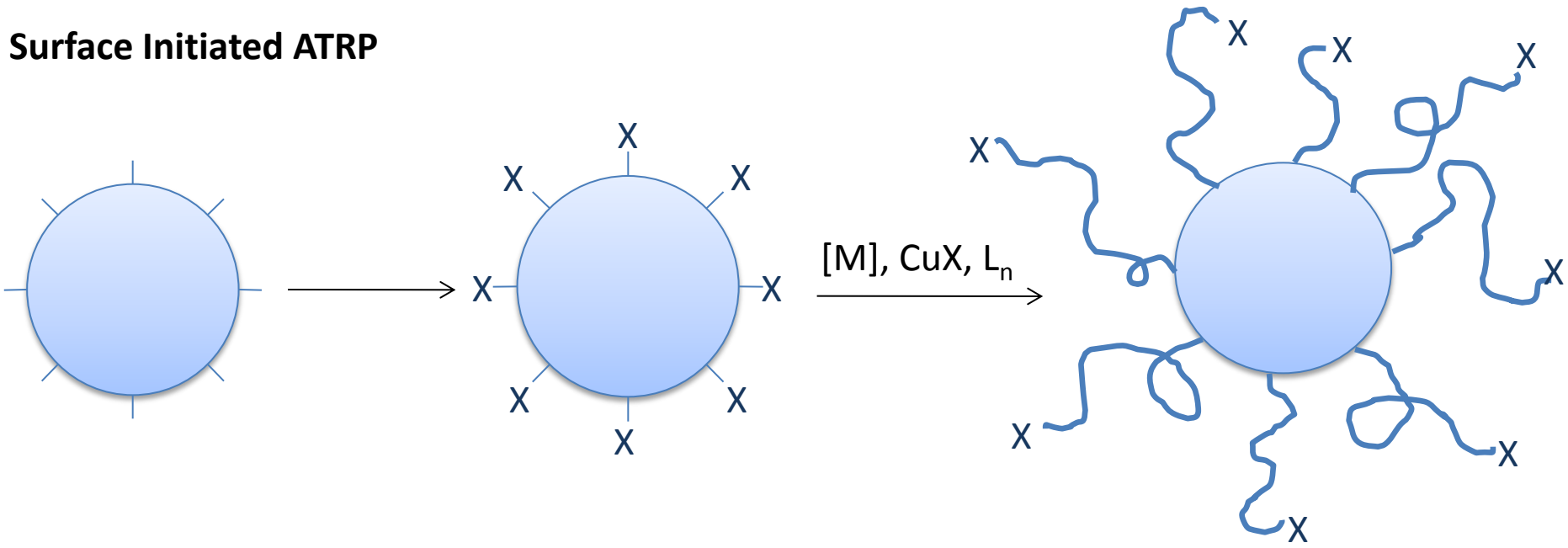
$$\sigma = \frac{\left(\frac{m_{poly.}}{M_n}\right) \times N_A}{m_{part.} \times \left(\frac{A}{m}\right)}$$

Atom Transfer Radical Polymerization (ATRP)

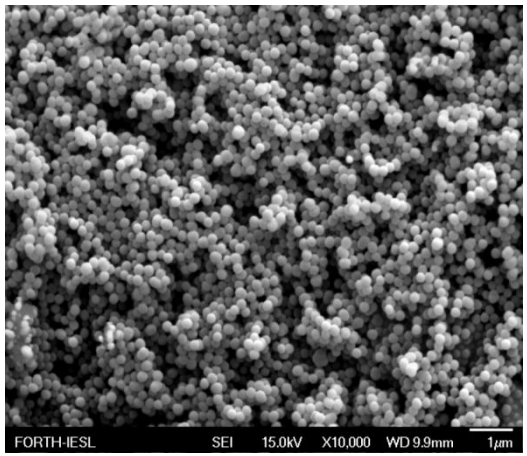


Mt^m= transition metal
L_n = complexing ligand
R- polymer chain
X = Br or Cl

Surface Initiated ATRP



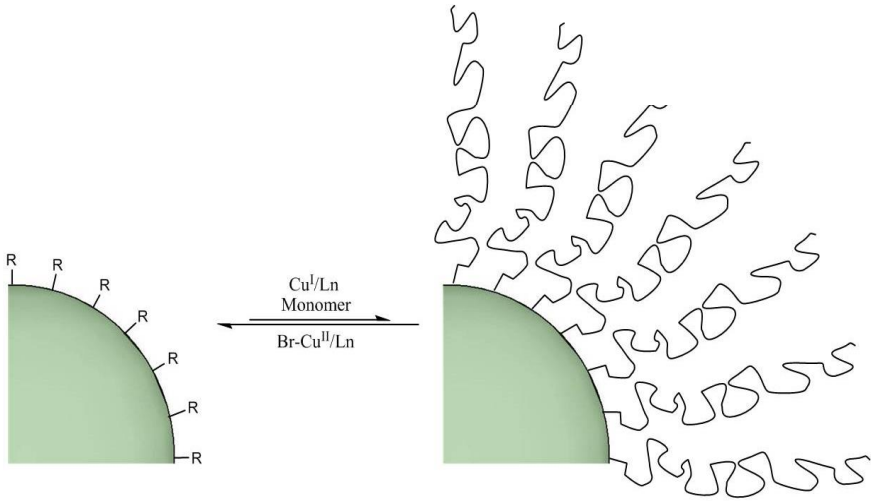
Work performed so far…

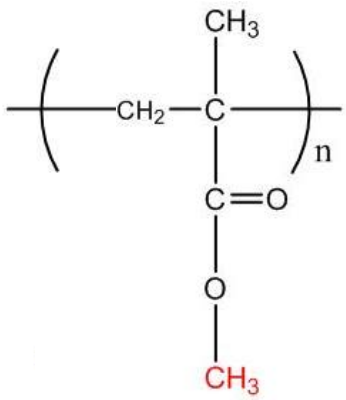


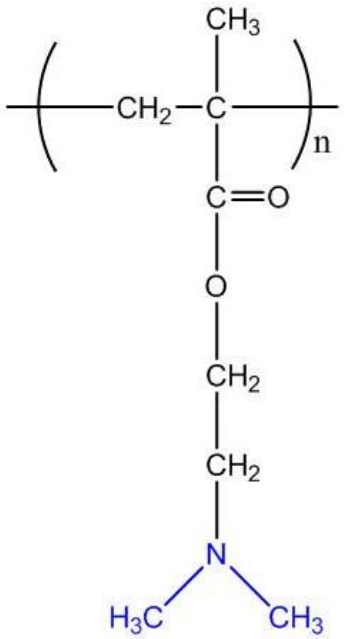
D = 200 nm SiO_2 particles
(different particles sizes possible)

- Poly(methyl methacrylate): inert
  - high grafting density
  - low grafting density

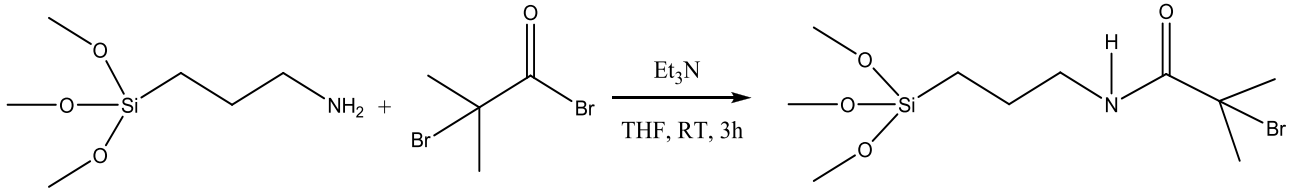
- Poly(2-(dimethylamino)ethyl methacrylate): pH and temperature responsive
  - Study the temperature responsive properties

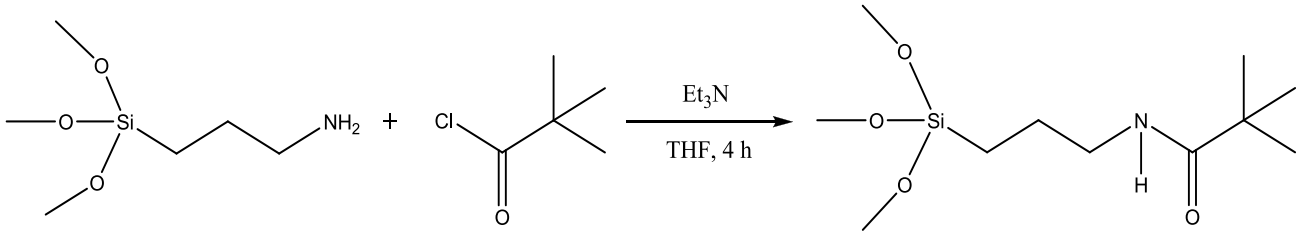






Step 1: Initiator Synthesis

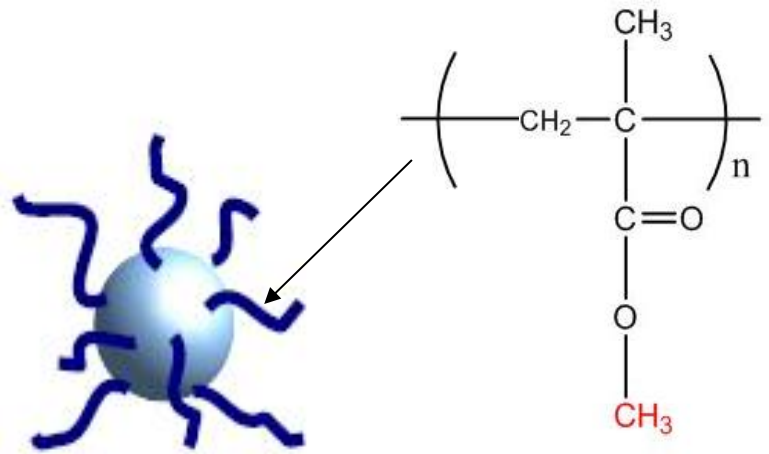


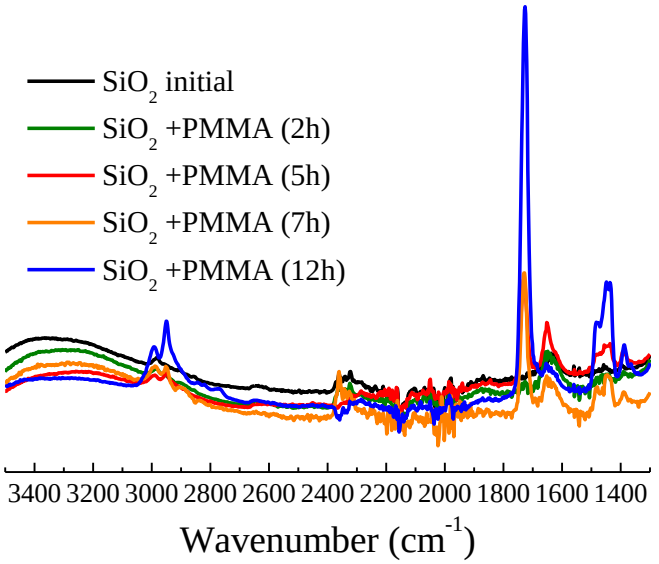


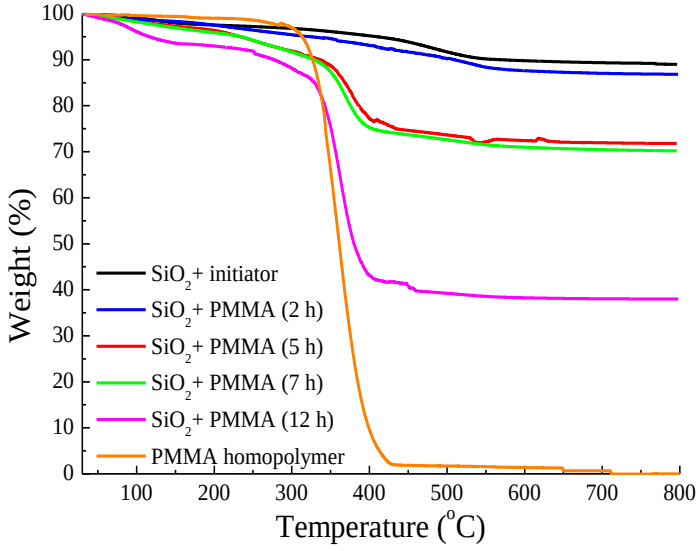
Step 2:

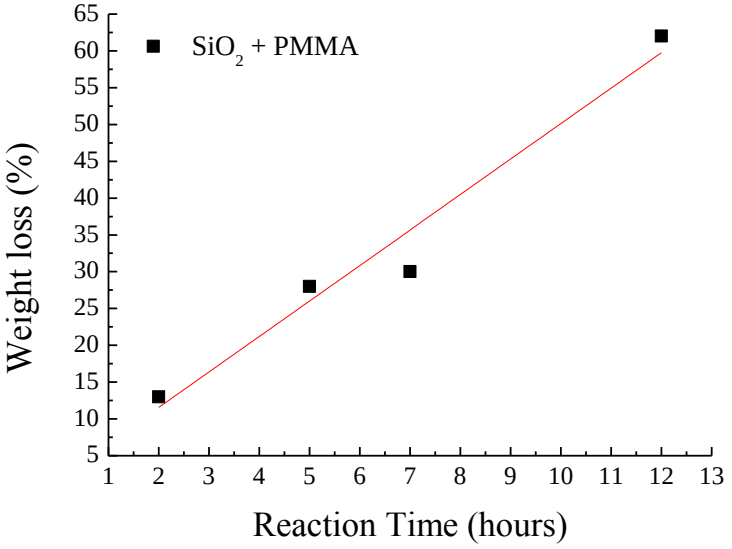
- Immobilization on silica surface via silane chemistry

Step 3: PMMA-coated silica nanoparticles



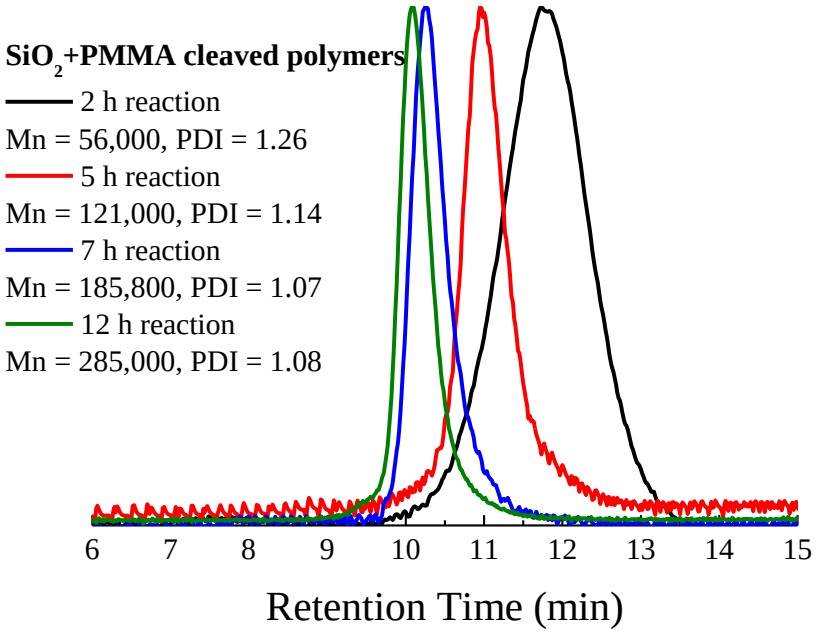


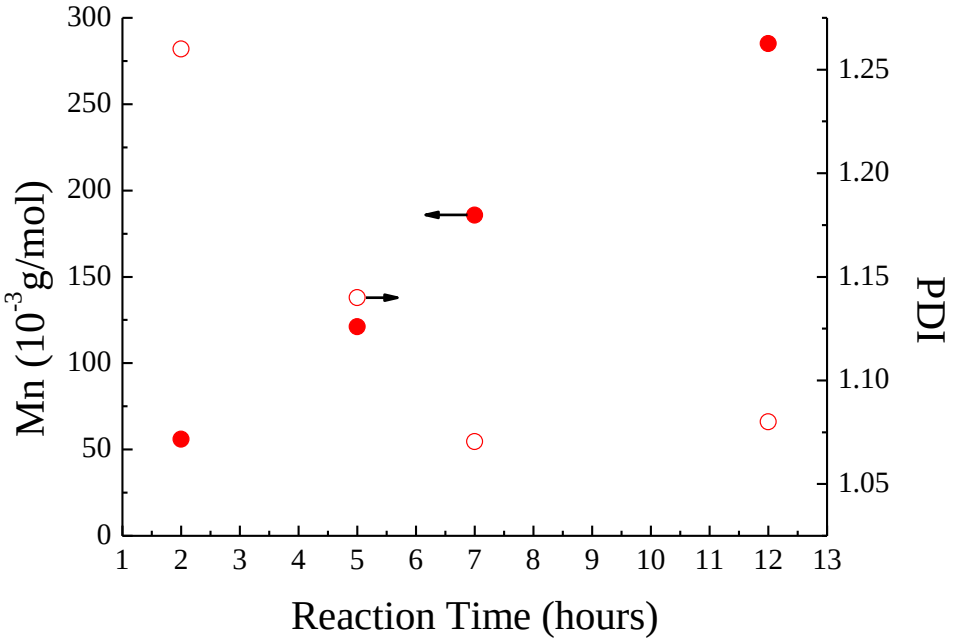




D. Moatsou

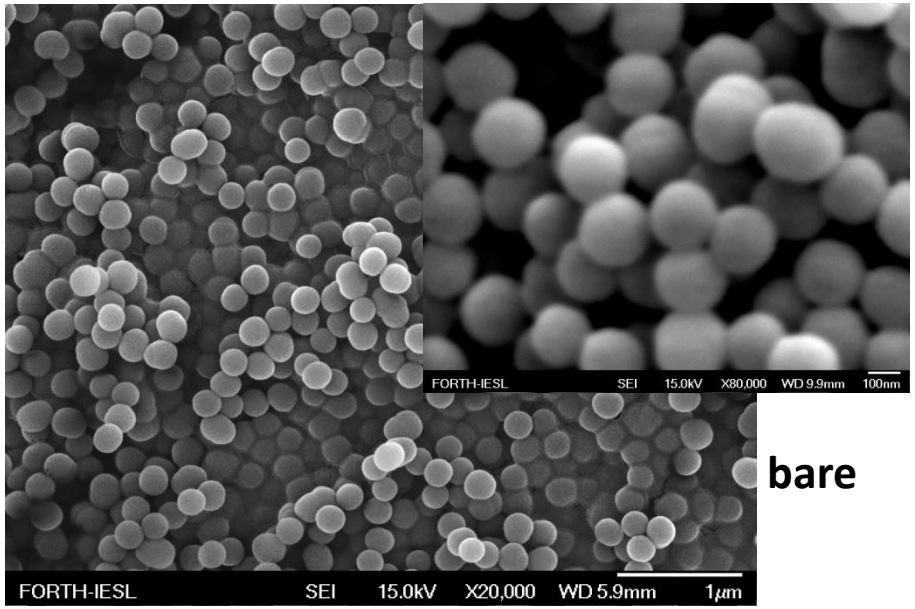
PMMA-coated silica nanoparticles





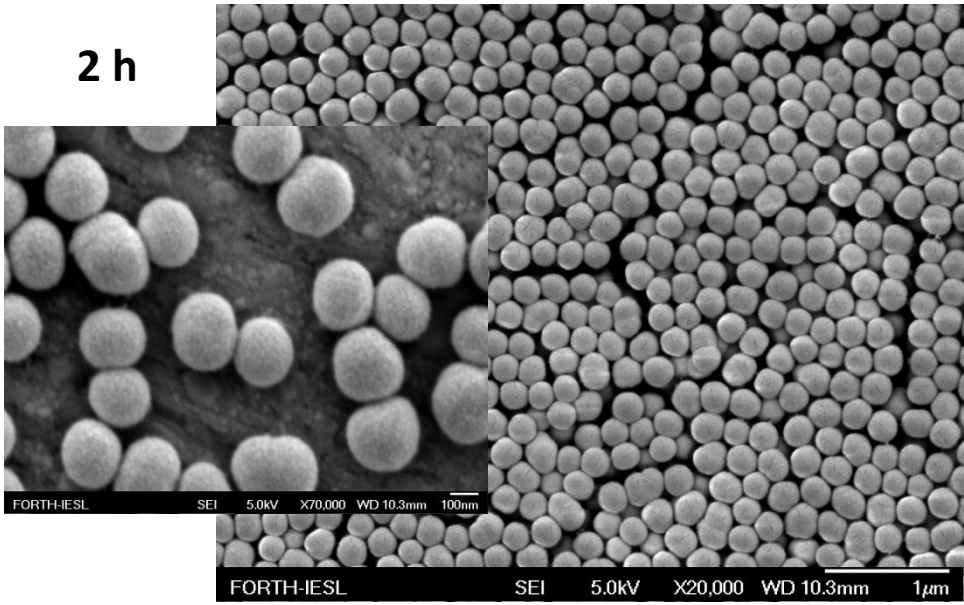
	# chains/ particle	σ (chains/nm^2)
SiO_2+PMMA (2 h)	25,526	0.13
SiO_2+PMMA (5 h)	31,416	0.16
SiO_2+PMMA (7 h)*	23,562	0.12
SiO_2+PMMA (12 h)	56,942	0.29
SiO_2+PMMA (LGD)	9,818	0.05

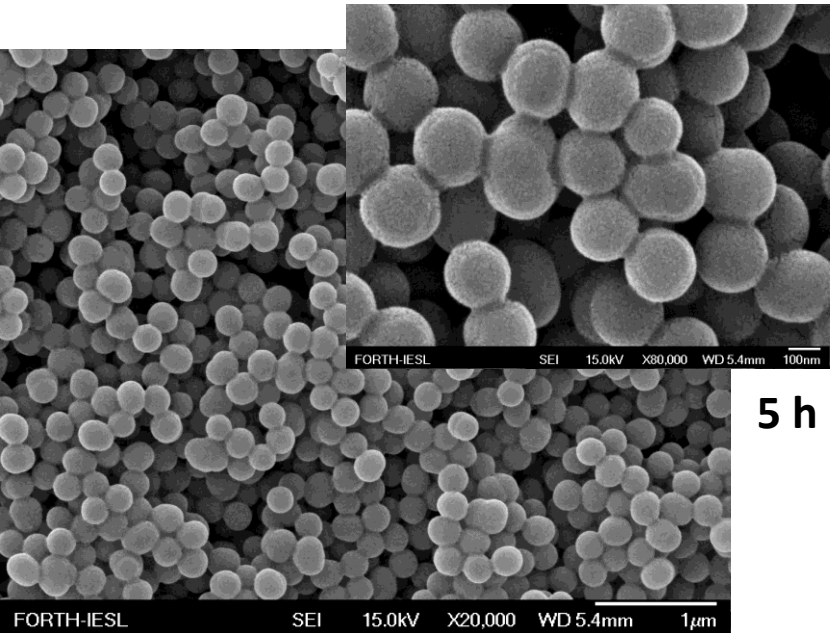
PMMA-coated silica nanoparticles



bare

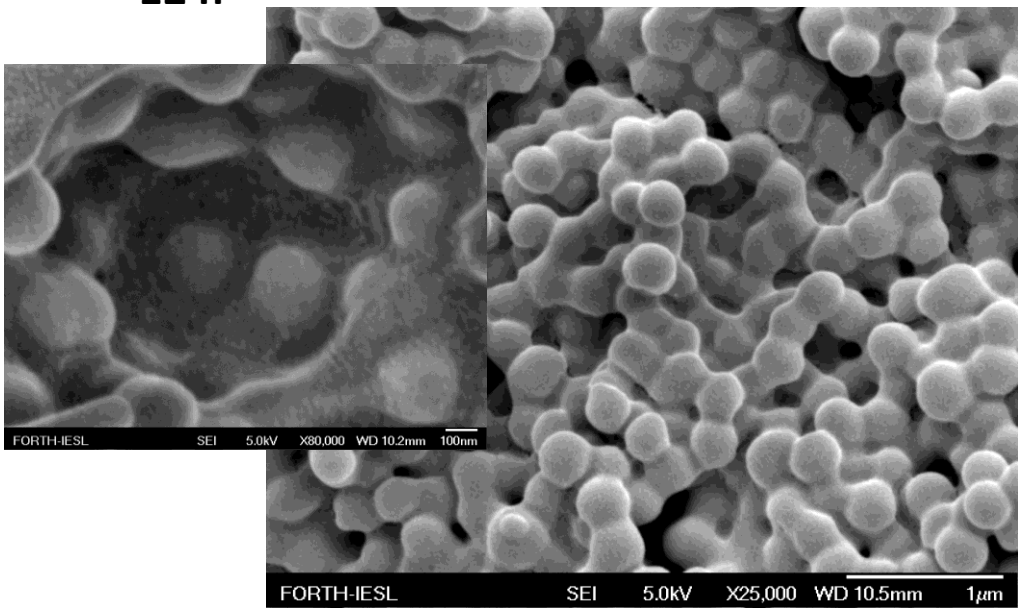
2 h





5 h

12 h



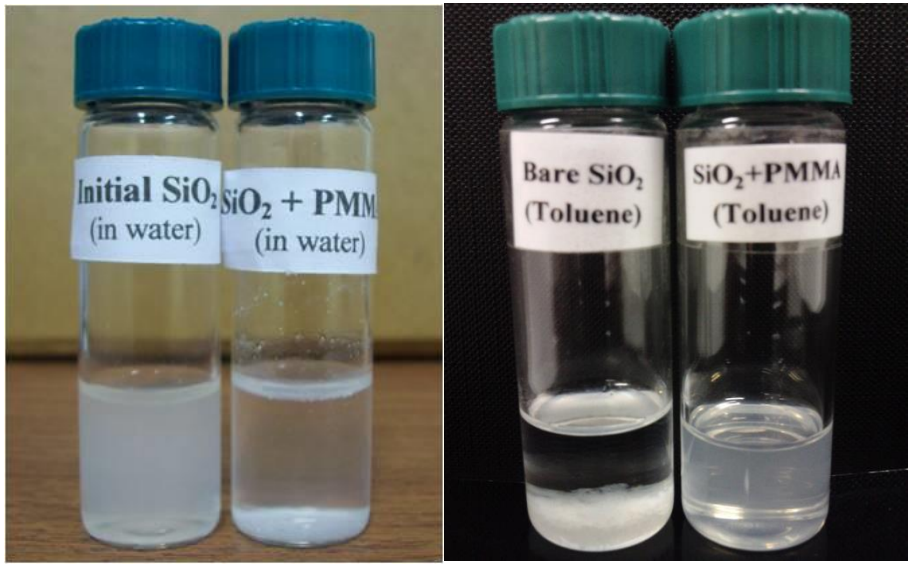
PMMA-coated silica nanoparticles

DLS measurements

	M_n (g/mol)	D_h (nm)
SiO_2 (initial)	-	242
SiO_2+PMMA (2 h)	56,000	450
SiO_2+PMMA (5 h)	121,000	520
SiO_2+PMMA (12 h)	285,000	1016
SiO_2+PMMA (LGD)	181,500	292

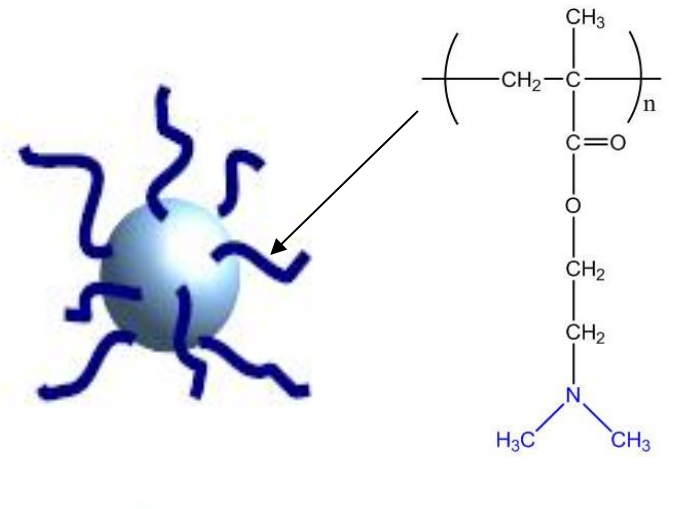
Dispersion Stability Tests

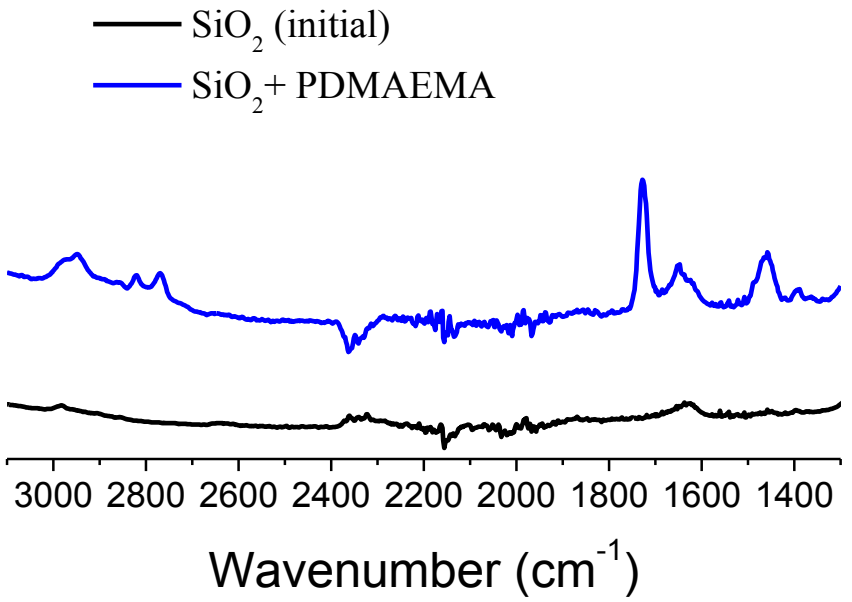
- Sedimentation in water

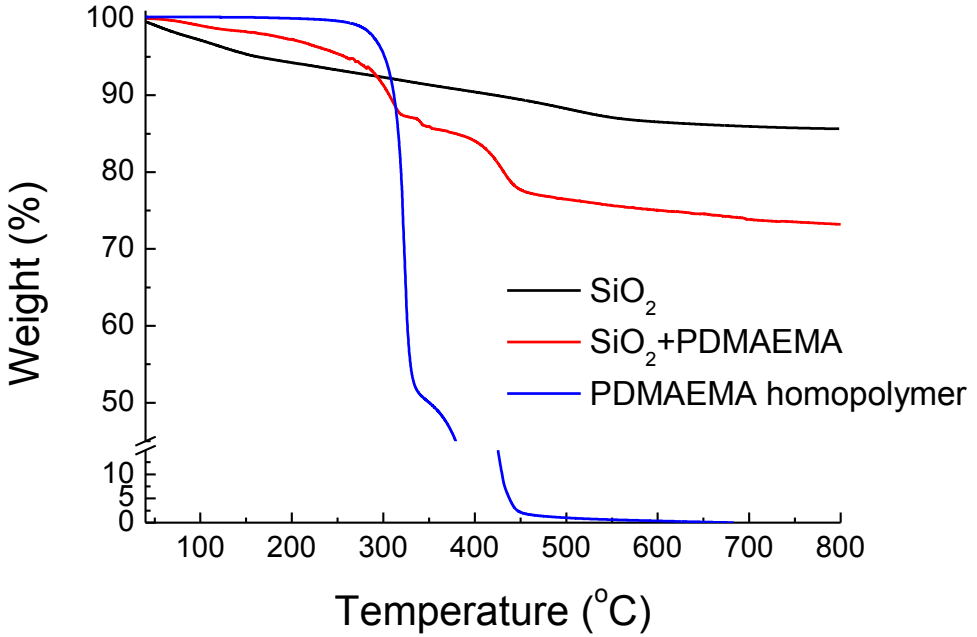


- Dispersion in toluene

PDMAEMA-coated silica nanoparticles







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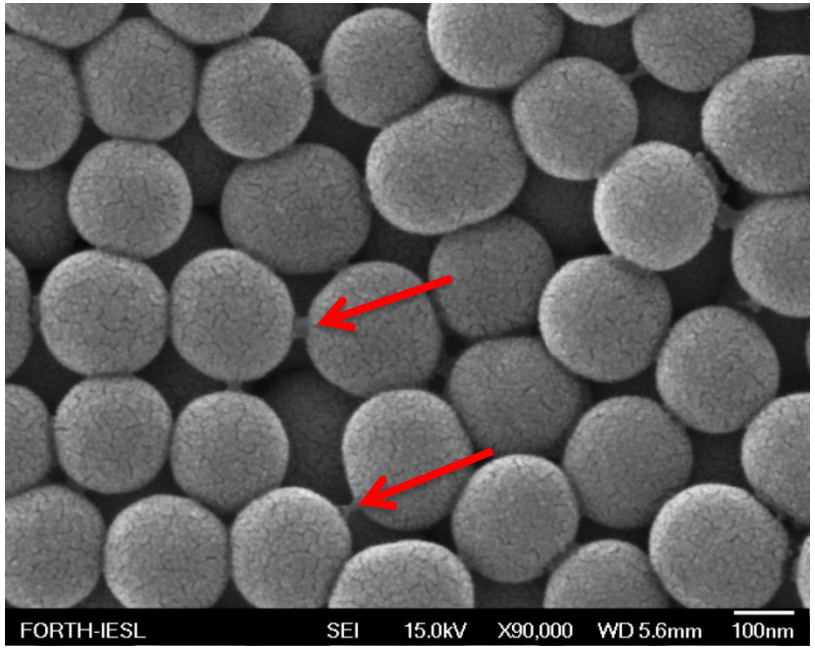
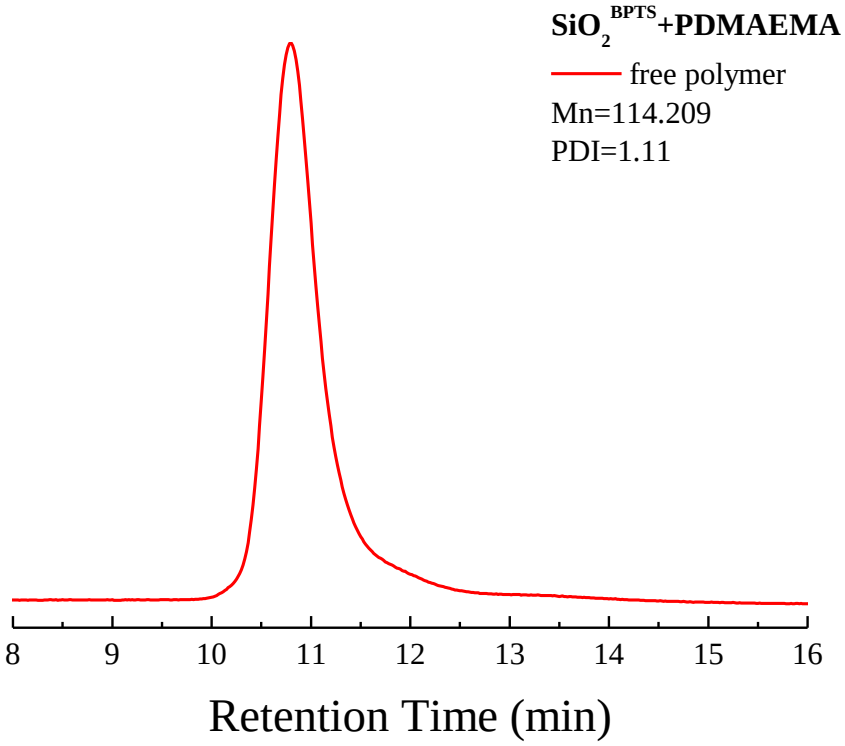
PDMAEMA-coated silica nanoparticles



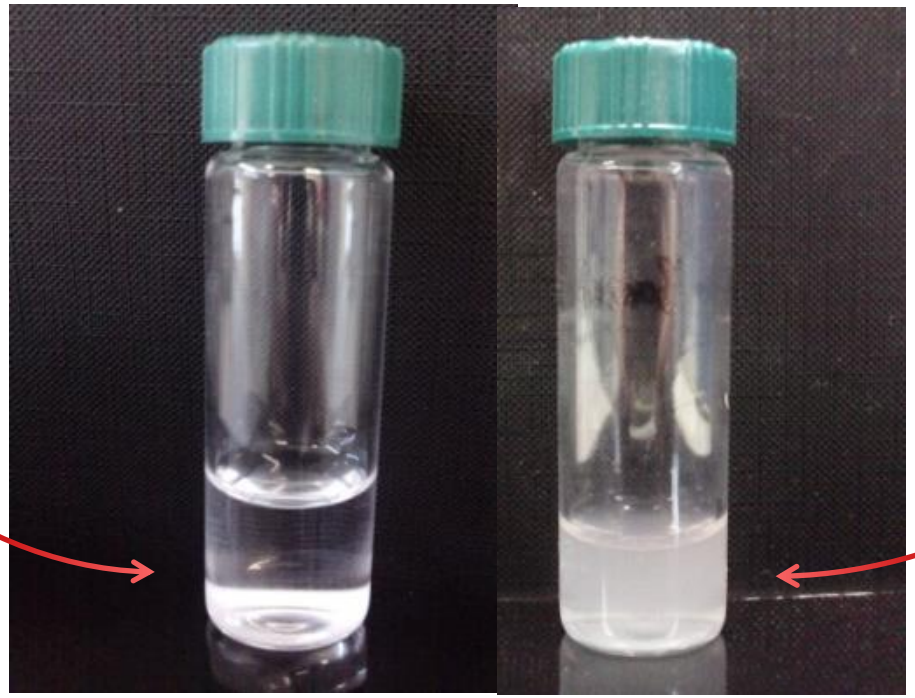


σ = 0.15 chains / nm²
~29,500 chains / nanoparticle

PDMAEMA-coated silica nanoparticles

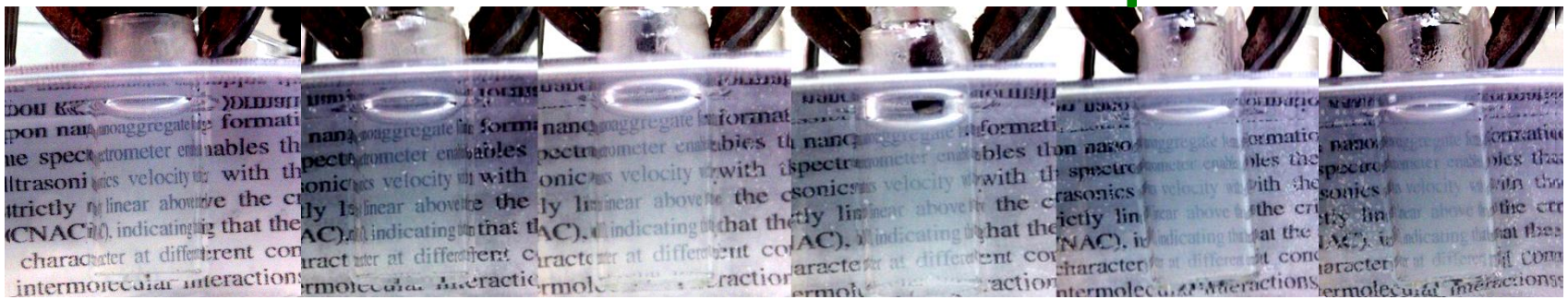
- Dispersion stability test in water after 2 weeks

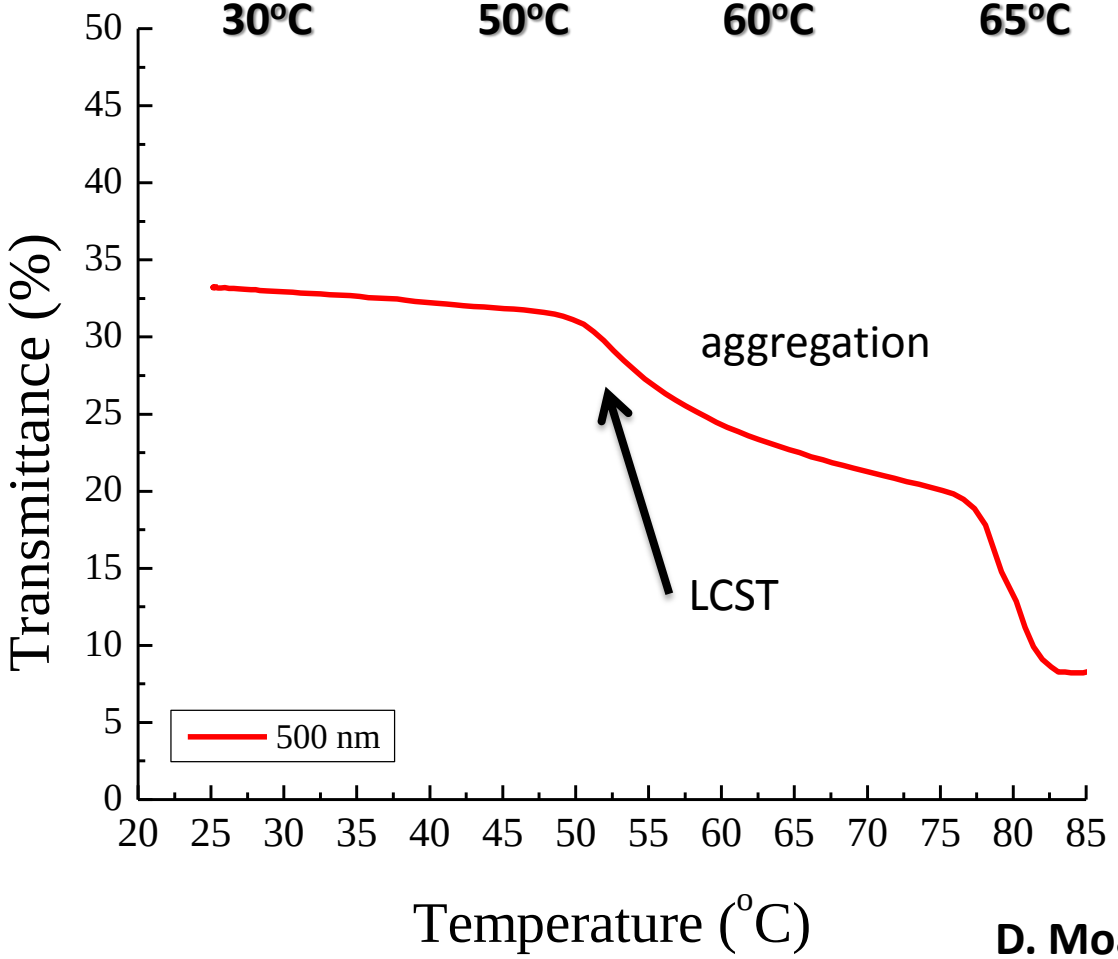
The bare nanoparticles have precipitated



The PDMAEMA-coated nanoparticles are stable

PDMAEMA-coated silica nanoparticles





- Gradual increase in turbidity from 50 ºC

D. Moatsou

Summary

- **Expertise:**
  - Polymer synthesis.
  - Polymer characterization and solution behavior.
  - Hybrid organic-inorganic materials.

- **Work until now:**
  - Successful synthesis of PMMA-coated silica nanoparticles
  - Vary the molecular weight of the grafted chains
  - Control the polymer grafting density

  - Successful synthesis of PDMAEMA-coated silica nanoparticles
  - Prolonged dispersion stability of the nanoparticles in water
  - Temperature responsive hybrid nanoparticles

Future Work

- Synthesis of PDMAEMA-coated nanoparticles of different grafting densities and various grafted polymer chain lengths
- Synthesize a thiol-based ATRP initiator for immobilization onto the Au prisms
- Synthesis of PMMA and PDMAEMA polymer brushes from the surface of the Au nanocolloids
- Characterization of the polymer-coated Au nanoparticles

➢ **Collaboration with Partners**

Thank You

Self-assembly and dynamics in metastable states

UoC-Contribution

Concepts

Report on structure & dynamics of the amphiphilic Hexaphenylbenzene-Poly(ethylene glycol) in water

Promising systems
Literature

Perspectives

Kick-off meeting
Thessaloniki Dec.2012

Why metastable ?

Multivalency
Shallow free energy landscape
Slow dynamics

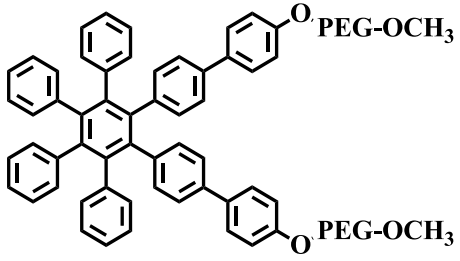
Controlling parameters ?

Association constants,
Interactions (T,solvent)
polydispersity
path dependence

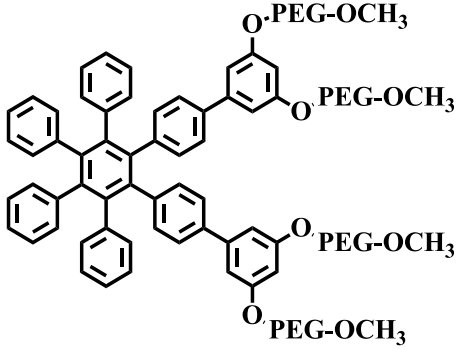
Solutions: Population diagram
Solid state: Phase diagram, external stimuli

Science **277**,1225,1997 & **335**,813,2012
Nature **481**,492,2012

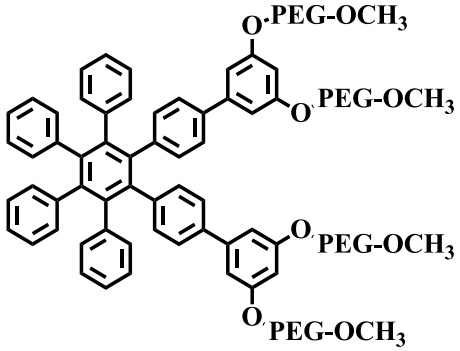
Hexaphenylbenzene-Poly(ethylene glycol) in water*



1 (PEG-750)



2 (PEG-750)



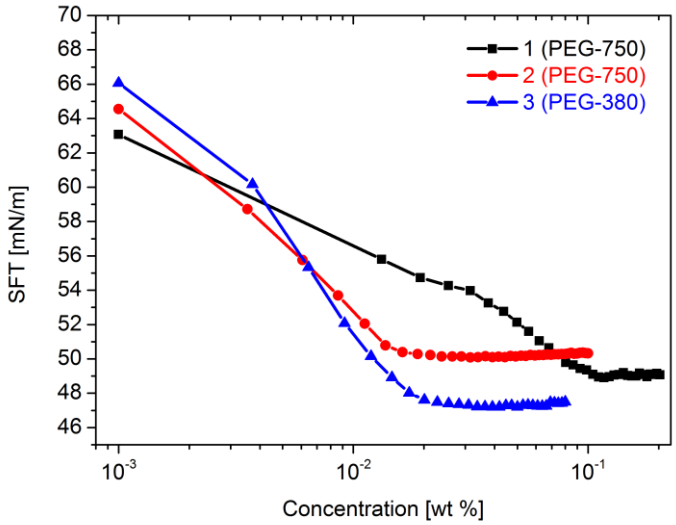
1 (PEG-380)

Molecular structure of molecules **1**, **2** and **3**.

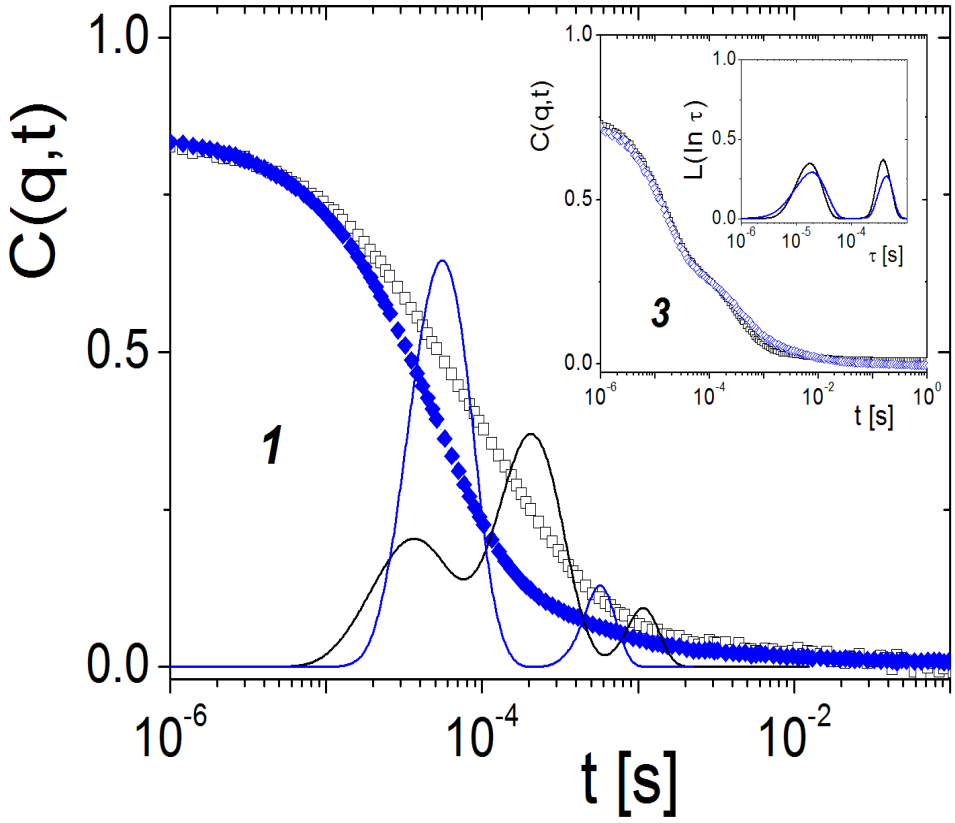
Solution study: Structure, Rheology UCLT?

* K.Wunderlich, M.Klapper,K.Müllen

1, 2 and 3: in aqueous solutions

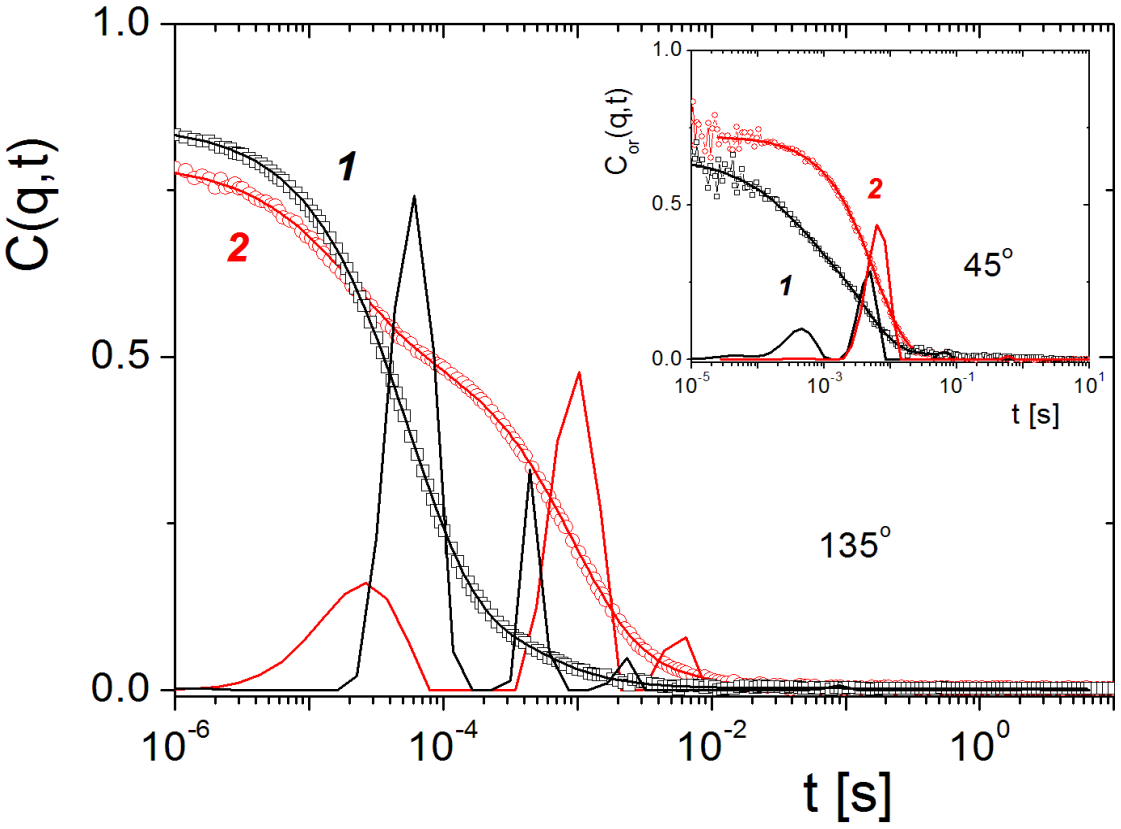


cmc of **1**, **2** and **3**.



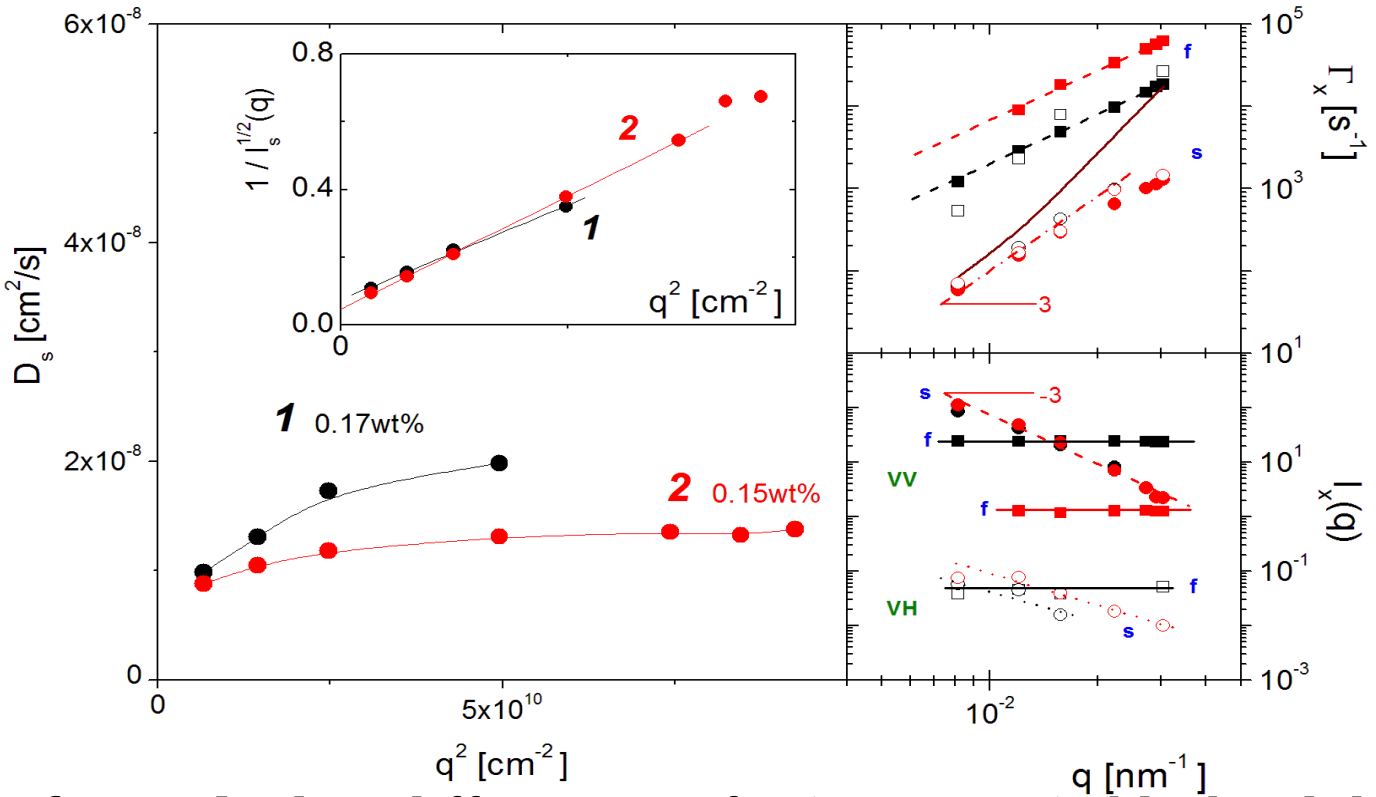
Metastability: PCS of 0.17 wt% aqueous solution of **1** at 20°C after dissolution at T=20°C (white squares) and after annealing at T = 50°C for few hours and subsequent slow cooling to T=20°C (blue solid rhombi). **Inset:** The corresponding behavior of **3** .

1, 2 and 3: in aqueous solutions



Assemblies: $C_{VV}(q,t)$ at $q=0.029nm^{-1}$) of **1** (0.17%) (black squares) and **2** (0.15 wt%) (red circles) at T=20°C recorded after annealing at T=50°C for few hours and subsequent slow cooling to T=20°C. **Inset**: $C_{or}(q,t)$ at $q=0.012nm^{-1}$ for the the same solutions of **1** (black squares) and **2** (at T=20°C .

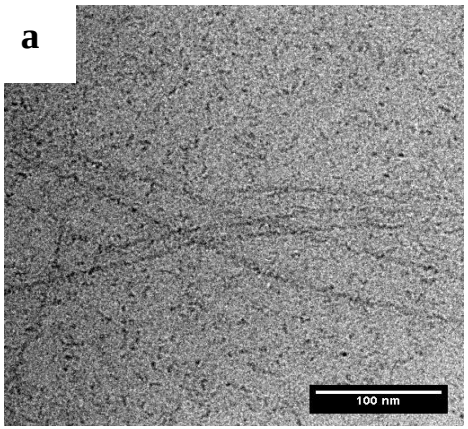
1, 2 and 3: in aqueous solutions

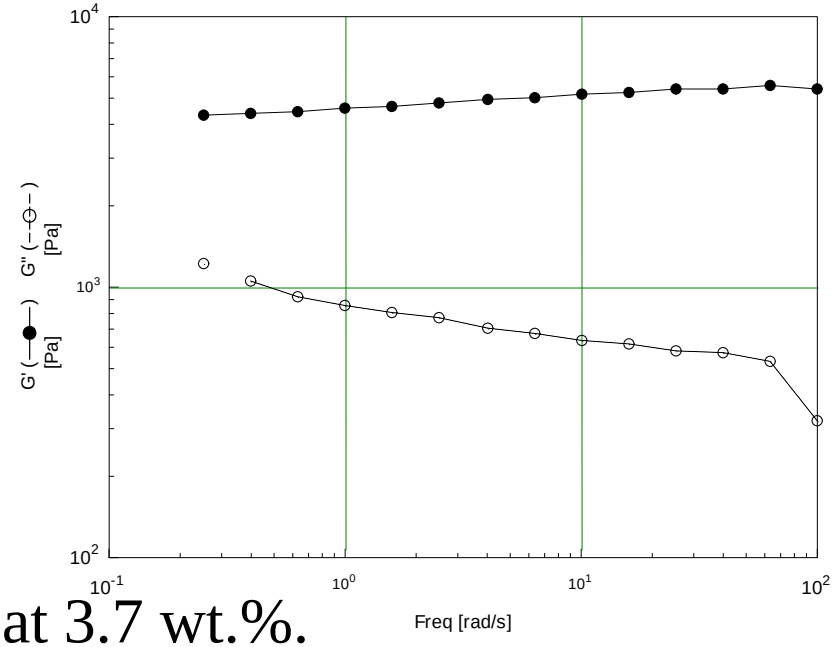


Left panel. Slow diffusion D_s of **1** (0.17 wt %) (black solid circles) and **2** (0.15 wt %) (red solid circles) at T=20°C. $I_s(q)$ (Debye-Bueche expression **Right panel.** Relaxation rates Γ_x and component intensities I_x from VV (solid) and VH (open symbols) relaxation functions ; f fast process and s ,slow process.

R_h and correlation length ξ of **1** to **3**

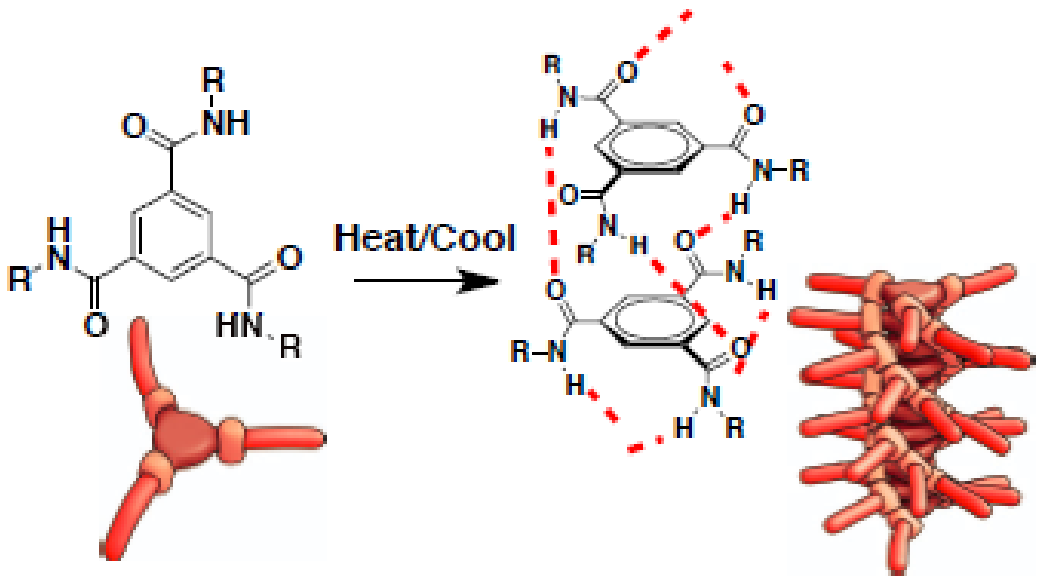
	1 (PEG-750)	**2 (PEG-750)**	**3 (PEG-380)**
R_h(fast)	11 nm	3 nm	3 nm
R_h(slow)	220 nm	260 nm	180 nm
ξ	84 nm	130 nm	60 nm





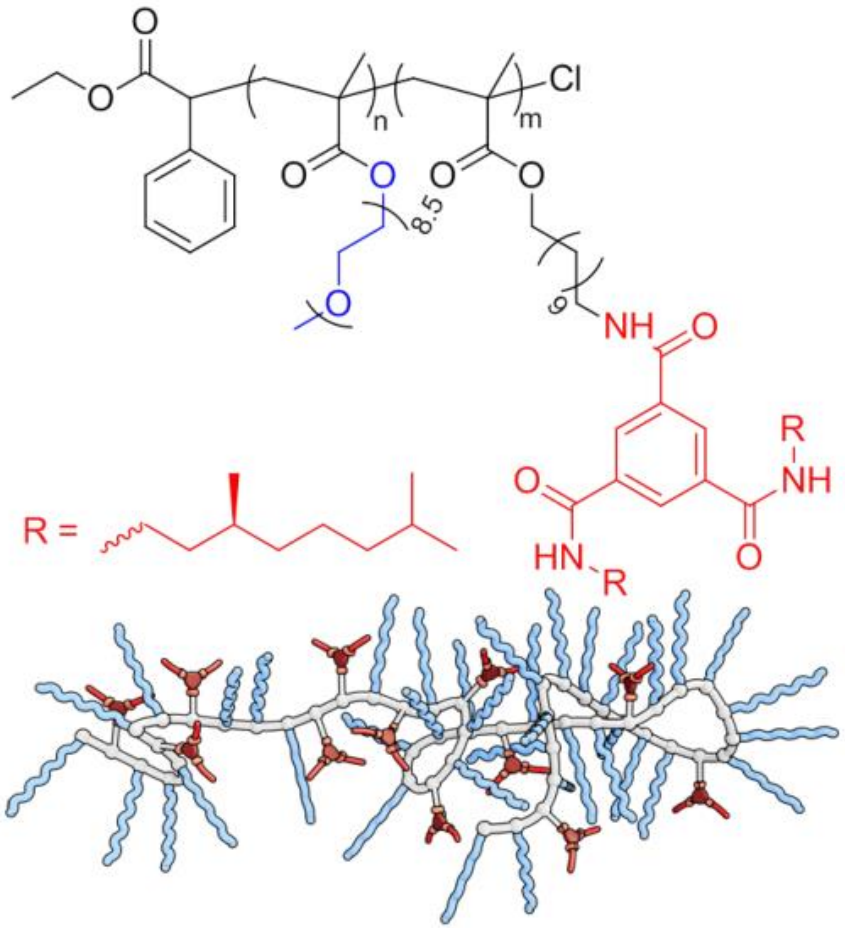
1 (**a**) in aqueous solution at 3.7 wt.%.

Promising systems- BTA based



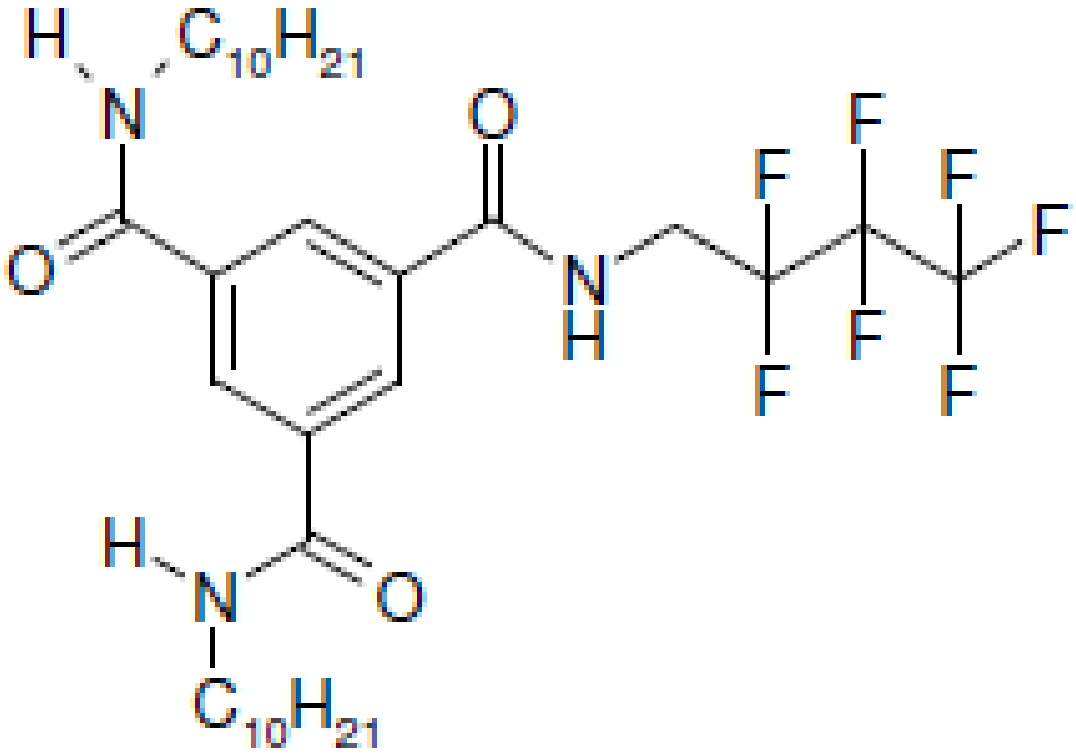
BTA: Benzene-1,3,5-tricarboxamide

I. Promising systems- BTA based



molecular structure & schematic representation: poly(oEGMA-*co*-BTAMA) P0% ,P10% and P20%

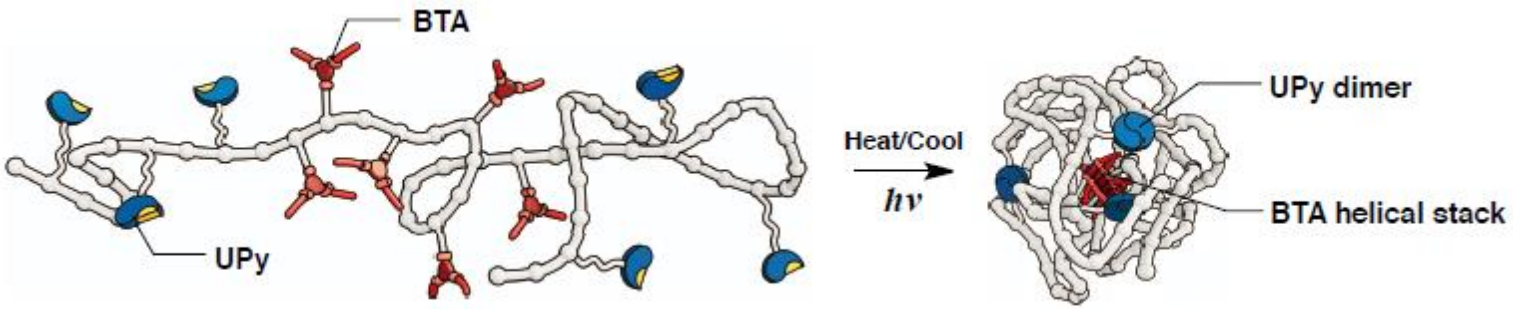
II. Promising systems- BTA based

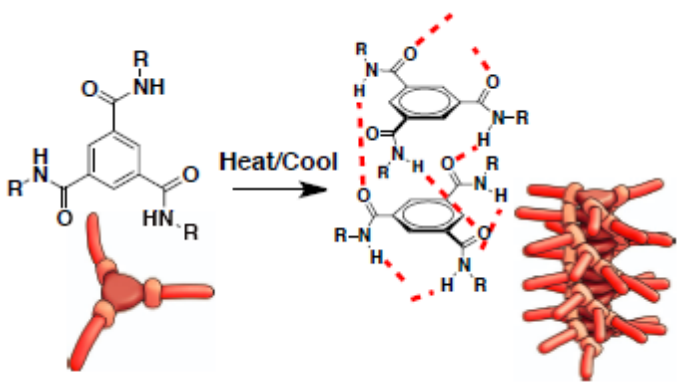


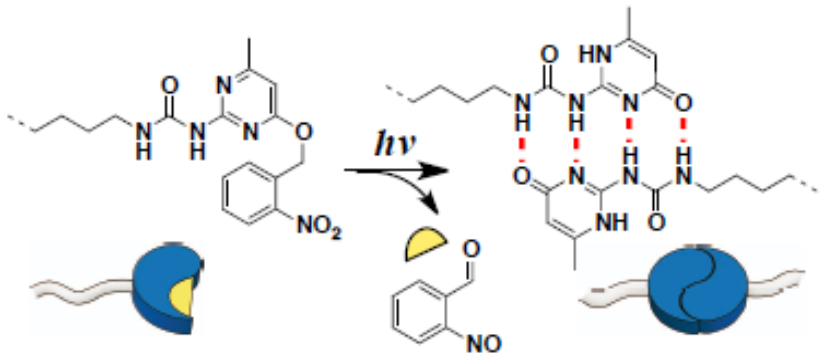
BTAF-x ; x=5, 7, 8

III. Promising systems- BTA based

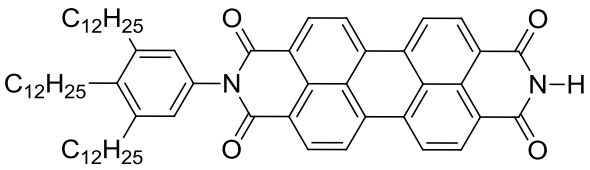
Folding block copolymers



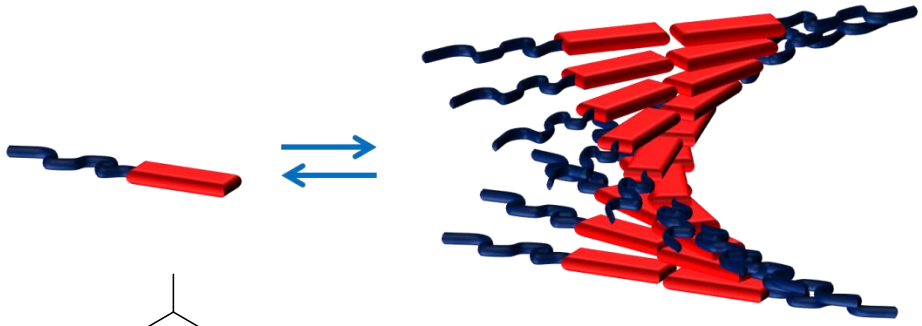




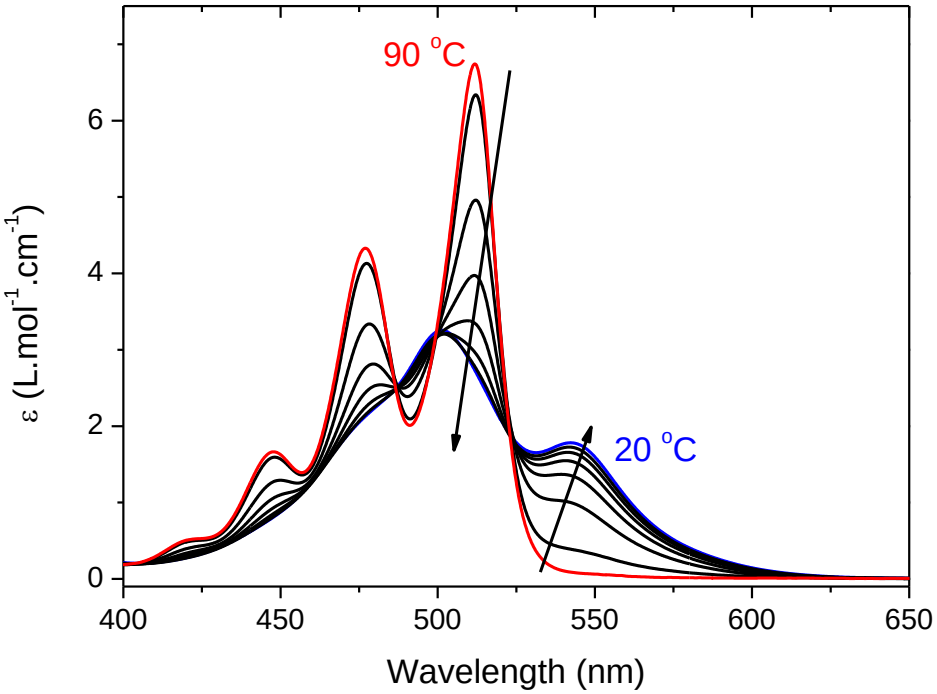
Cooperative self-assembly of PBI

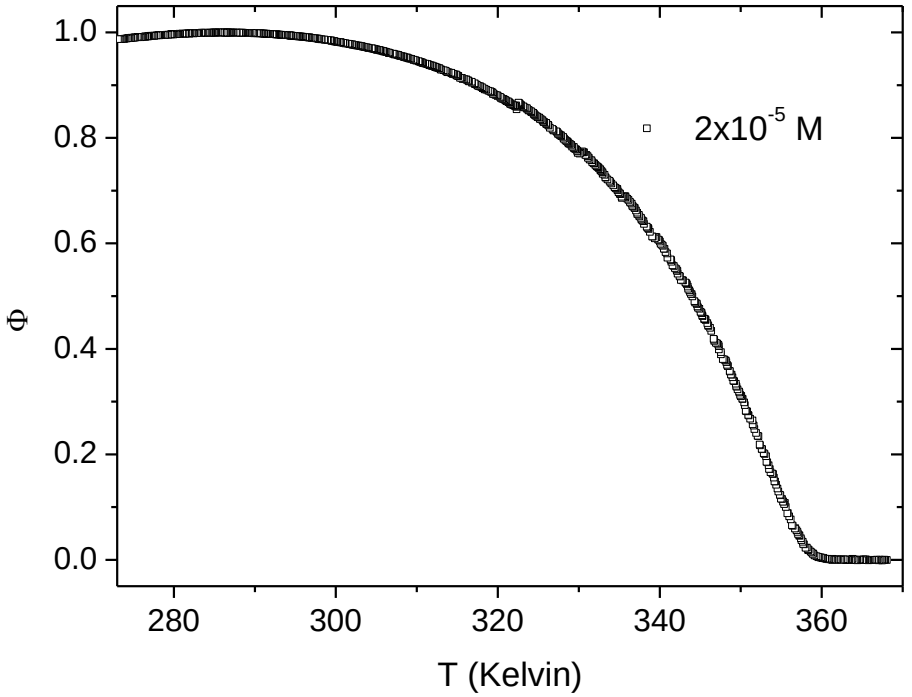


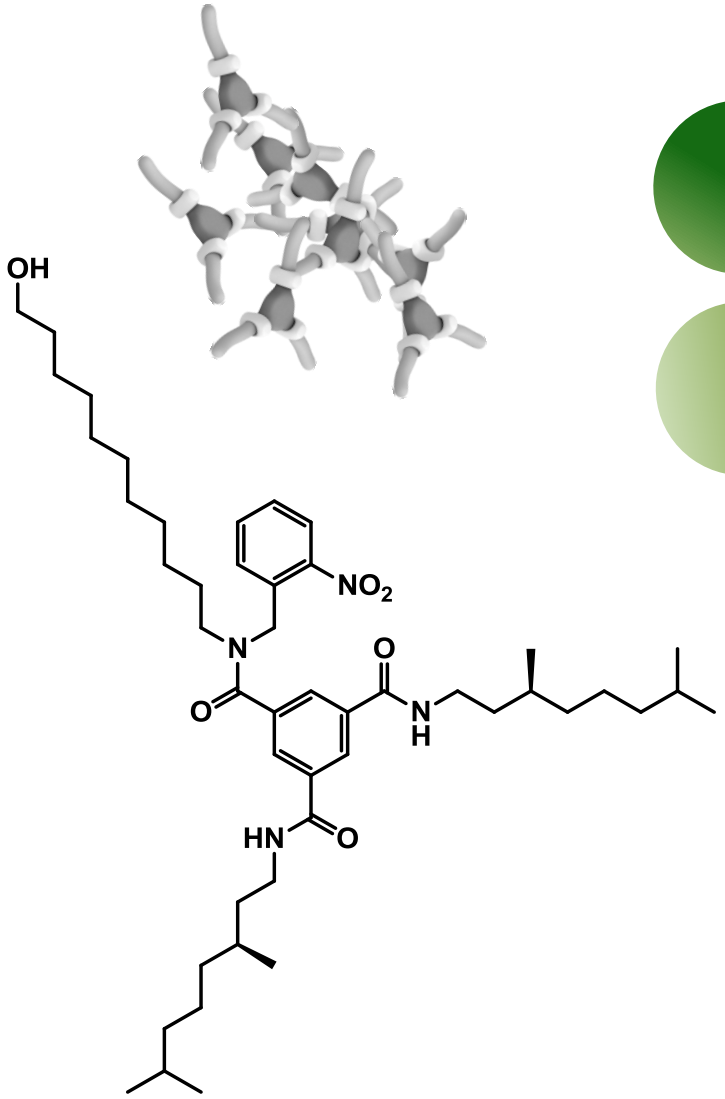
FT-IR: ν(NH) = 3174 cm^{-1}

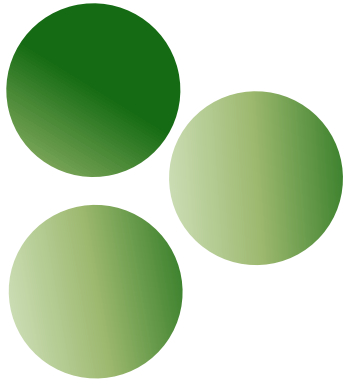


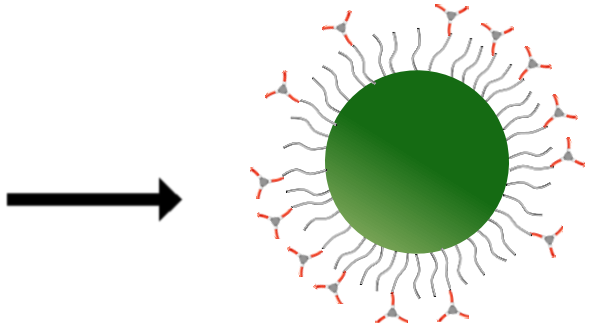
Solvent:











Silica colloids

d = 26 nm (AS-40)

d = 500 nm, green fluorescent core

META-ASSEMBLY AT NTU ATHENS

Orestes Ziogos, Ph.D. Student[1]

Leonidas Tsetseris, Assistant Professor[2]

Doros Theodorou, Professor[1]

[1]School of Chemical Engineering

[2]School of Applied Mathematics and Physical Sciences

RESEARCH PLANS

WP19: Atomistic simulation of discotic liquid crystals (DLCs) of graphene with electric dipoles

Task 19.1: Atomistic simulation of structure and thermodynamic properties

- Molecular arrangement at equilibrium
- Degree of orientational order
- Mass density and its dependence on *T*, *P*
- Elastic constants of solid phase
- Molar enthalpies of LC, solid phases
- Phase transition between LC and solid phases

Task 19.2: Atomistic simulation of DLC dynamics

- Characterization of short-time (1 μs) dynamics through computation of time autocorrelation functions for characteristic vectors
- Dependence of dynamics on the phase (crystalline-liquid crystalline)
- Comparison against spectroscopic measurements

RESEARCH PLANS

WP20: Mesoscopic simulation of discotic liquid crystals with electric dipoles

Task 20.1: Coarse-graining of DLC molecular models

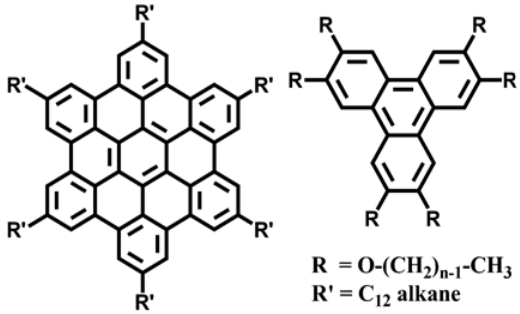
- Choose coarse-grained representations for the systems under study
- Develop effective potential energy functions for the coarse-grained models
- Validate against atomistic model predictions and experiment

Task 20.2: Prediction of phase diagrams and collective dynamics

- Conduct coarse-grained simulations to address long length and time scales
- Predict phase diagram
- Predict self-diffusivity and viscosity
- Validate against experimental measurements

PREVIOUS WORK

Atomistic simulations of triphenylene and hexabenzocoronene derivatives



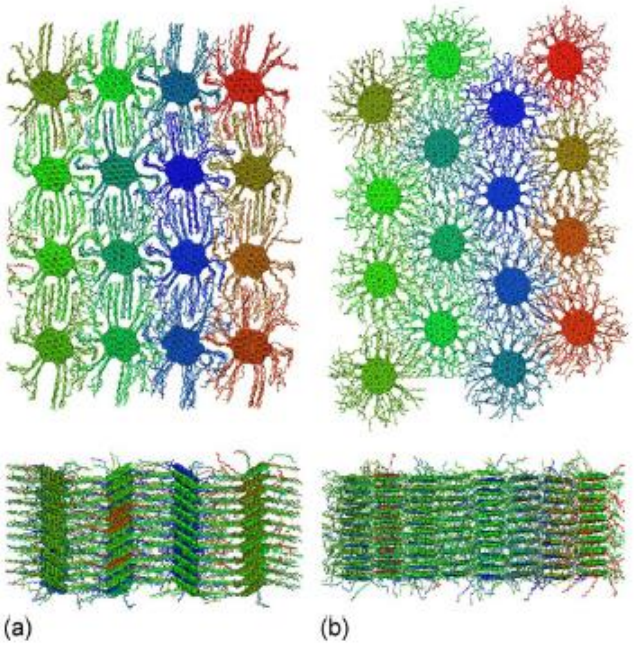
- Monitoring of phase transitions (from solid herringbone to liquid crystalline hexagonal) and their dependence on side chain length
- Characterization of structure in the columnar mesophase
- Estimation of charge carrier mobility in the columnar state
- Study of translational dynamics in the columnar state

Andrienko, D.; Marcon, V.; Kremer, K. *J. Chem. Phys*. **2006**, *125*, 124902.

Marcon, V.; Vehoff, T.; Kirkpatrick, J.; Jeong, C.; Yoon, D.Y.; Kremer, K.; Andrienko, D. *J. Chem. Phys*. **2008**, *129*, 094505.

Kirkpatrick, J.; Marcon, V.; Kremer, K.; Nelson, J.; Andrienko, D. *J. Chem. Phys*. **2008**, *129*, 094506.

Cinacchi, C.; Colle, R.; Tani, R. *J. Phys. Chem. B* **2004**, *108*, 7969-7977.

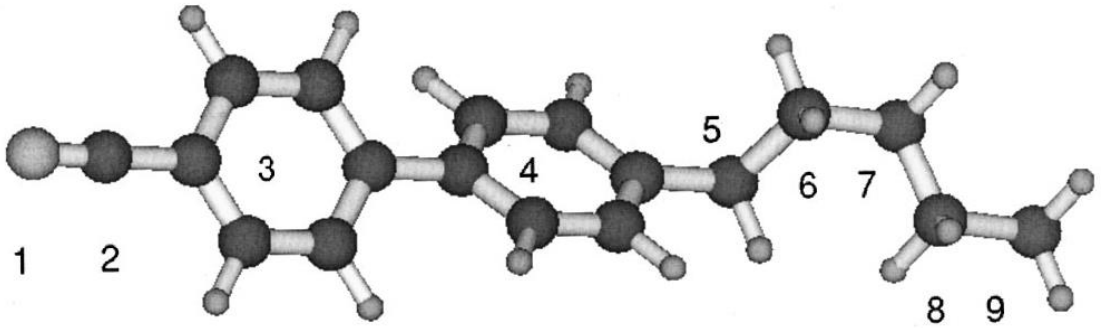


Configurations of HBCs in the "herringbone" arrangement encountered in the crystalline state (a) and in the columnar arrangement of the liquid crystalline state (b)

MNIBS: Multiscale Modelling of Nanostructured Interfaces for Biological Sensors

Antonia Vyrkou, Grigoris Megariotis, Adrien Leygue, DNT

5CB: 4-cyano-4'-pentyl biphenyl



Archetypal example of small molecule thermotropic Liquid Crystal (LC)

First synthesized 1973 (Gray, Harrison, Nash)

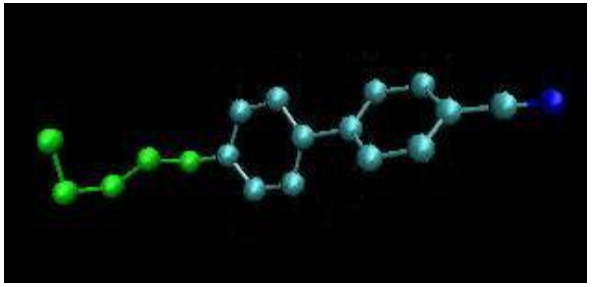
Used extensively in commercial applications (LC displays)

At p = 1 bar: T_m (crystal to nematic) = 294.1 K

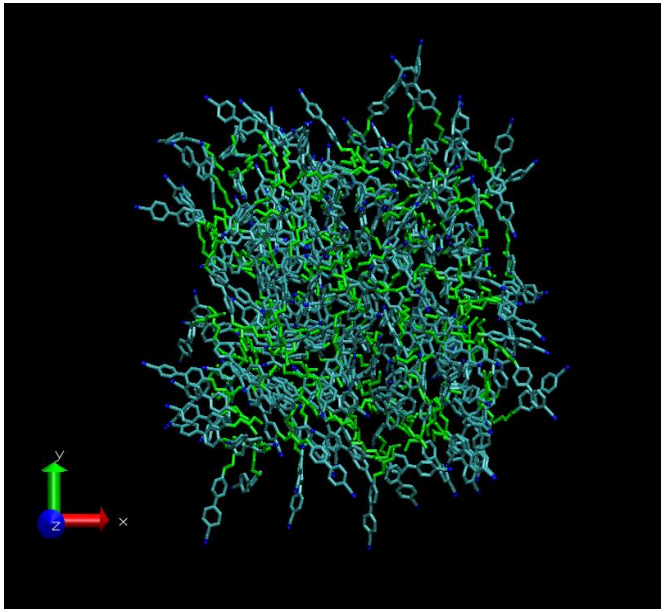
T_{NI} (nematic to isotropic) = 308.4 K

5CB: DETAILED SIMULATIONS

- United atom model:
  Tiberio, G.; Muccioli, L.; Berardi, R.; Zannoni, C. *Chem. Phys. Chem.* **2009**, *10*, 125.

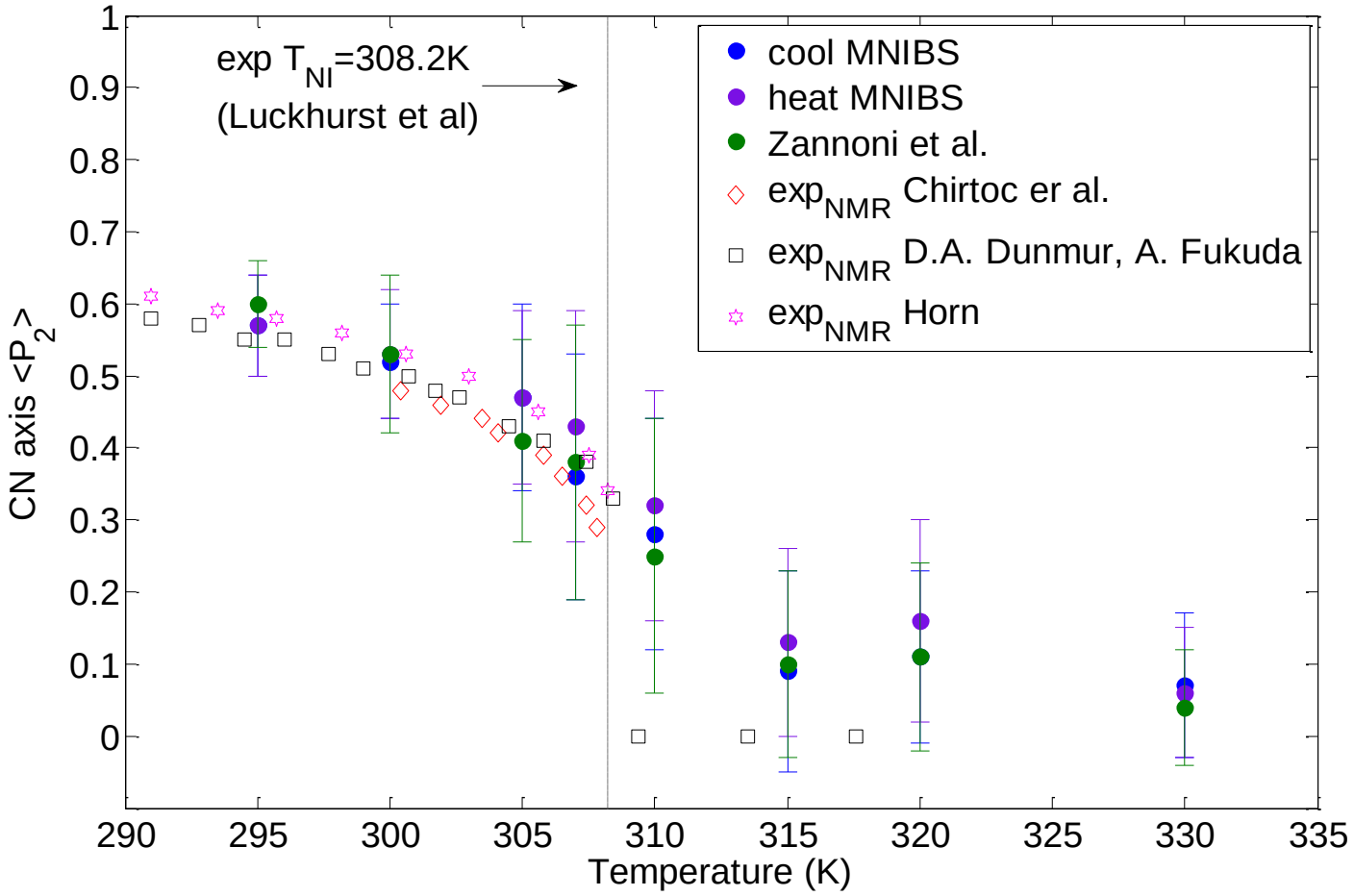


- Model optimized for the n-CB series
- Cubic box (216, 1728 molecules)
  NPT ensemble
  (*P*=1atm, *T*=295-330K)
  timestep=2fs
  Parrinello-Rahman, Nosé-Hoover
  PME
- GROMACS 4.0.3



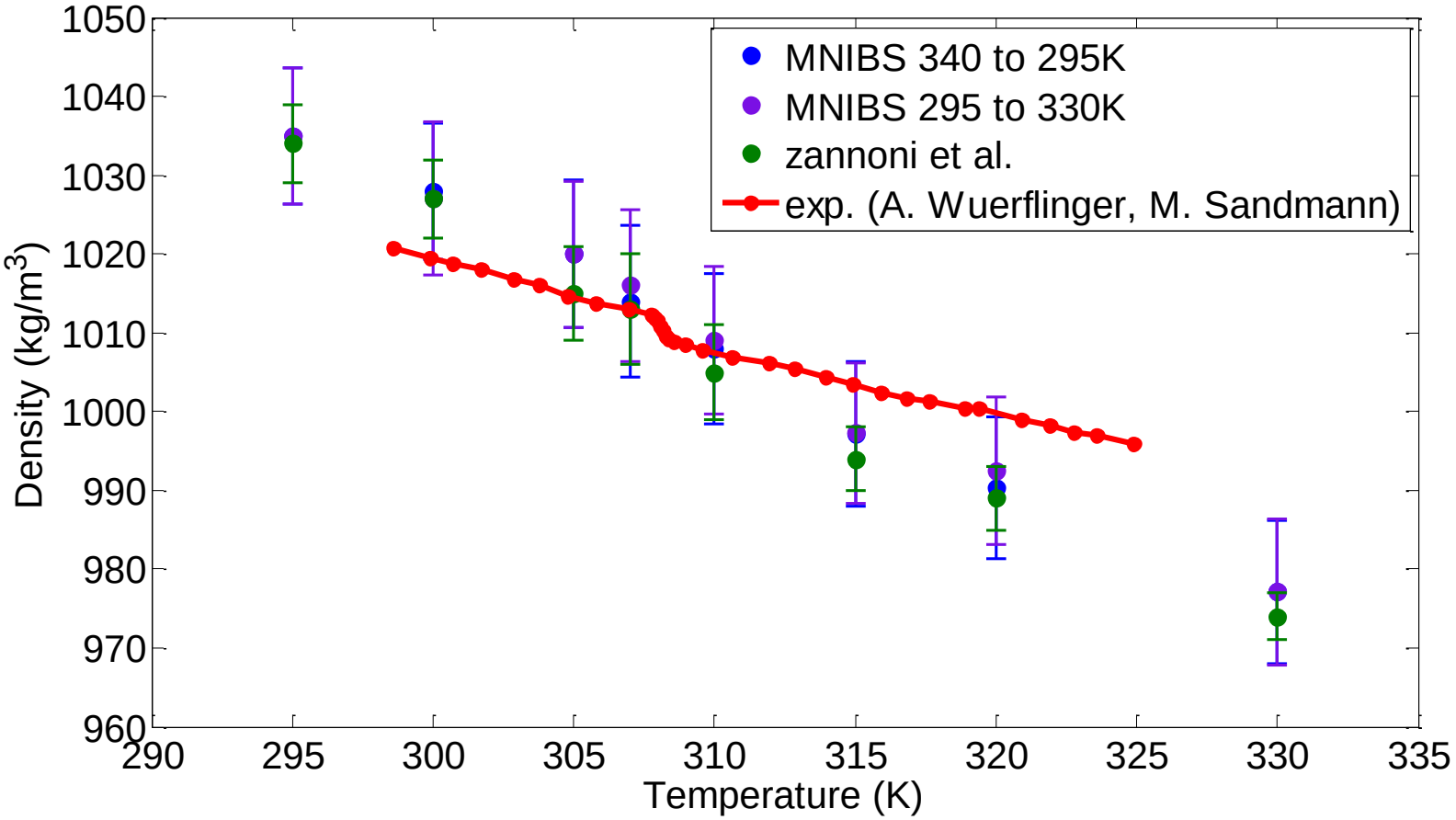
TEMPERATURE DEPENDENCE OF THE ORDER PARAMETER

Detailed 5CB model, 216 molecule system, 1 atm



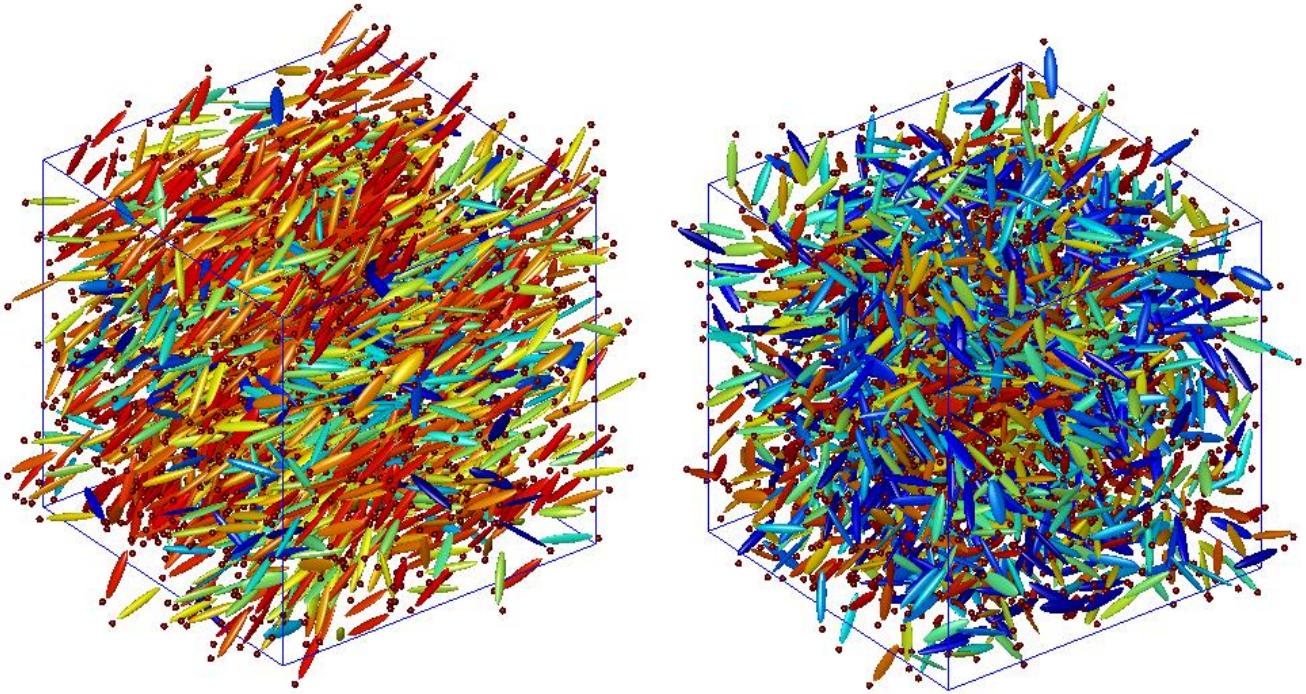
TEMPERATURE DEPENDENCE OF THE DENSITY

Detailed 5CB model, 216 molecule system, 1 bar



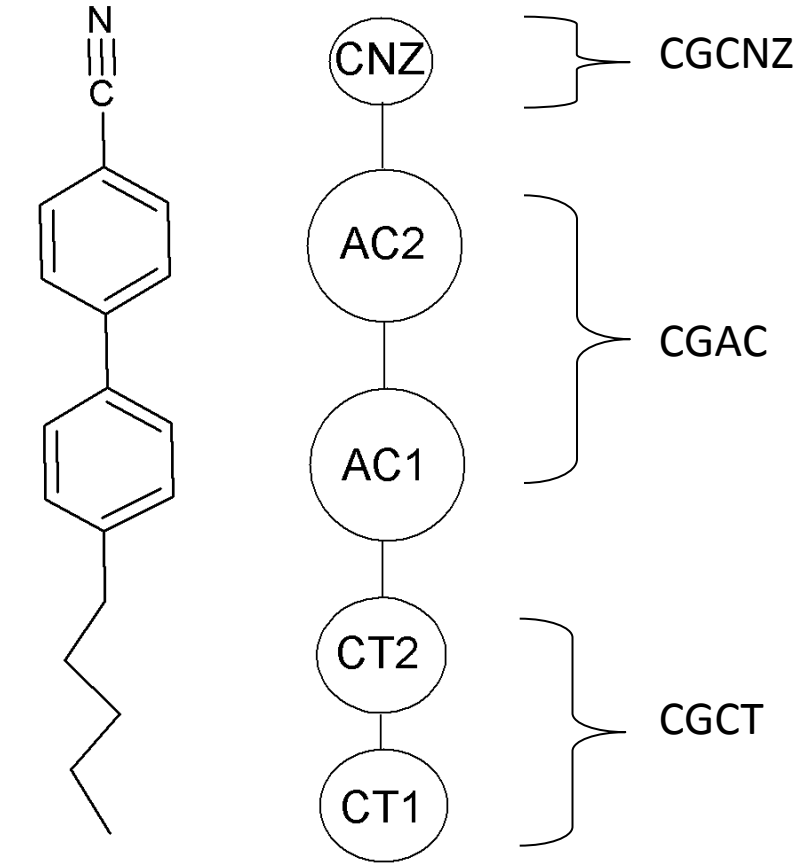
MOLECULAR CONFIGURATIONS

Detailed 5CB model, 1728 molecule system, 1 atm



- Representation as ellipsoids
  300K - Nematic phase (left)
  320K – Isotropic phase (right)

CHOICE OF A COARSE-GRAINED MODEL

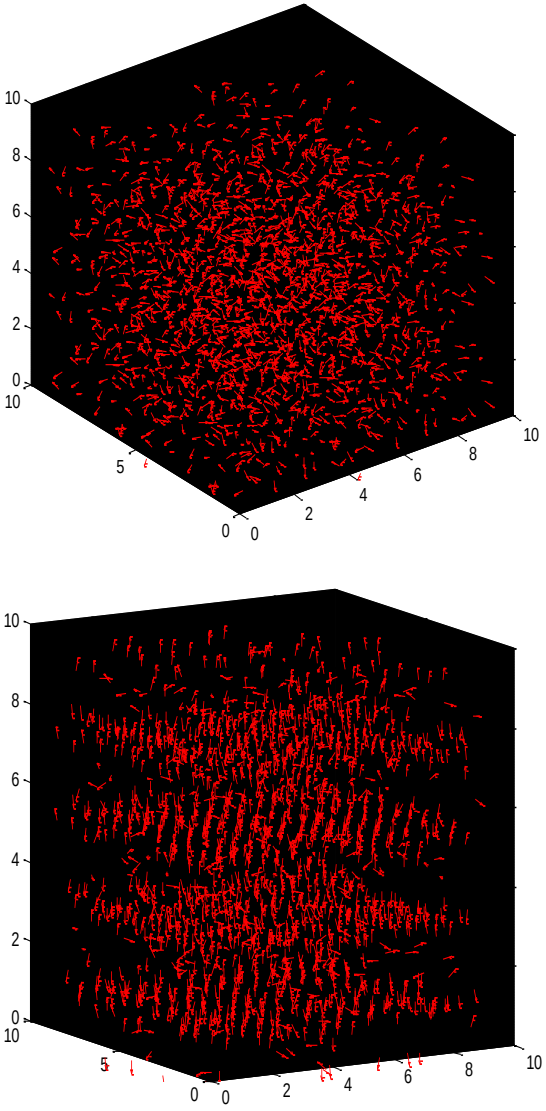


- **Five superatoms per molecule in place of 19 sites of the united-atom model**[1]
- **Three types of superatoms**
- **Development of the coarse-grained model at 315K (isotropic phase)**
- **Effective bonds constrained to their equilibrium values**
- **Reproduction of six RDFs and three distributions of effective bond angles**
- **Ramp correction for the pressure**

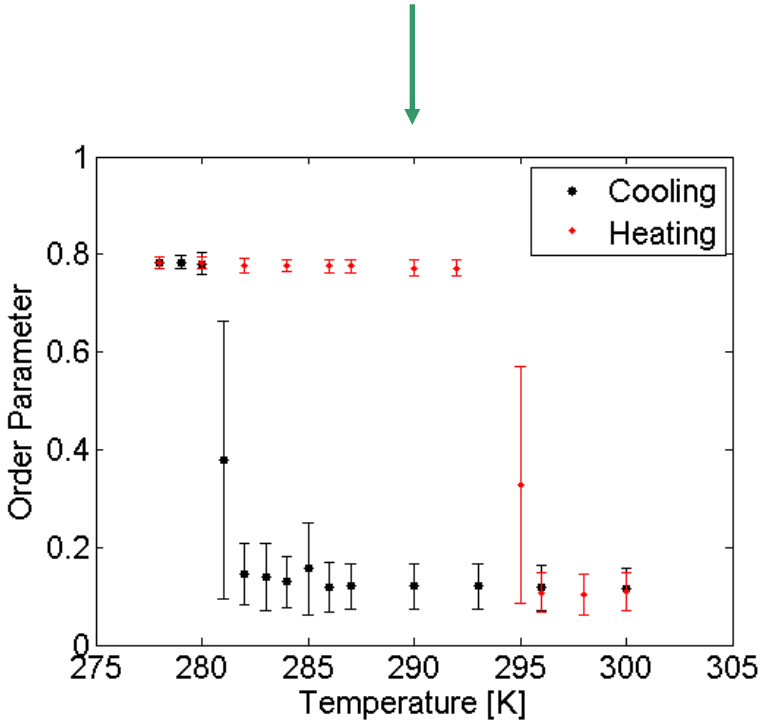
[1] G. Tiberio, L. Muccioli, R. Berardi, and C. Zannoni, *ChemPhysChem* **2008**, *10*, 125.

Megariotis, G.; Vyrkou, A.; Leygue, A.; DNT *Ind. Eng. Chem*. Res. **2011**, 50, 546.

STUDY OF THE COARSE-GRAINED MODEL IN THE LIQUID CRYSTALLINE REGION

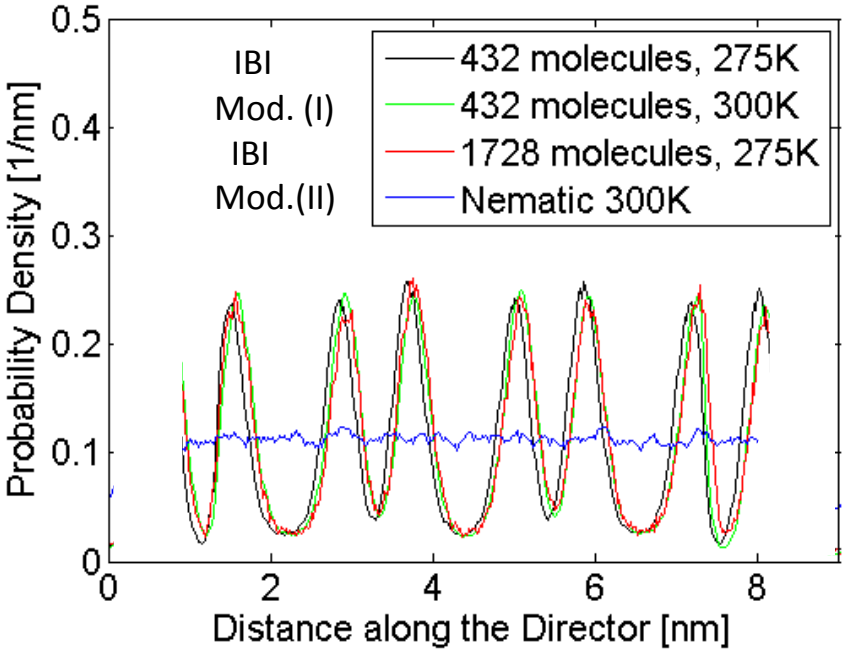


Estimate of transition points through CG Molecular Dynamics simulations at increasing and decreasing temperatures (rate of heating/cooling 0.3K/ns)



CHARACTERIZATION OF ORDERED STRUCTURE FOR THE MODIFIED COARSE-GRAINED MODELS

Distribution of molecular centres



T (K)	D_{II} / $D_{\perp}$
IBI 275	0.049±0.027
Mod. (I) 300	0.22±0.06
Mod. (II) 300	1.149±0.450

	Modified CG Model (II)	United-atom Model	Exp[1]
Density [kg/m^3]	1035±3	1028	1020
Order parameter	0.512±0.004	0.54	0.54

Smectic phase: Bilayer structure
Nematic phase: Flat distribution

[1] M. Hird, *Physical Properties of Liquid Crystals*, Vo1 1: *Nematics*, IEE (London, 2001 pp. 3-16).

AdvCarbonMatls: PREDICTING THE PROPERTIES OF CARBONACEOUS PITCHES VIA MOLECULAR MODELING

Marie Curie IIF, Project No 234999, 1/3/2009-31/8/2011

Professor Mark C. Thies, Clemson University

Relevant Objectives:

- Develop molecular dynamics force fields needed to model the dominant polyaromatic hydrocarbons present in petroleum pitches. Evaluate force-field candidates with pure-component density and heat of vaporization data.

- Simulate crystalline state for representative pure-component polycyclic aromatic hydrocarbons.

FORCE FIELDS EVALUATED

- OPLS/AMBER

  Jorgensen, W.L.; Maxwell, D.S.; Tirado-Rives, J. *J. Am. Chem. Soc*. **1996**, *118*, 11225-11236.

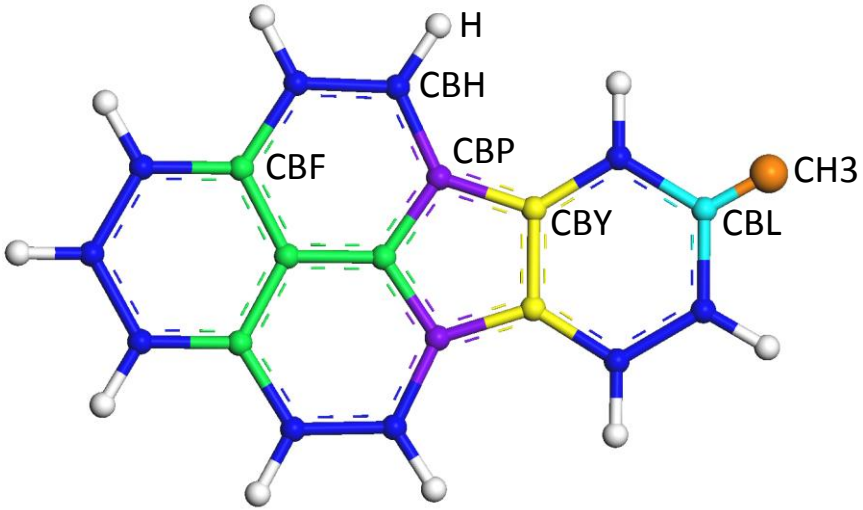
- KRE

  Andrienko, D.; Marcon, V.; Kremer, K. *J. Chem. Phys*. **2006**, *125*, 124902.

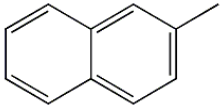
$$\mathcal{V}(\mathbf{r}) = \sum_{bonds} \frac{1}{2} k_{bond} \left(r - r_0\right)^2 + \sum_{angles} \frac{1}{2} k_\theta \left(\theta - \theta_0\right)^2 + \sum_{torsions} k_\varphi \left[1 + \cos(n\varphi - \delta)\right] +$$

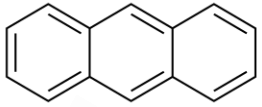
$$\sum_{torsions} k'_\varphi \cos^x(\Psi_i) + \sum_{impropers} k_\xi \left(\xi - \xi_0\right)^2 + \sum_i \sum_{j>i} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{1}{4\pi\varepsilon\varepsilon_0} \frac{q_i q_j}{r_{ij}} \right\}$$

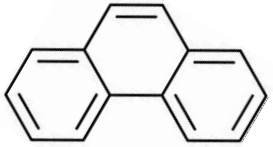
TYPES OF INTERACTION SITES CONSIDERED

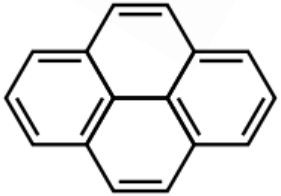


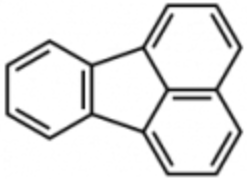
- H : Aromatic hydrogen
- CH3: Methyl group bonded to aromatic carbon
- CBH: Aromatic carbon bonded to hydrogen
- CBF: Fused aromatic carbon
- CBL: Aromatic carbon bonded to an alkyl group
- CBY: Benzene carbon belonging to 5-membered ring
- CBP: Naphthalene carbon belonging to 5-membered ring











Component	ρ(kg/m^3)				ΔH^{vap}(kJ/mol)		
	OPLS	KRE	Expt		OPLS	KRE	Expt
Benzene							
298.15 K, 1.01325 bar	863	884	874[a]		33.2	34.1	33.8[a]
2-Methylnaphthalene							
373.15 K, 1.01325 bar	932	954	945[b]		53.2	54.8	54.5[b]
473.15 K, 0.375 bar	847	867	865[b]		47.3	48.5	48.5
573.15 K, 3.23 bar	746	771	769[b]		41.1	42.5	41.6[b]
673.15 K, 12.4 bar	600	629	644[b]		33.5	34.9	31.2[b]
Anthracene							
493.15 K, 0.056 bar	954	974	972[c]		62.7	64.0	62.1[c]
593.15 K, 0.67 bar	866	885	901[c]		55.4	56.7	56.0[c]
Phenanthrene							
373.15 K, 0.0003 bar	1064	1084	1069[c]		72.1	73.6	70.3[c]
493.15 K, 0.0581 bar	971	988	982[c]		63.3	64.4	62.4[c]
593.15 K, 0.691 bar	884	904	910[c]		56.2	57.4	55.8[c]
Pyrene							
423.81 K, 0.00058 bar	1067	1094	...		74.8	77.1	77.9[d]
573.15K, 0.152 bar	951	979	...		64.2	66.4	67[d]
667.95K, 1.01325 bar	858	898	...		56.8	59.9	58[d]
Fluoranthene[f]							
383.33 K, 0.00016 bar		1091	...			77.5	73.53[e]
473.15 K, 0.0105 bar		1022	...			70.5	67.4[e]
573.15 K, 0.193 bar		943	...			63.5	62.4[e]
655.95 K, 1.01325 bar		866	...			57.3	57.8[e]

Liquid ρ within 1%

ΔH^{vap} within 2%

of experiment

[a,b,c,d,e]Superscipts denote data sources.

a. Jorgensen et al., *J. Comp. Chem.* **1993**, *14(2)*, 206-215.

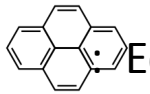
b. API Monograph Series. 1- and 2-Methylnaphthalene and Dibenzanthracenes. Publ. 724, 1985.

c: API Monograph Series. Anthracene and Phenanthrene. Publ. 708, 1979.

d: API Monograph Series. Four-ring Condensed Aromatic Compounds. Publ. 709, 1979.

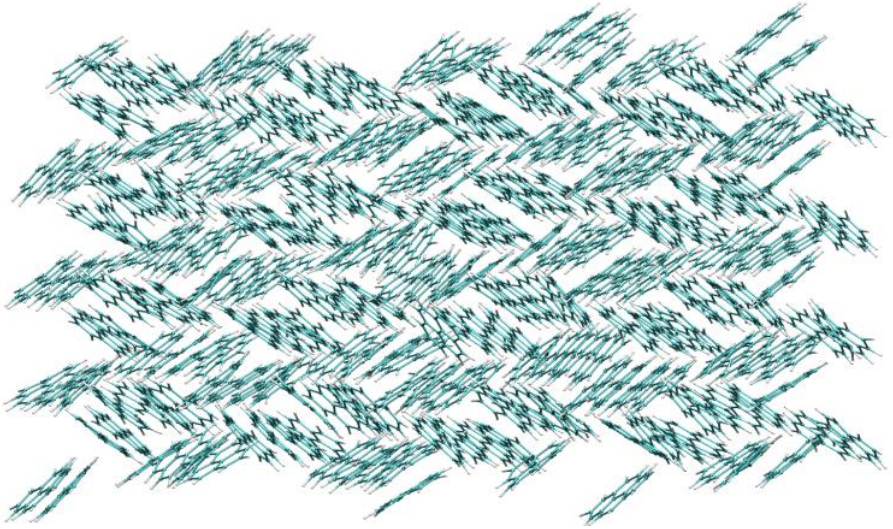
e: API Monograph Series. Acenaphthylene, Acenaphthene, Fluorene, and Fluoranthene. Publ. 715, 1981

VALIDATION IN THE CRYSTALLINE STATE

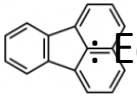
Pyrene  Equilibrates at structure close to that determined by X-ray diffraction.

KRE: Unit cell parameters off by 0.06%
Unit cell volume off by 0.24%

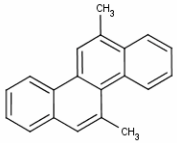
OPLS: Unit cell parameters off by 0.28%
Unit cell volume off by 0.71%



256 pyrene molecules in 4×4×4 unit cells (OPLS).

Fluoranthene  Equilibrates at structure close to that determined by XRD

KRE: Unit cell parameters off by 0.69%
Unit cell volume off by 2%

5,12-Dimethylchrysene 

KRE: Unit cell parameters longer than expt. by 1.50%
Unit cell volume larger by 4.5%. Partial melting of crystalline structure

OPLS: Unit cell parameters longer shorter than expt. by 1.2%
Unit cell volume smaller by 3.5%. Integrity of crystal remains unchanged.

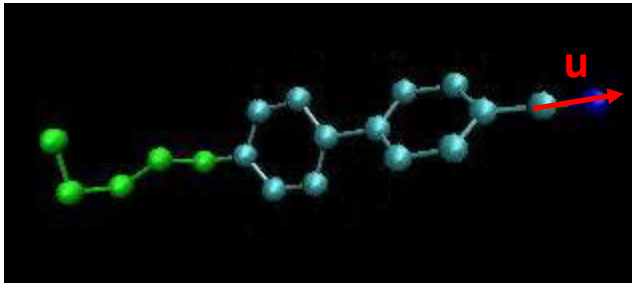
MEASURES OF ORDER

- Second order parameter P_2

$$P_2 = \langle -2\lambda_2 \rangle$$

λ_2 = middle eigenvalue[1] of the Saupe ordering tensor:

$$\mathbf{Q}(t) = \sum_{i=1}^{N} \left[3\mathbf{u}_i(t)\mathbf{u}_i(t) - \mathbf{I} \right] / 2N$$



u taken as the CN bond vector

- Director **n**: Unit eigenvector corresponding to largest eigenvalue of **Q**

[1] Epenga, R.; Frenkel, D. *Mol. Phys.* **1984**, *52*, 1303

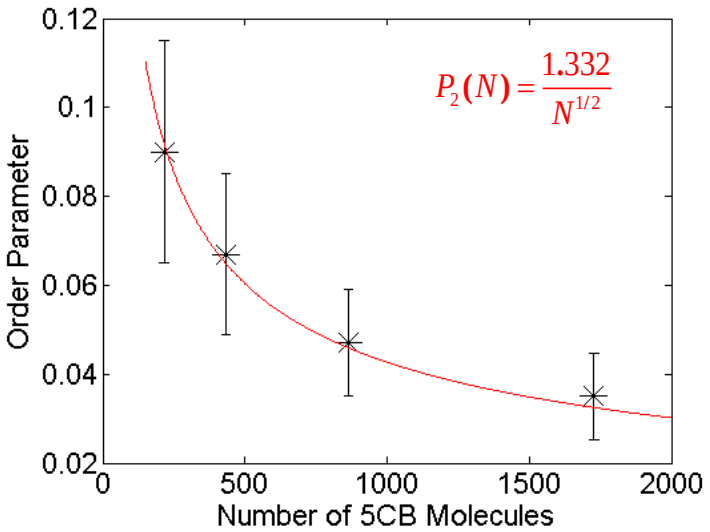
QUANTIFICATION OF IBI CONVERGENCE AND SYSTEM SIZE EFFECTS

Relative errors %

$$RE_i = \frac{\int_0^{1.5\,nm} w_{\alpha\beta}(r)\left[g_{\alpha\beta,i}(r) - g_{\alpha\beta}(r)\right]^2 dr}{\int_0^{1.5nm} w_{\alpha\beta}(r)\left[g_{\alpha\beta}(r)\right]^2 dr} \times 100 \qquad w_{\alpha\beta}(r) = \exp(-r/1nm)$$

$\alpha\beta$	CGCT-CGCT	CGCT-CGAC	CGCT-CGCNZ	CGAC-CGAC	CGAC-CGCNZ	CGCNZ-CGCNZ
RE_1[a]	2.56	0.71	1.93	1.00	0.294	2.08
RE_2[b]	1.08	0.340	0.861	1.40	1.76	0.751
RE_{15}[c]	0.111	0.0862	0.0584	0.153	0.100	0.104

System size effects in the order parameter (coarse-grained model, isotropic phase)



Megariotis, G.; Vyrkou, A.; Leygue, A.; DNT *Ind. Eng. Chem. Res.* **2011**, 50, 546.

MODIFIED COARSE-GRAINED MODELS FOR THE DESCRIPTION OF THE LC-PHASE

- Modified model (I): Rescaling of all intermolecular effective potentials by factor α=1.05. Smectic phase with a transition point equal to 302 K (close to the experimental ordering temperature).

- Modified model (II): Rescaling of two effective potentials, CGCT-CGCT (tail-tail) and CGCNZ-CGCNZ (head-head), by α=1.20. Nematic phase for systems consisting of more than 500 molecules.

Megariotis, G.; Vyrkou, A.; Leygue, A.; DNT *Ind. Eng. Chem*. **2011**, 50, 546.

Hierarchical Multi-scale Modeling of Core-Shell Nanoparticles

THALIS "META-ASSEMBLY" Project: Self-assembly and dynamics in metastable states. From molecular and supramolecular to mesoscopic systems.

TEAM 3: Sub-team of the *Department of Applied Mathematics, University of Crete*

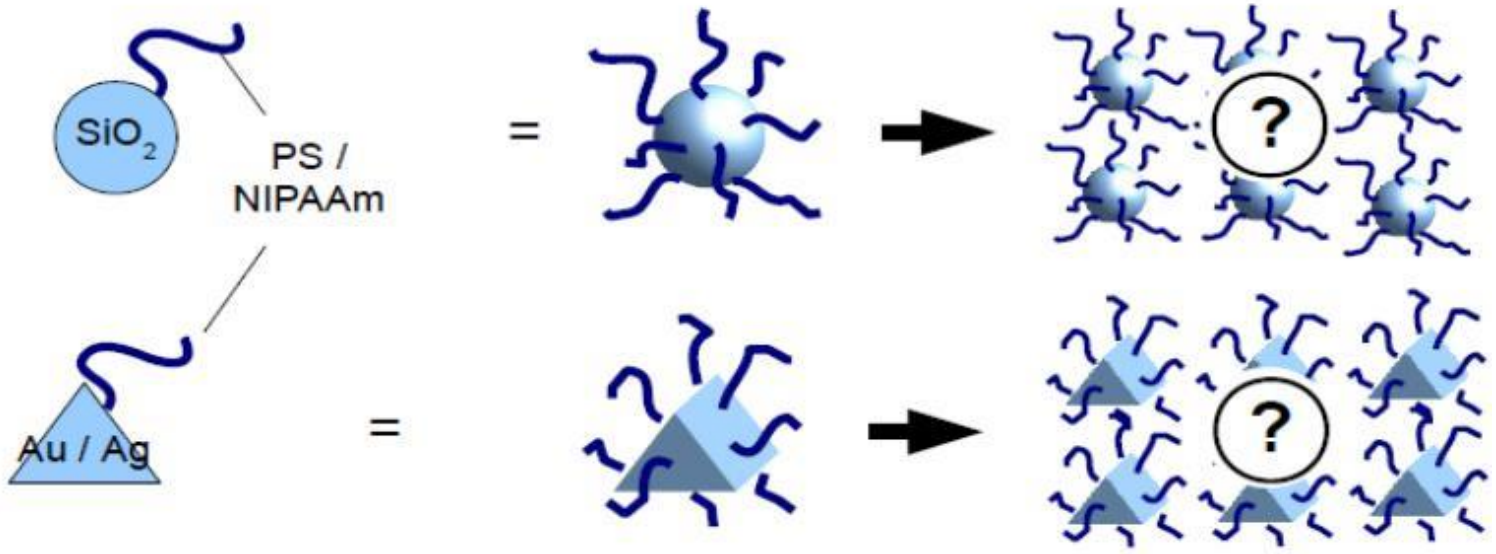
First Meeting Thessaloniki, 01/12/12

Proposed Work - Work Packages

- **WP 21: Atomistic simulation of core-shell type nanoparticles**
  - **Task 21.1: Atomistic simulation of structure, thermodynamics and computation of interaction potentials for core-shell type nanoparticles.**
  - **Task 21.2: Atomistic simulation of the dynamics of core-shell nanoparticles.**
- **WP 22: Mesoscopic simulation of core-shell hybrid nanoparticles**
  - **Task 22.1: Derivation of a coarse-grained model for core-shell nanoparticles.**
  - **Task 22.2: Study of self-organization and collective dynamics of core-shell nanoparticles.**
- **WP 25: Collaboration with Prof. Likos (Mesoscopic model and cooperativity of core-shell nanoparticles).**

Systems

❑ **Model Systems:**



❑ **Proposed core/shell systems:**

➢ **Core: Au (prism structure), SiO2**

➢ **Shell: PS, PNIPAAm**

Hierarchical Multi-scale Modeling of Core-shell Nanoparticles

❑ **STAGES:**

1. **(?) Ab-initio (DFT) calculations of small fragments (e.g. monomers/solid layers):**
   - **Study of structure in the most detailed level.**
   - **Development of accurate classical force field.**

2. **Microscopic (atomistic) simulations of small (low M) systems for short times.**

3. **Development of the effective CG force field using the atomistic data-configurations.**

4. **CG simulations (MD or MC) with the new coarse-grained model of large systems for longer times.**

5. **Re-introduction (back-mapping) of the atomistic detail if needed.**

Relevant Work: Polymer/Metal Interfaces

Hierarchical multiscale modelling

Quantum calculations (DFT)

↓

Develop surface potentials

↓

Atomistic MD simulations

↓

Coarse-grained MD simulations

Develop atomistic surface potentials

- Assume PS = benzene + ethane
- DFT adsorption energy vs. distance from surface for several molecular orientations
- Fit classical pair potentials to DFT data

Polystyrene (PS)

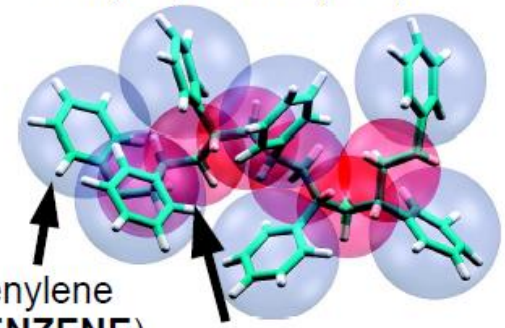


Image from Macromol. **42** 7579 (2009)

[K. Johnston and VH, J. Phys. Chem. C, 115, 1407 (2011); Soft Matter 8, 6320 (2012)]

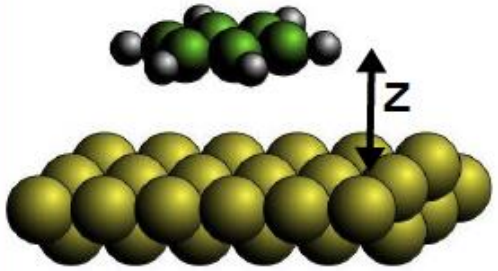
Molecule/Surface Interaction

- Customised VASP code
- DFT + vdW-DF using PBE exchange [1,2]
- Adsorption is due to vdW forces

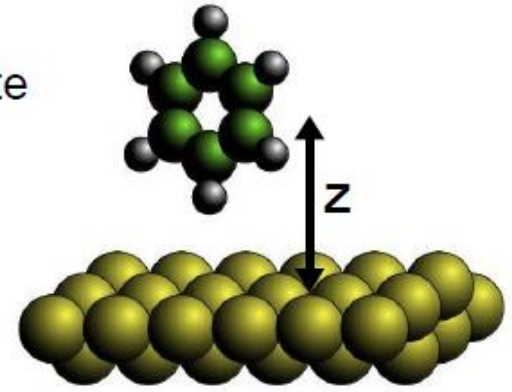
$E_{adsorption}$ (kJ/mol)	
Present [3]	**82.1**
Ref [4]	77.2
DFT+D [5]	73.3
Expt TDS [6]	61.8

[1] Dion PRL **92** (2004)
[2] Gulans PRB **79** (2009)
[3] Johnston JPCC **115** (2011)
[4] McNellis PRB **80** (2009)
[5] Tonigold JCP **132** (2010)
[6] Syomin JPC 105 (2001)

Lowest energy structure:
Benzene flat on hollow site

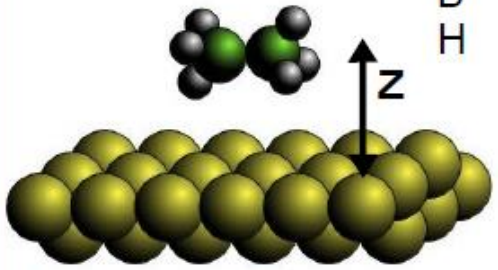


Benzene flat

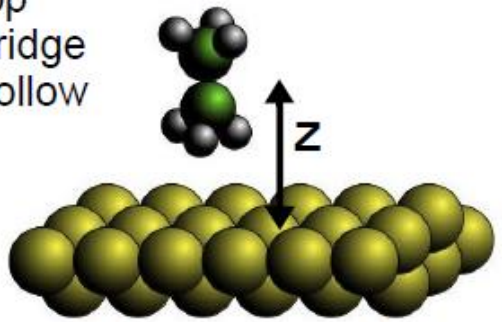


Benzene vertical

Sites:
T top
B bridge
H hollow



Ethane flat



Ethane vertical

Polymer/Metal Interfaces: From Ab-initio to Atomistic Scale

✓ DFT calculations can be used for modeling the interaction of a few atoms with the solid surface: We need to "build a bridge" between ab-initio and classical simulations.

❑ New microscopic (atomistic) interaction potential : Parameterization of DFT data E_{ads}^{DFT}

➢ For *N* polymer atoms interacting with *M* surface atoms we have: $E_{ads}^{AT} = \sum_{i=1}^{N}\sum_{j=1}^{M} V(r_{ij})$

➢ $V(r_{ij})$ is the classical non-bonded potential (e.g. LJ type)

❑ Needed: Optimization over many parameter space, i.e. a highly complex numerical problem. Idea: Use a Simulated Annealing code.

✓ Minimized (Cost) function is defined as the difference between atomistic and DFT obtained polymer/metal interaction energy:

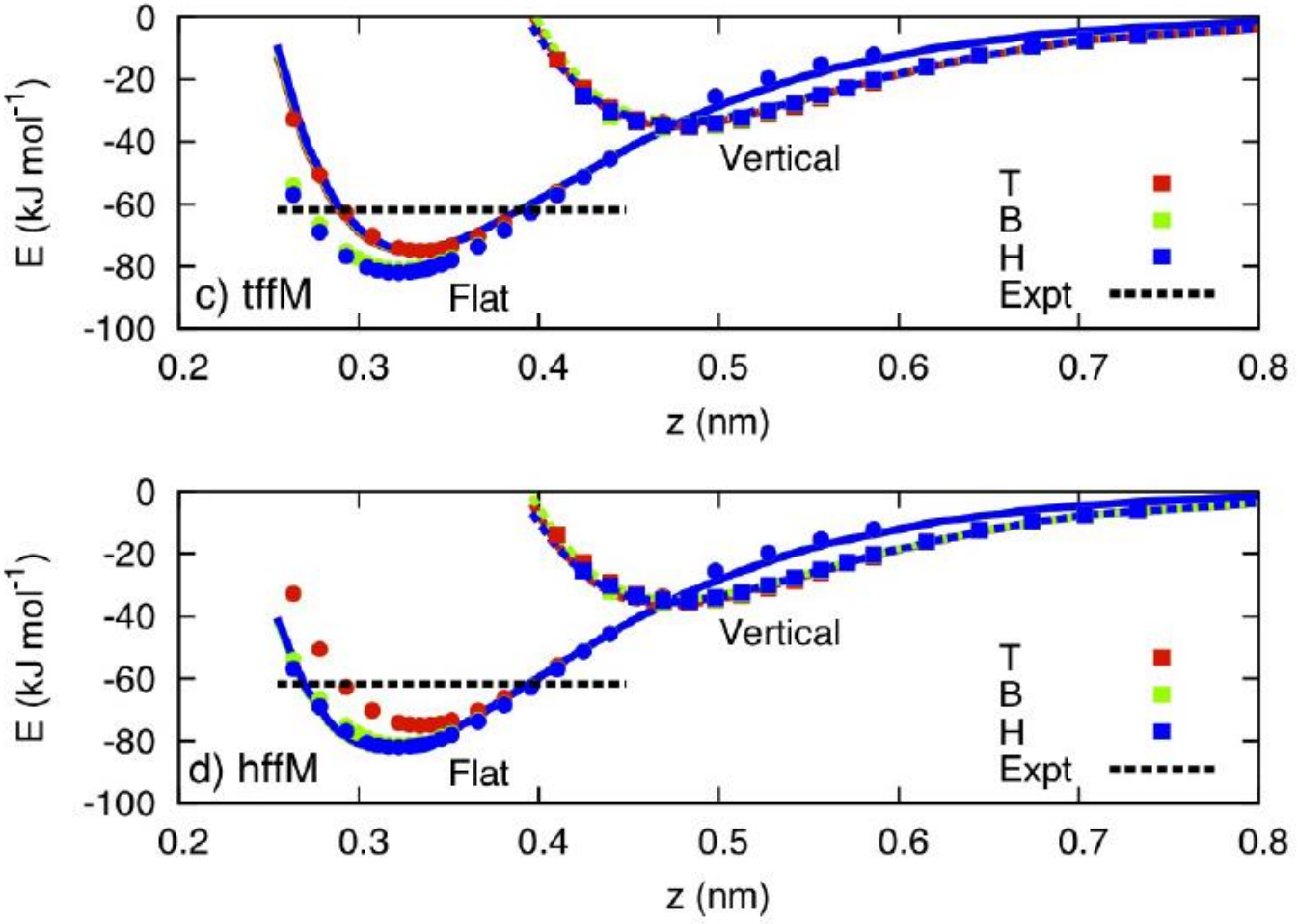
$$F = \sum_{i=1}^{n_{confs}} \sum_{j=1}^{n_k} \left[\left(E_{ads}^{DFT}\left(i, z_j\right) - E_{ads}^{AT}\left(i, z_j\right) \right)^2 W\left(i, z_j\right) \right]$$

-- n_{confs}: number of molecule conformations.
-- n_k: number of molecule-surface distances (z_j) for each conformation.
-- $W(i,z_j)$: statistical weights.

Polymer/Metal Interfaces: Parameterization of DFT data using a SA code

➢ **Benzene/Au interaction - use a more detailed Morse potential:**

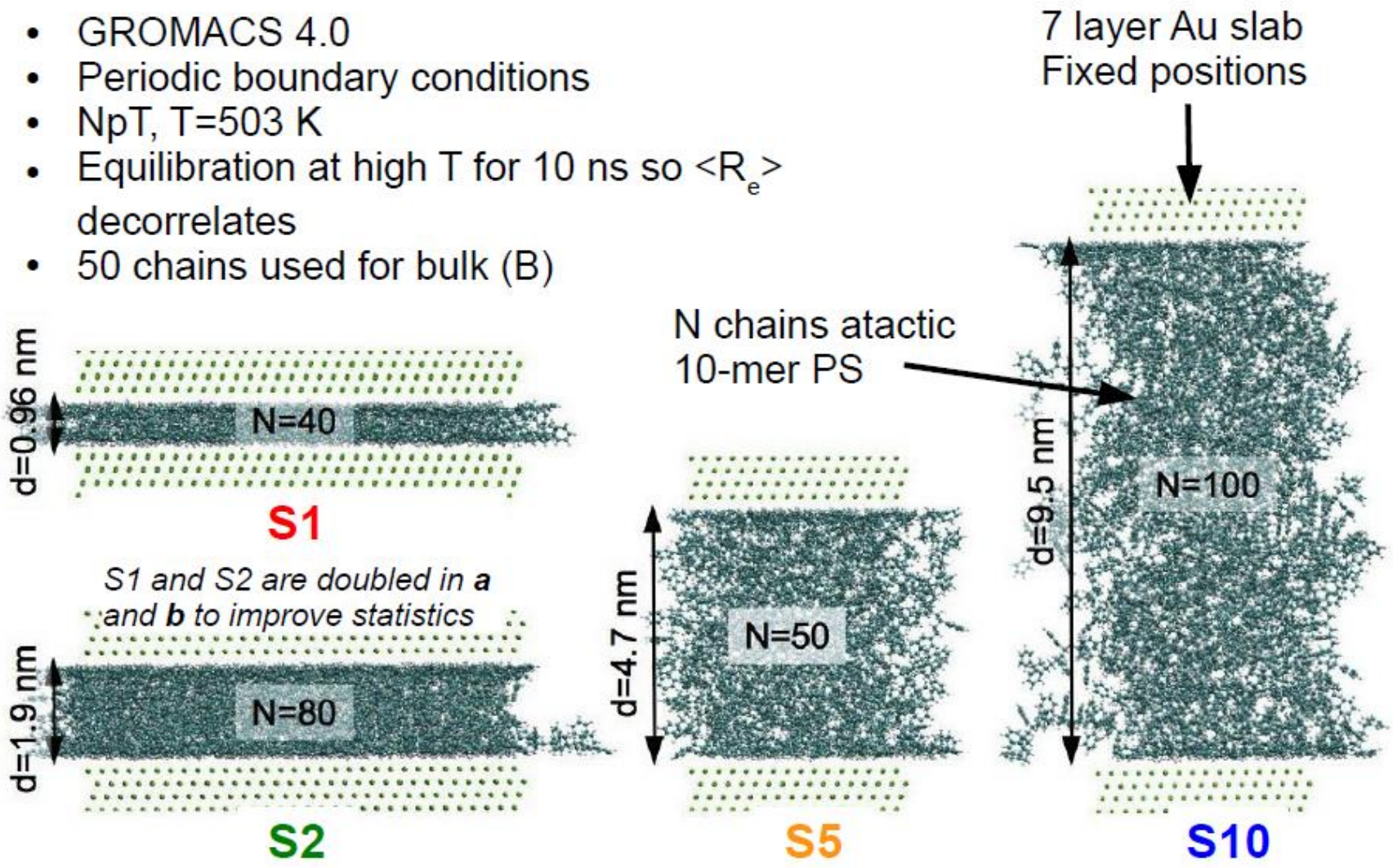
$$V_{LJ}(r_{ij}) = \varepsilon_{ij}\left[\exp\left(-2\alpha_{ij}\left(r_{ij}-r_{0,ij}\right)\right)-2\exp\left(-\alpha_{ij}\left(r_{ij}-r_{0,ij}\right)\right)\right]$$



Very good agreement between DFT and Atomistic data at all distances!

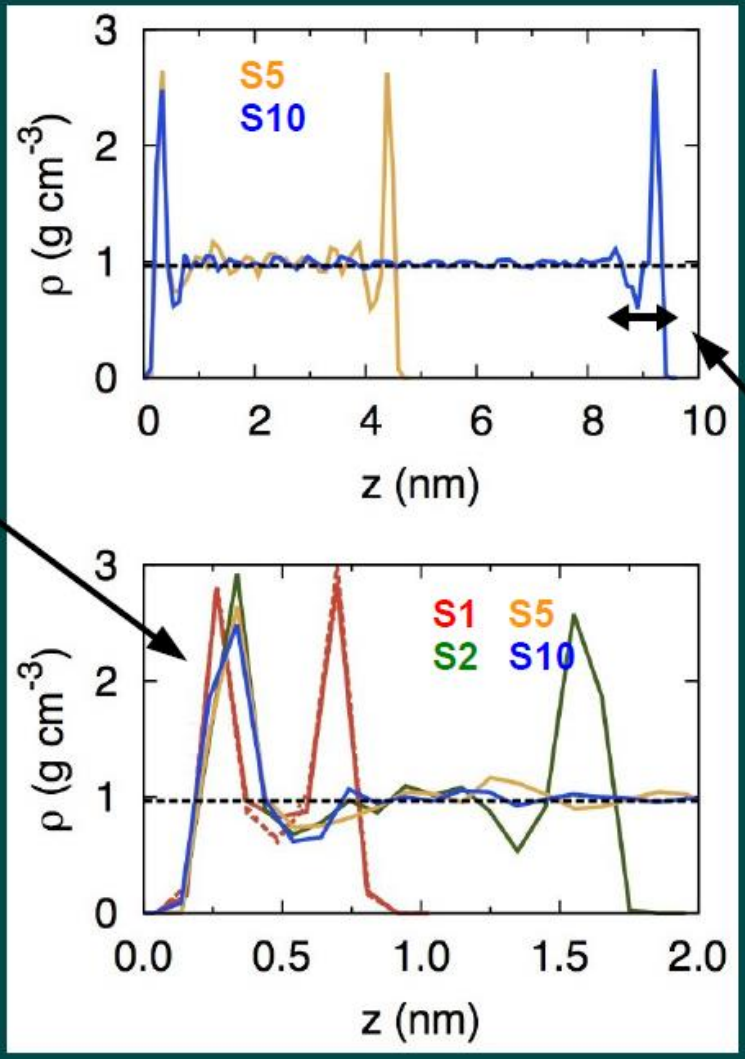
Hybrid Polystyrene/Au Systems: Atomistic Model Systems

- GROMACS 4.0
- Periodic boundary conditions
- NpT, T=503 K
- Equilibration at high T for 10 ns so $\langle R_e \rangle$ decorrelates
- 50 chains used for bulk (B)



Hybrid Polystyrene/Au Systems: Density - Structure

Density profiles



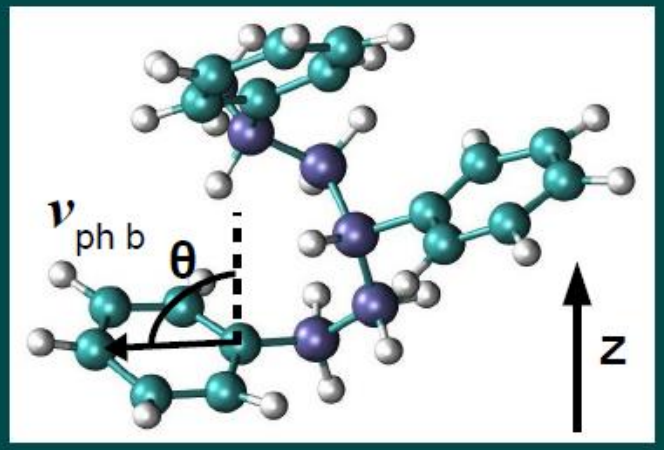
Single peak at surface (adsorption layer)

Film reaches bulk density ≈1.5 nm from surface

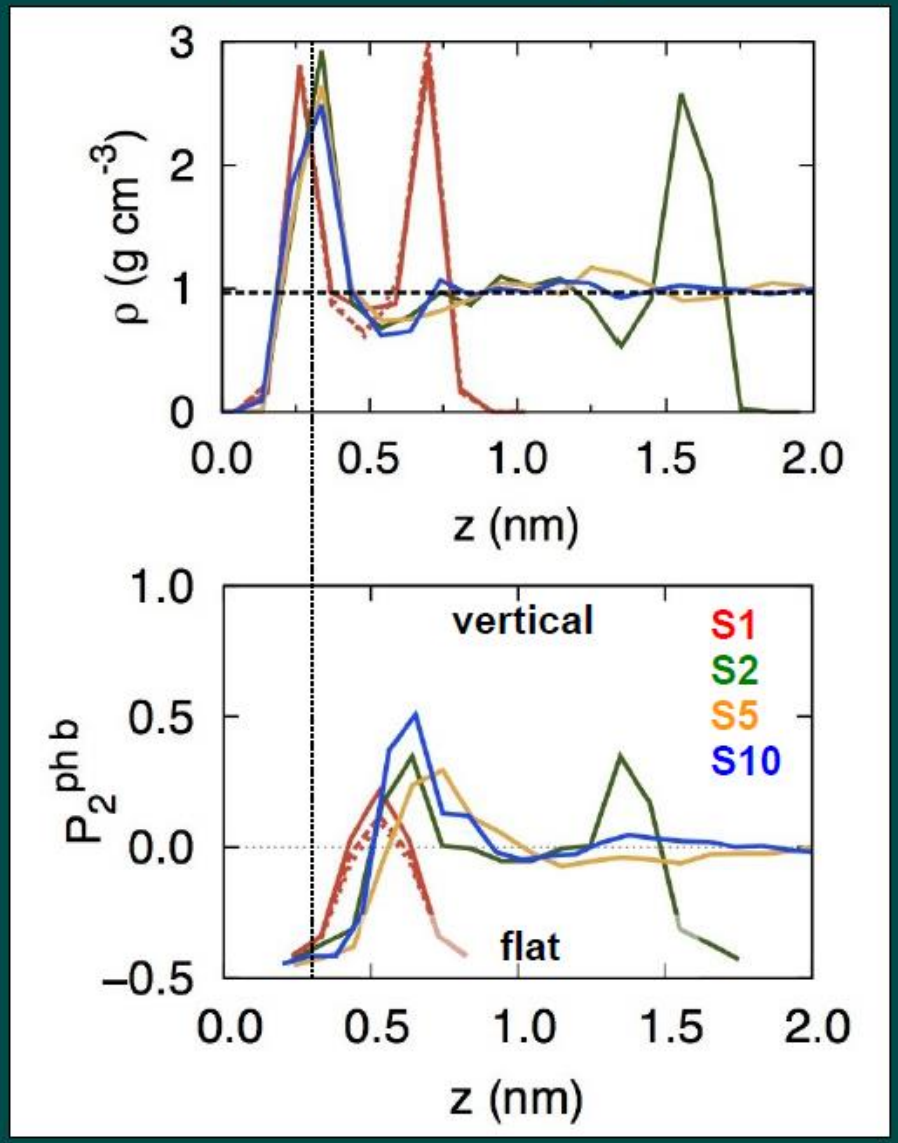
Structure – Orientation parameter P_2

$$P_2 = \frac{3}{2}\langle \cos(\theta) \rangle - \frac{1}{2}$$

= +1.0 perpendicular
-0.5 parallel

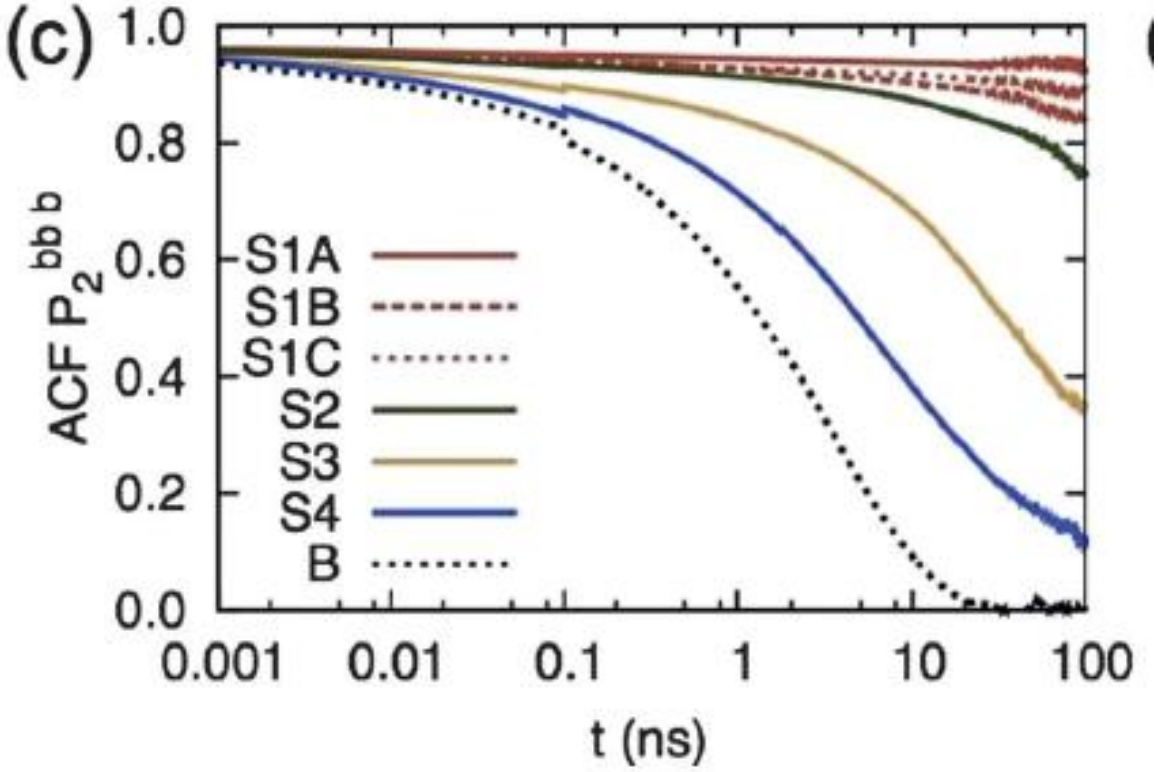


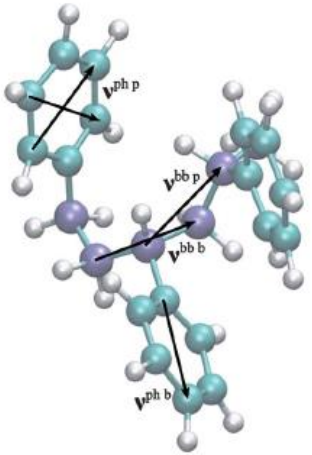
Phenyl rings in adsorption layers align parallel to surface



PS Local Dynamics as a function of distance from the Au surface

- **Local dynamics of different vectors along the monomer**





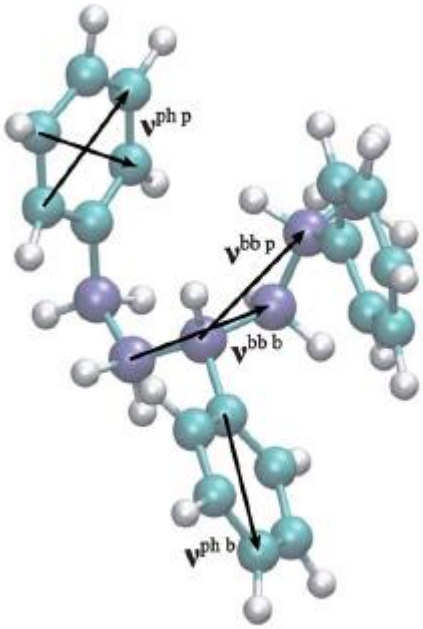
$$P_2(t) = \frac{1}{2}\left(3\left\langle \cos^2\left(\theta(t)\right)\right\rangle - 1\right)$$

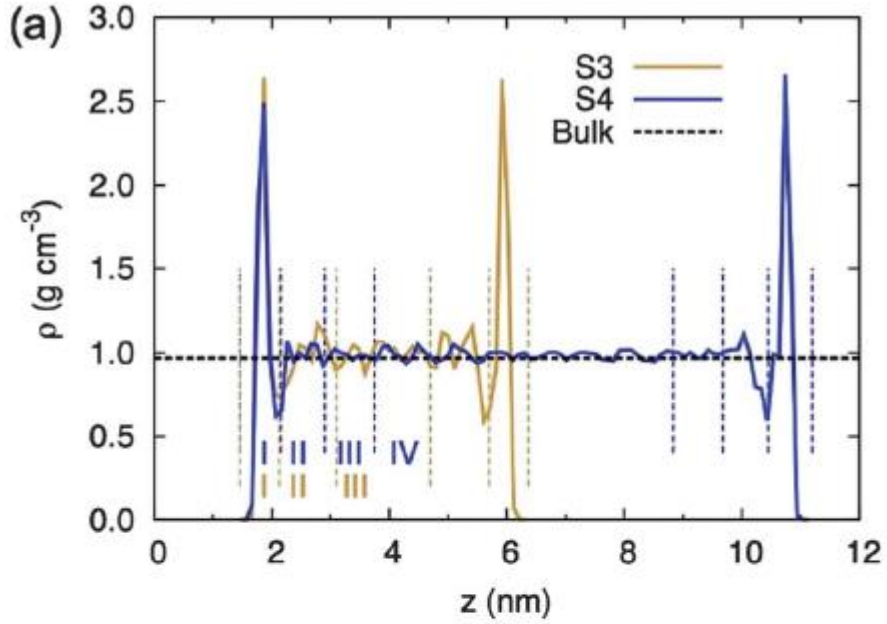
- **P_2(t) can be fitted with stretched exponential functions:**

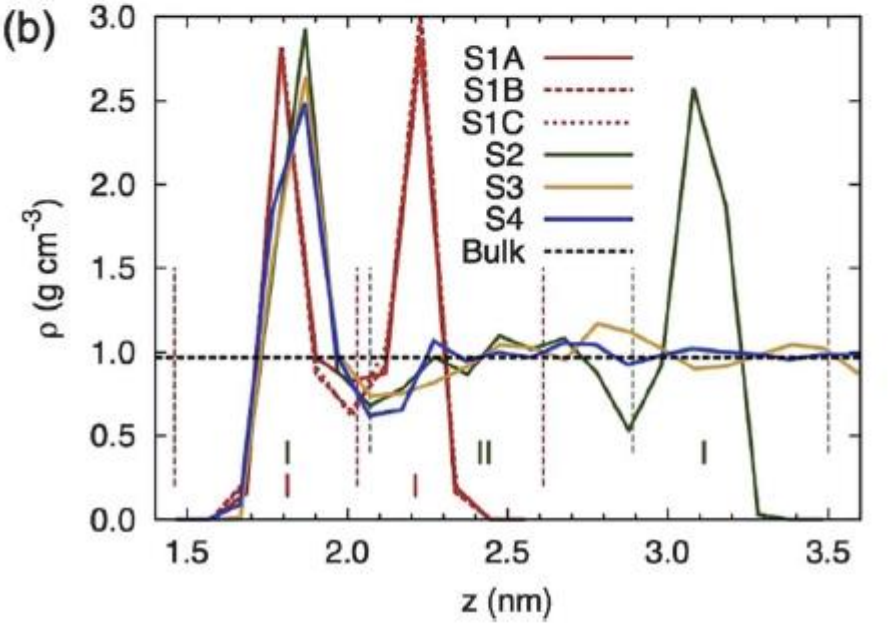
$$P_2(t) = A\exp\left\{-\left(\frac{t}{t_{KWW}}\right)^{\beta}\right\}$$

Polystyrene/Au Systems: Analysis as a function of distance from the Au surface

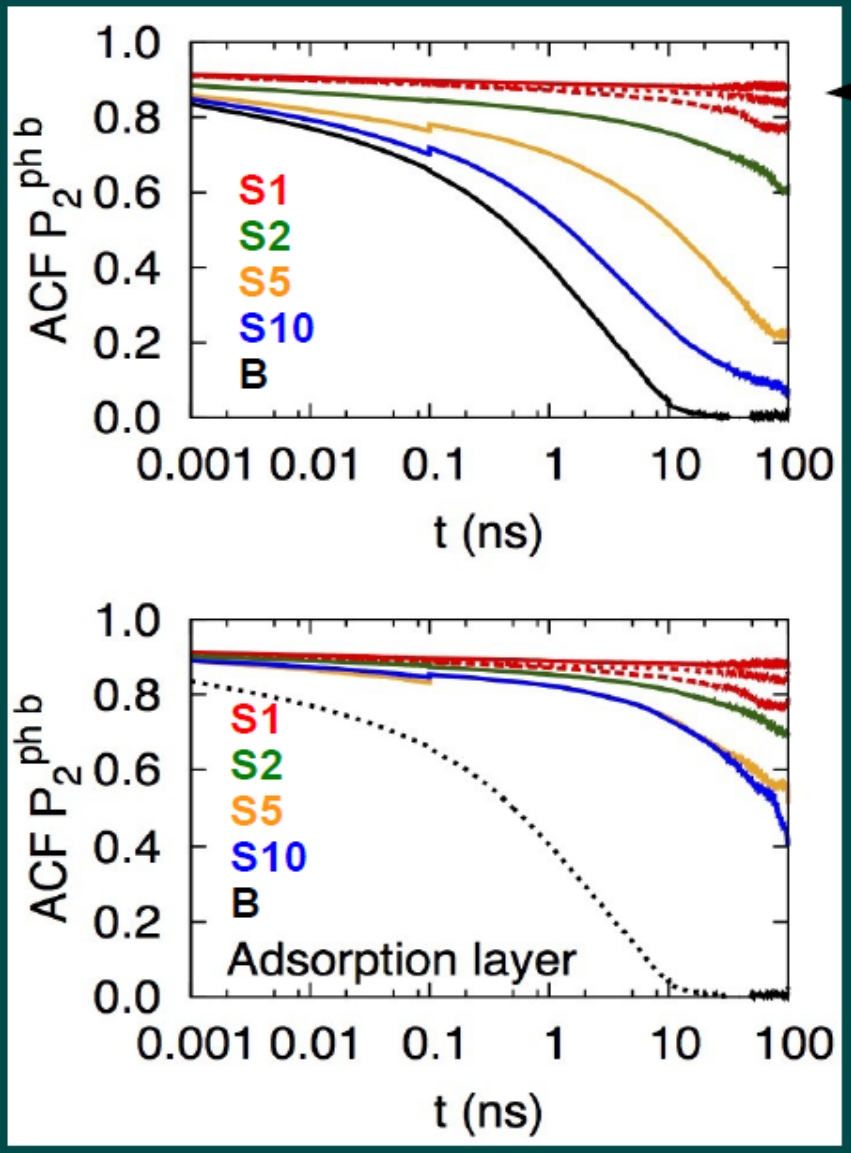
- Define adsorption layers I - IV







Dynamics – Time autocorrelation function for P2



S1 films almost frozen

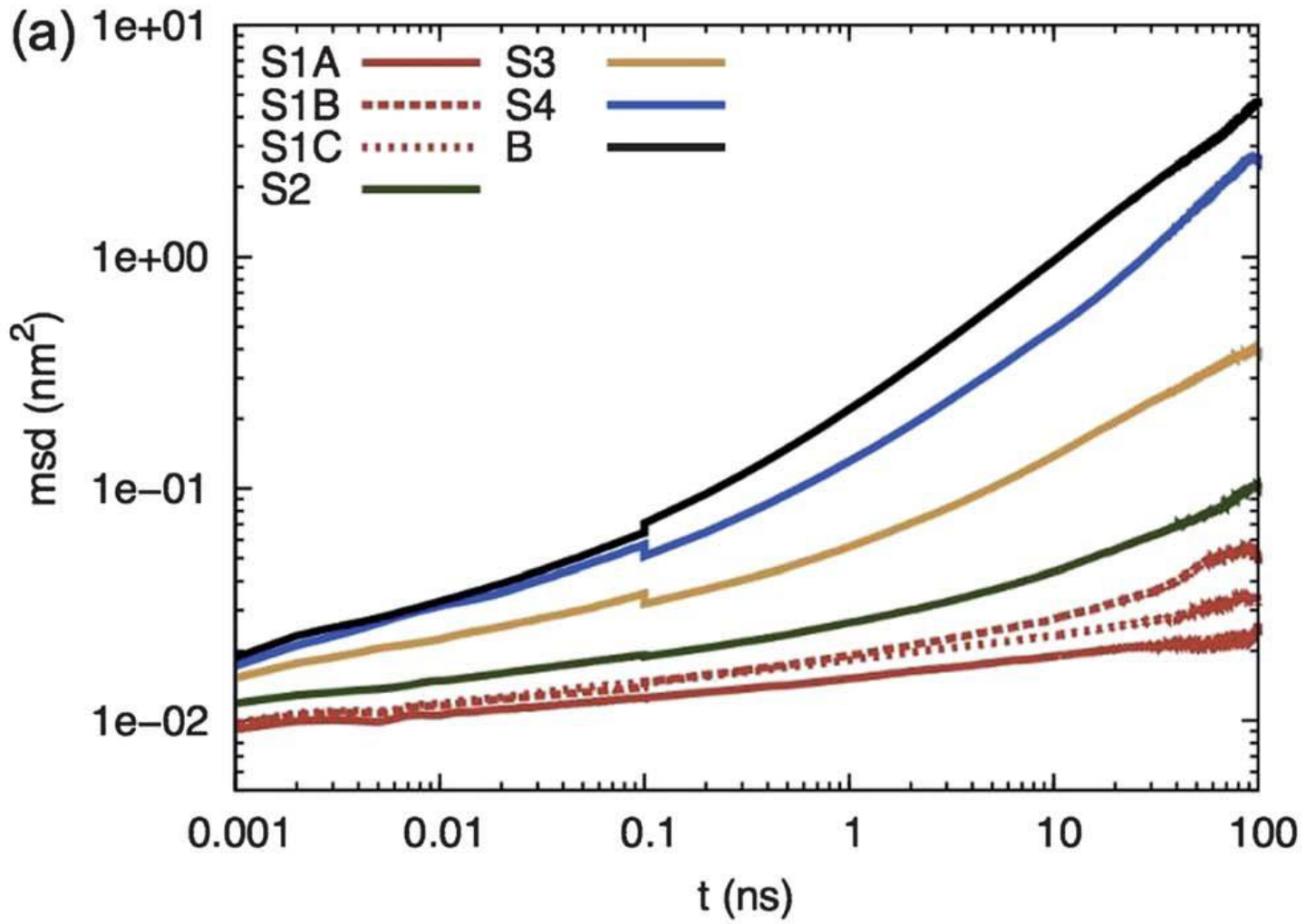
Confinement increases decorrelation time

Dynamics slowest in adsorption layer

Similar trend in mean square displacements

Polymer/Metal Interfaces: Chain Center-of-mass Dynamics

[K. Johnston and VH, Soft Matter 8, 6320 (2012)]



❑ **Strongly confined systems : practically frozen.**

Current Work: (C) Realistic Polymer Nanocomposites

➢ Polymer/solid interfaces are models of a single nanoparticle embedded in a polymer matrix.

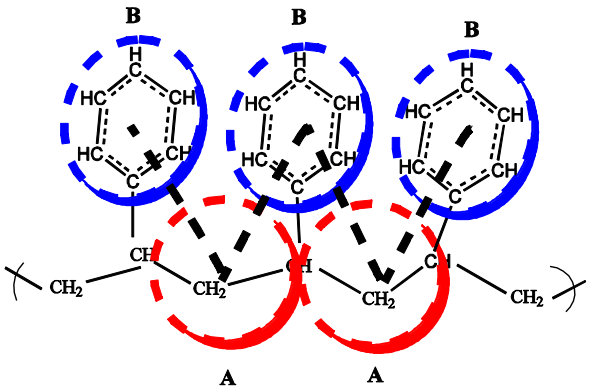
➢ Full study of realistic nanocomposites requires modeling of huge systems.

Mesoscopic (coarse-grained, CG) models of nanocomposites, based on:

CG Polymer models developed directly from the chemistry

[Harmandaris, et al. Macromolecules, 39, 6708 (2006); Macromol. Chem. Phys. 208, 2109 (2007); Macromolecules 40, 7026 (2007)]

➢ Example CG PS 2:1 model: Each chemical repeat unit replaced by two spherical beads (PS: 16 atoms or 8 "united atoms" replaced by 2 beads).



➢ CG operator T: from "CH_x" to "A" and "B" description.

$\sigma_A = 4.25$ Å, $\sigma_B = 5.10$ Å

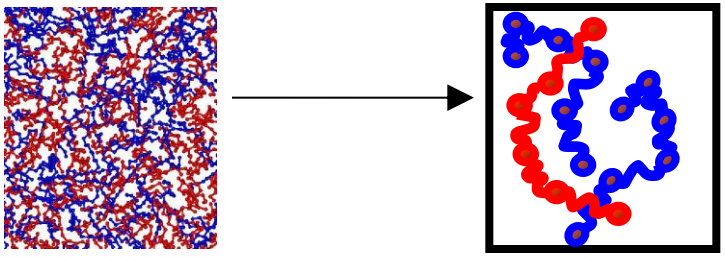
➢ Chain tacticity is described through the effective CG potentials.

➢ Possible to re-introduce atomistic detail if needed.

GENERAL PROCEDURE FOR DEVELOPING MESOSCOPIC PARTICLE MODELS DIRECTLY FROM THE CHEMISTRY

1. Choice of the proper mesoscopic description.

-- number of atoms that correspond to a 'super-atom' (coarse grained bead)



2. Microscopic (atomistic) simulations of short chains (oligomers) for short times.

3. Develop the effective mesoscopic force field using the atomistic data.

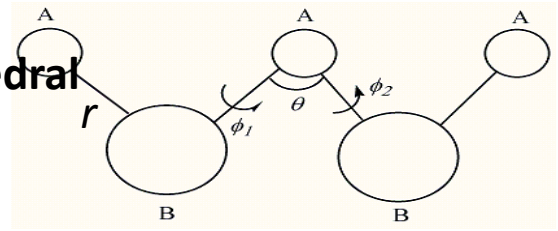
4. CG (MD or MC) simulations with the new CG model.

Re-introduction (back-mapping) of the atomistic detail if needed.

DEVELOP THE EFFECTIVE MESOSCOPIC CG POLYMER FORCE FIELD

$$U_{total}^{CG}(\mathbf{Q}) = U_{bonded}^{CG}(\mathbf{Q}) + U_{non-bonded}^{CG}(\mathbf{Q})$$

BONDED POTENTIAL



- **Degrees of freedom:** bond lengths (r), bond angles (ϑ), dihedral angles (ϕ)

PROCEDURE:

- From the microscopic simulations we calculate the **distribution functions** of the degrees of freedom in the mesoscopic representation, $P^{CG}(r,\vartheta,\phi)$.

- $P^{CG}(r,\vartheta,\phi)$ follow a **Boltzmann distribution:**

$$P^{CG}(r,\theta,\phi) = \exp\left[-\frac{U^{CG}(r,\theta,\phi)}{kT}\right]$$

- **Assumption:**

$$P^{CG}(r,\theta,\phi) = P^{CG}(r)\,P^{CG}(\theta)\,P^{CG}(\phi)$$

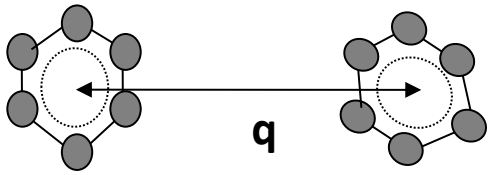
- **Finally:**

$$U^{CG}(x,T) = -k_B T \ln P^{CG}(x,T), \qquad (x = r,\theta,\phi)$$

NONBONDED INTERACTION PARAMETERS: REVERSIBLE WORK

➢ **CG Hamiltonian – Renormalization Group Map:**

$$e^{-\beta U_{nb}^{CG}(\mathbf{q},T)} = \int e^{-\beta U^{AT}(\mathbf{r},T)} P_N\left(d\mathbf{r}\,|\,\mathbf{q}\right)$$



Reversible work method [McCoy and Curro, *Macromolecules*, 31, 9362 (1998)]

➢ **By calculating the reversible work (potential of mean force) between the centers of mass of two isolated molecules as a function of distance:**

$$e^{-\beta U_{nb}^{CG}(\mathbf{q},T)} = \frac{\int \ldots \int \exp\left[-\beta U^{AT}\left(\mathbf{r},T\right)\right] d\mathbf{r}_1, \ldots \mathbf{r}_N}{Z_N}$$

$$\beta U_{nb}^{CG}(\mathbf{q},T) = -\ln\left\langle \exp\left(-\beta U^{AT}\left(\mathbf{r},\Gamma\right)\right)\right\rangle \qquad U^{AT}\left(\mathbf{r},\Gamma\right) = \sum_{i,j} U^{AT}\left(\mathbf{r}_{ij}\right)$$

➢ **Average < > over all degrees of freedom Γ that are integrated out (here orientational) keeping the two center-of-masses fixed at distance *r*.**

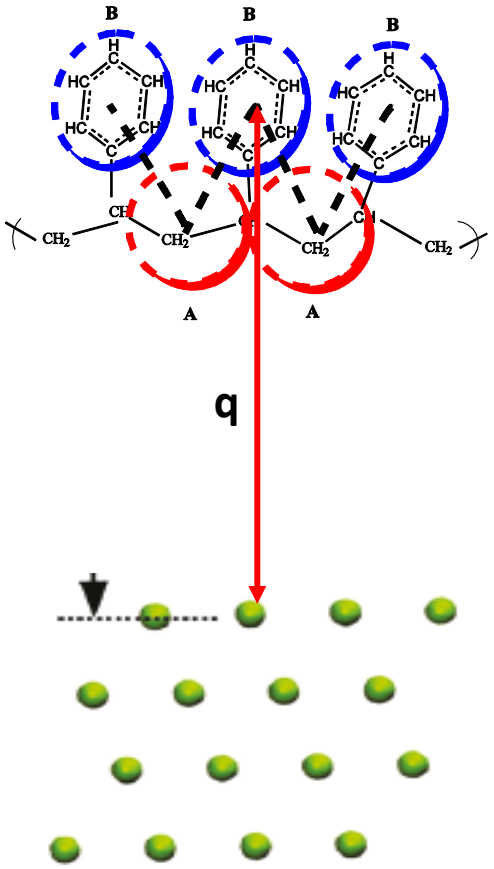
Polymer/Metal Interfaces: Coarse-Grained Model

$$U^{CG}_{total}(\mathbf{Q}) = U^{CG}_{bonded}(\mathbf{Q}) + U^{CG}_{non-bonded}(\mathbf{Q}) + U^{CG}_{superatom/surface}(\mathbf{Q})$$

- **We need the CG superatom / Au surface interaction potential (free energy) .**

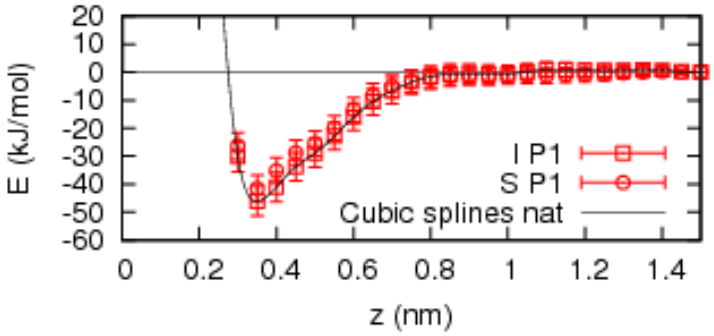
- **Develop it as a PMF between molecule and surface:**

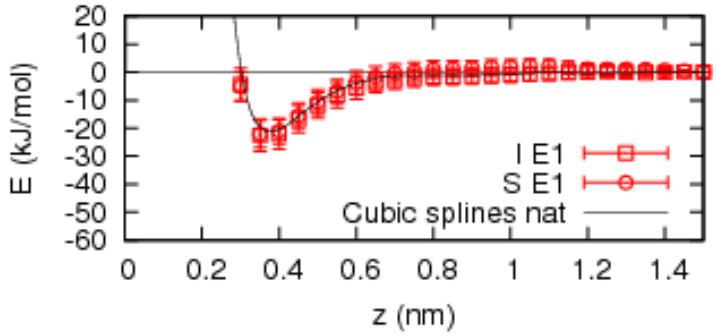
$$U^{CG}_{superatom/surface}(\mathbf{q})$$

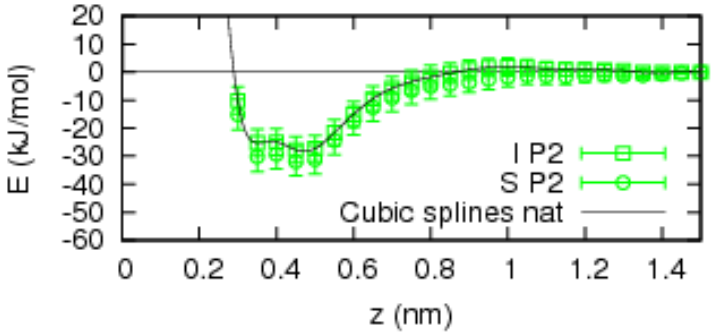


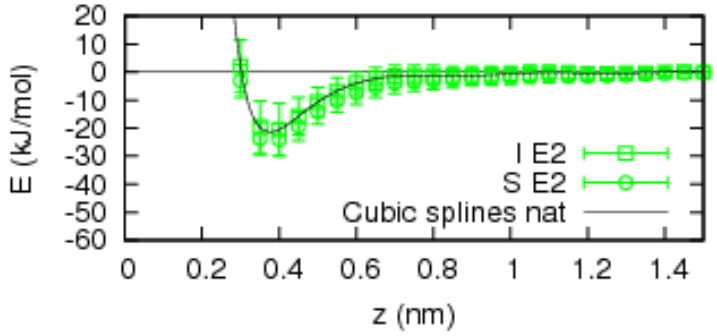
Polymer/Metal Interfaces: Coarse-Grained Effective Interaction

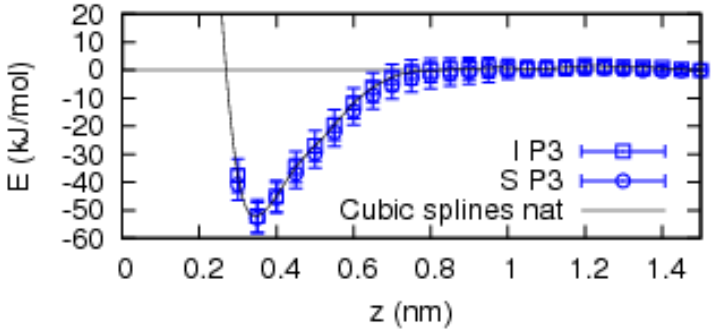
❑ Parameterization of CG effective interaction

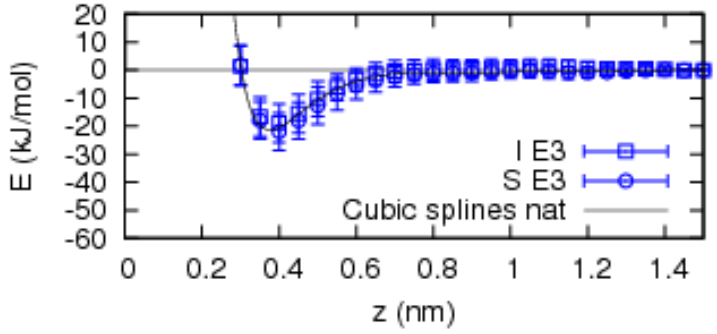








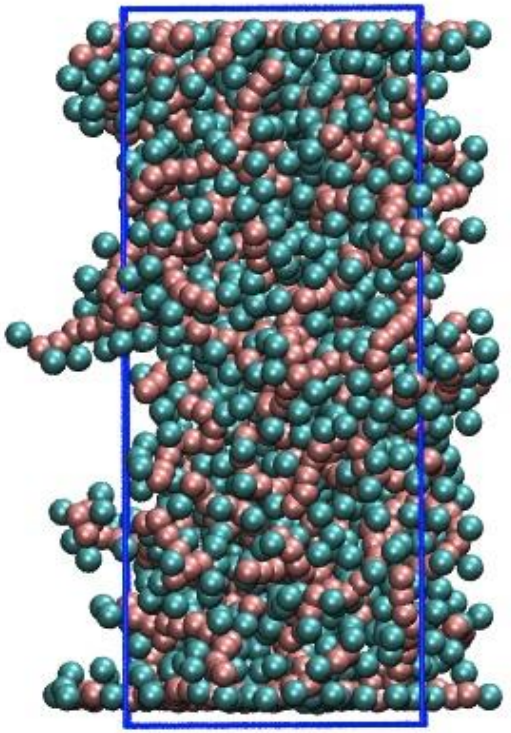




Current work: CG Simulations of PS/Au Hybrid Systems

- **Systems Studied: Atactic PS melts with molecular weight from 1kDa (10 monomers) up to 50kDa (1kDa = 1000 gr/mol).**

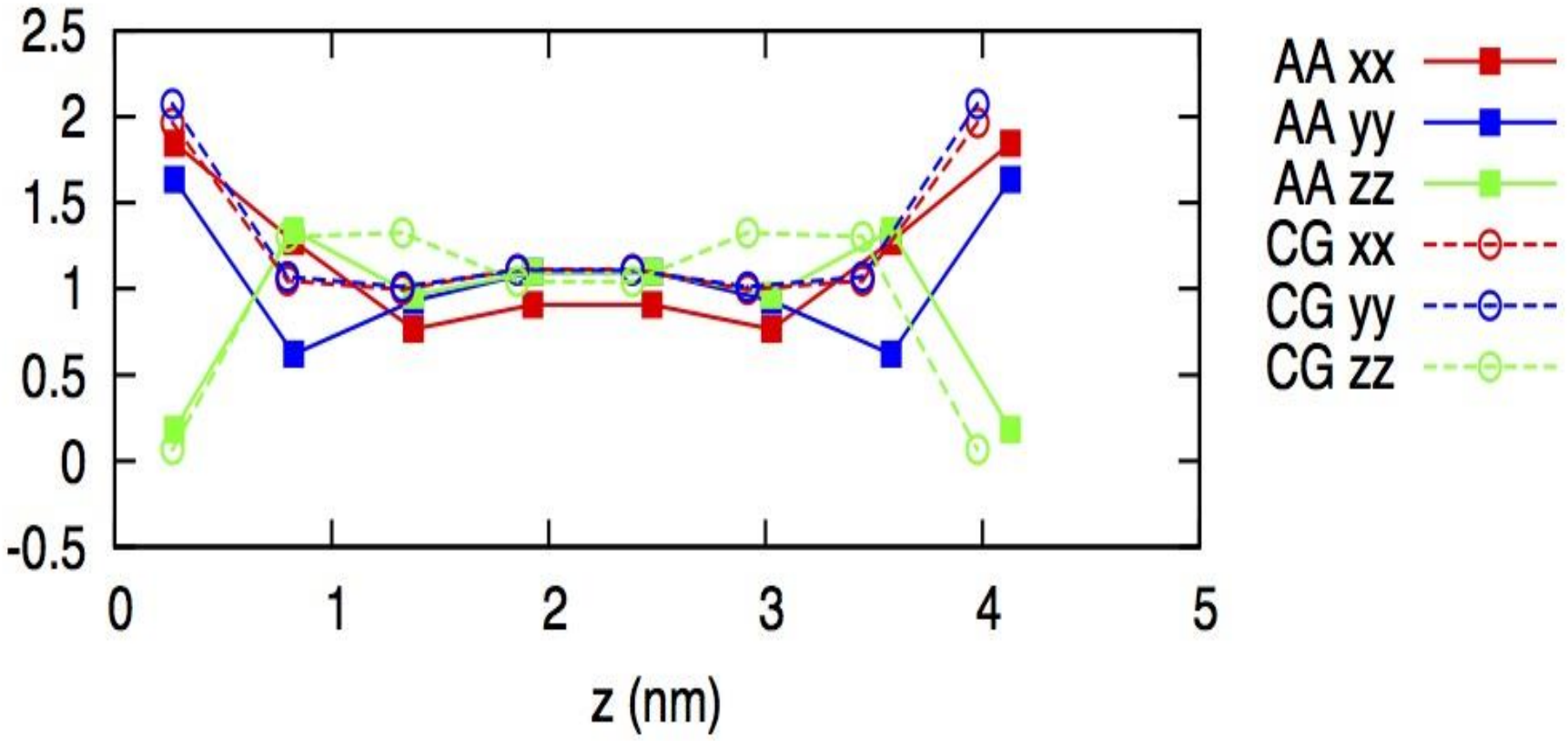
$$m_i \frac{\partial^2 \mathbf{q}_i}{\partial t^2} = -\frac{\partial U^{CG}}{\partial \mathbf{q}_i} - \Gamma \frac{\partial \mathbf{q}_i}{\partial t} + W_i(t)$$



- **NVT Ensemble.**
- **Langevin thermostat (T=463K).**
- **Periodic boundary conditions.**

CG Simulations of PS/Au Hybrid Systems: Structure

➢ **Conformation tensor: comparison between atomistic and CG PS/Au systems of short PS chains (10mers).**



Current work: Dynamics of PS/Au systems

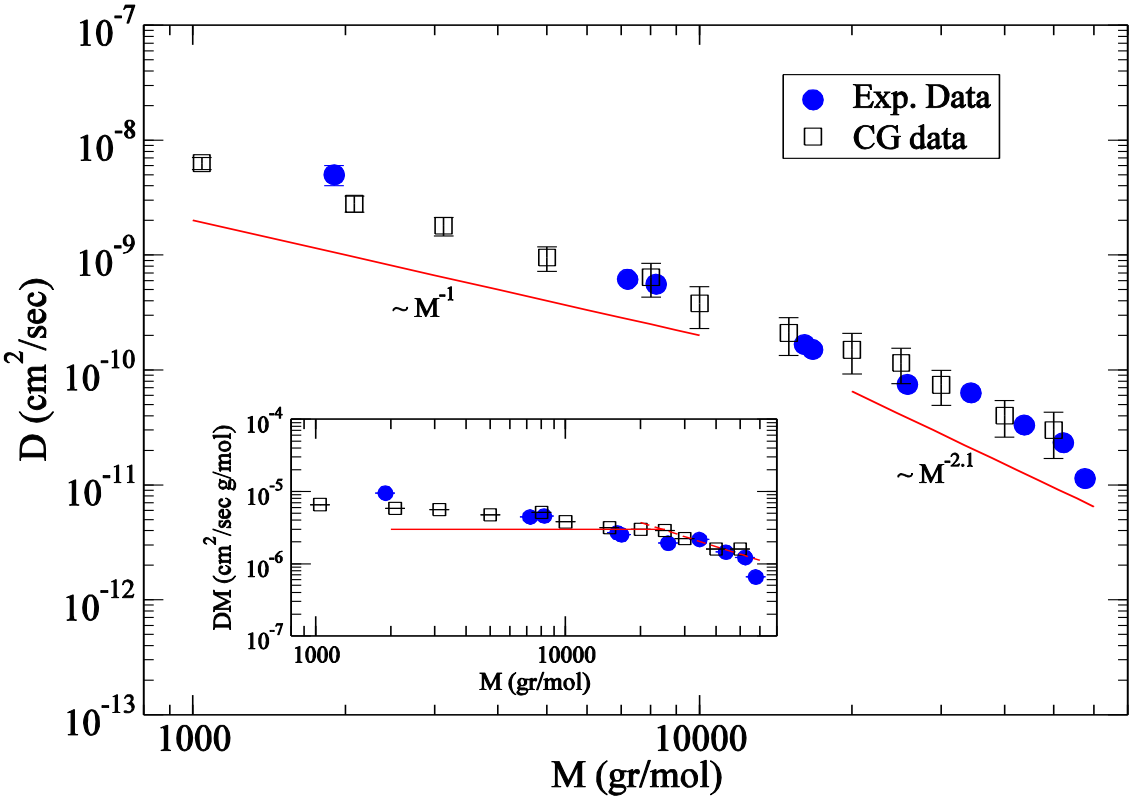
➢ **Hierarchical Multi-scale MD simulations:**

– **Time scales: up to few ms (10^{-3} sec)**

– **Molecular weight: up to 50000-100000 g/mol**

$$D \equiv \lim_{t\to\infty} \frac{\left\langle \left(R_{cm}(t) - R_{cm}(0)\right)^2 \right\rangle}{6t}$$

-- Bulk system:



-- Exp. Data (full symbols): [Sillescu et al. Makromol. Chem. 1987, 188, 2317]

CONCLUSIONS

➢ **Modeling of realistic hybrid multi-phase nanocomposites requires multi-scale simulation approaches.**

❑ **Hierarchical systematic computer simulation approach coupling:**

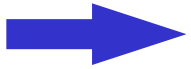
- ➢ **quantum (DFT),**
- ➢ **microscopic (atomistic) and**
- ➢ **mesoscopic (coarse-grained) techniques**

for the study (structure, conformation, dynamics, mechanical properties, etc.) of polymer interfaces.

➢ **Length scales: from ~ 1 Å (10^{-10} m) up to 100 nm (10^{-7} m)**

➢ **Time scales: from ~ 1 fs (10^{-15} sec) up to about 1 ms (10^{-3} sec)**

❑ **Polymer Nanocomposites: Size of the organic/inorganic interface depends on the properties considered.**



MORE CONCLUSIONS …

Examples:

- ✓ PS/Metal,
- ✓ PS/Graphene
- ✓ PE/Graphite,
- ✓ … etc.

In overall: Effect of interface on polymer properties

- ✓ density ~ 2-3 nm,
- ✓ conformations ~ 2-3 R_G
- ✓ local (segmental) dynamics ~ 1 nm
- ✓ global dynamics ~ 6-7 R_G

CURRENT WORK - OPEN QUESTIONS

- Polymer/solid interfaces are models of confined systems or a single nanoparticle embedded in a polymer matrix.

- Study of realistic many particles polymer nanocomposites systems requires CG modeling of huge systems.

- Model different systems. Example: PMMA/Graphene interfaces.

- DFT calculations of molecule/Graphene system.

- Effect of solid interface on glass transition temperature, T_g.

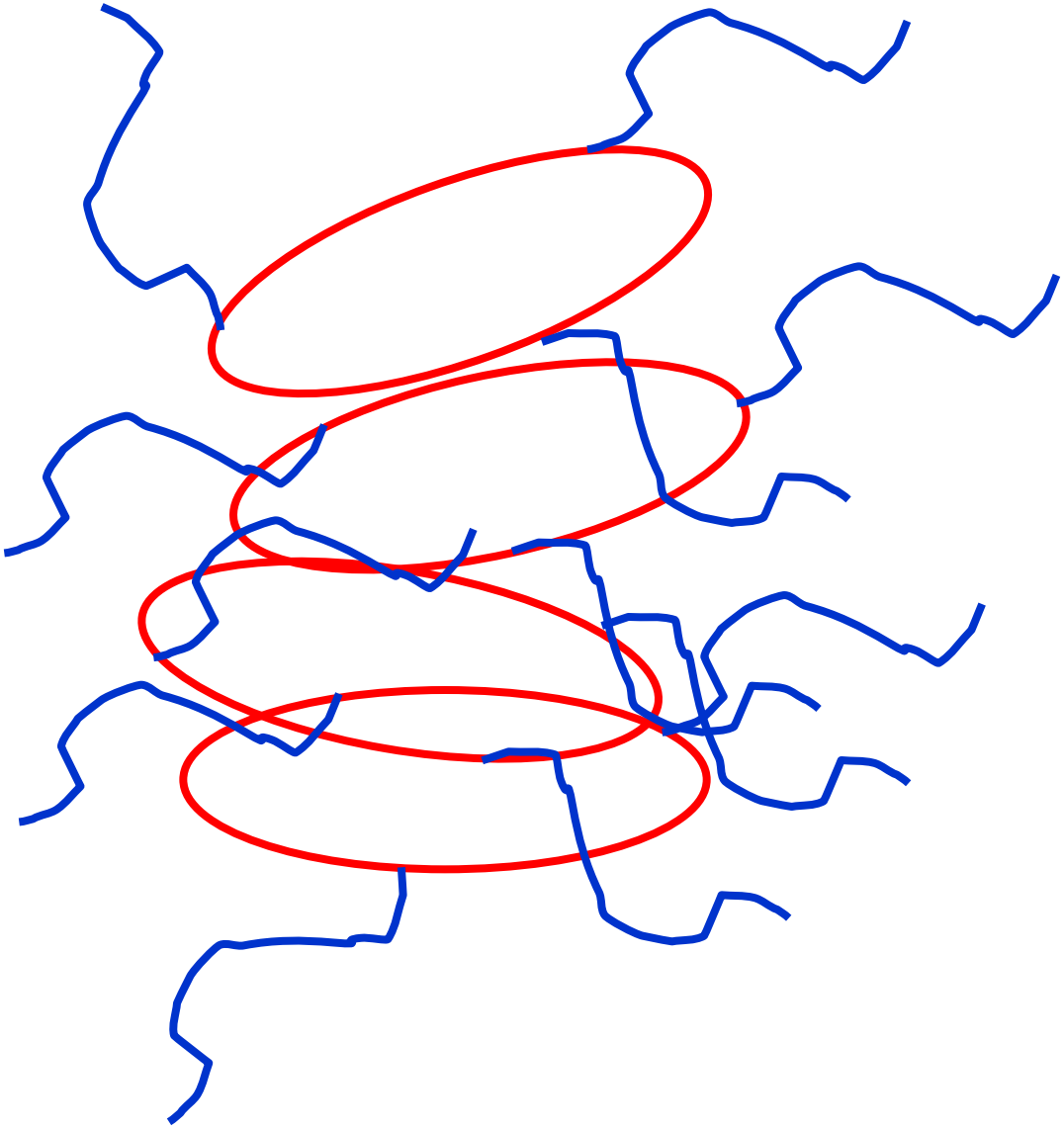
- …

Θεωρητική Μελέτη Επίδρασης Πολυμερικών Αλυσίδων στην Συμπεριφορά Δισκοτικών Υλικών

Π. Ευθυμιόπουλος, Μ. Κοσμάς

Τμήμα Χημείας, Πανεπιστήμιο Ιωαννίνων

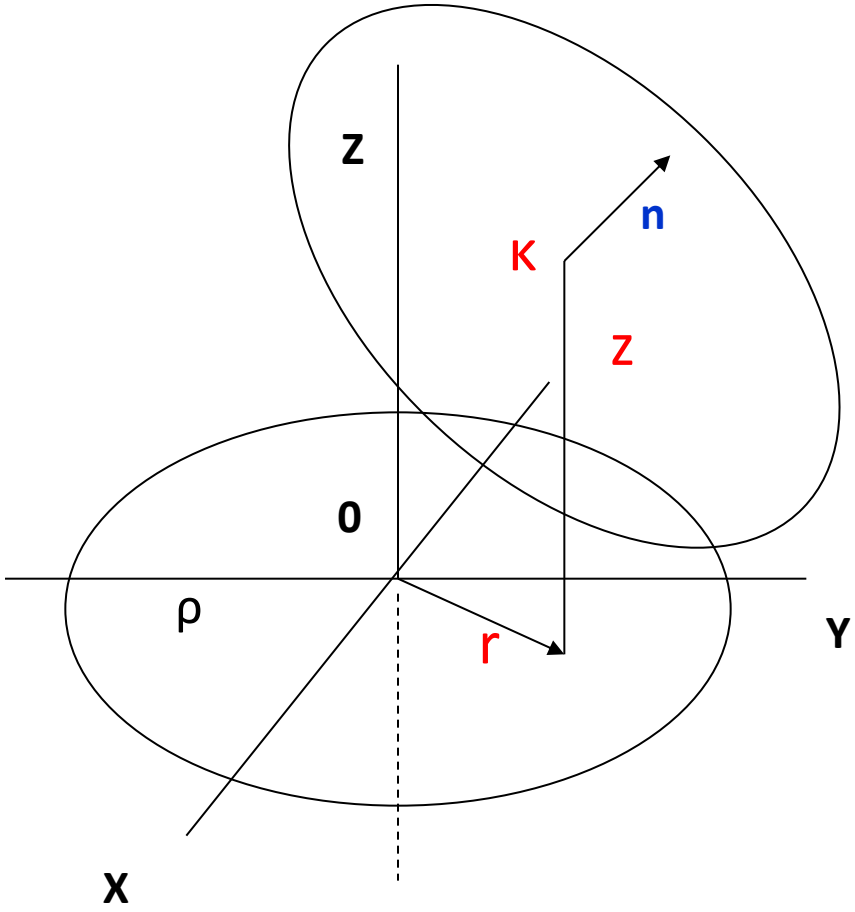
Δισκοτικά υλικά, επίδραση πολυμερικών αλυσίδων



Σκληροί Δίσκοι

Ευλύγιστες αλυσίδες

Ζεύγος δίσκων



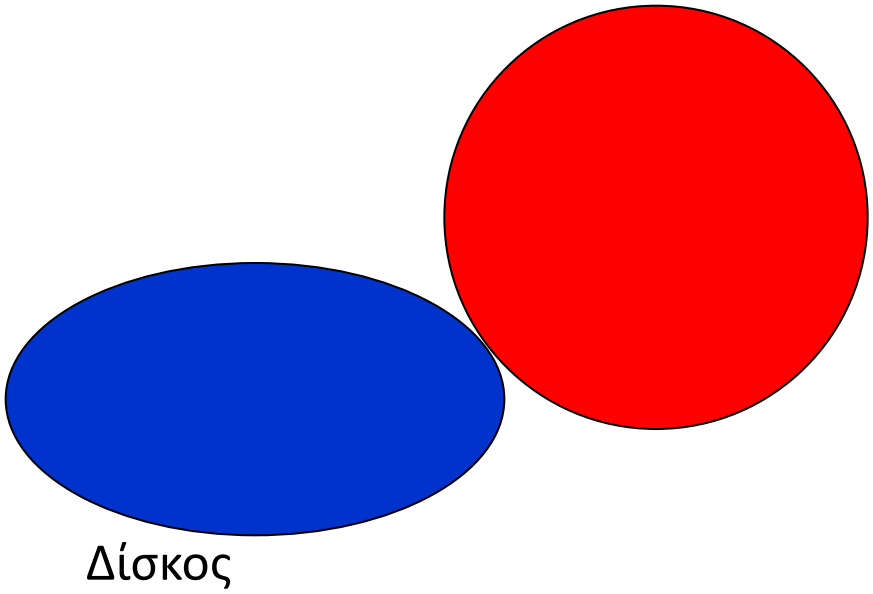
Δυναμικό εξαιρετέου όγκου

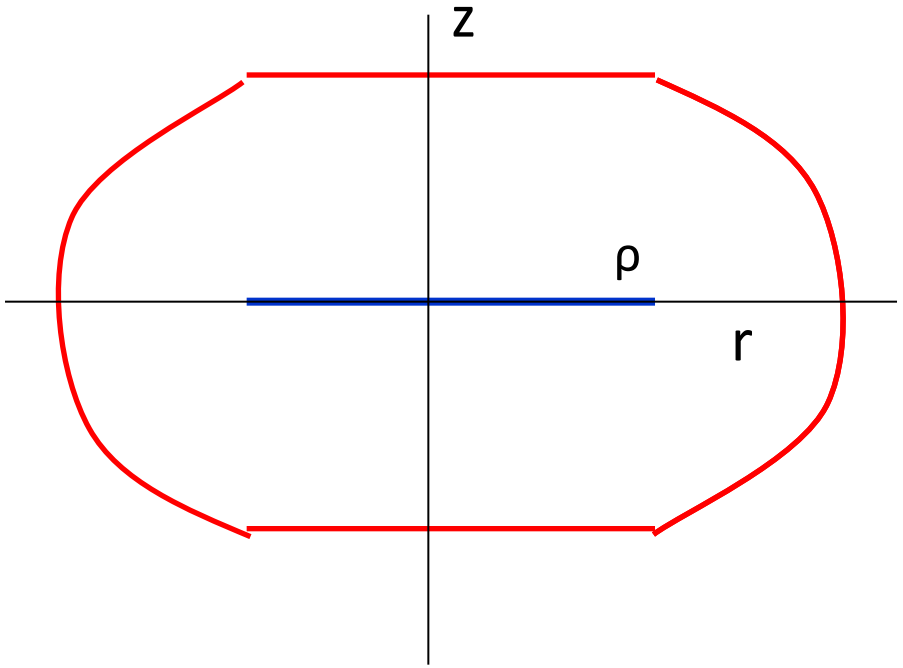
K(z,r)

n(θ,ϕ)

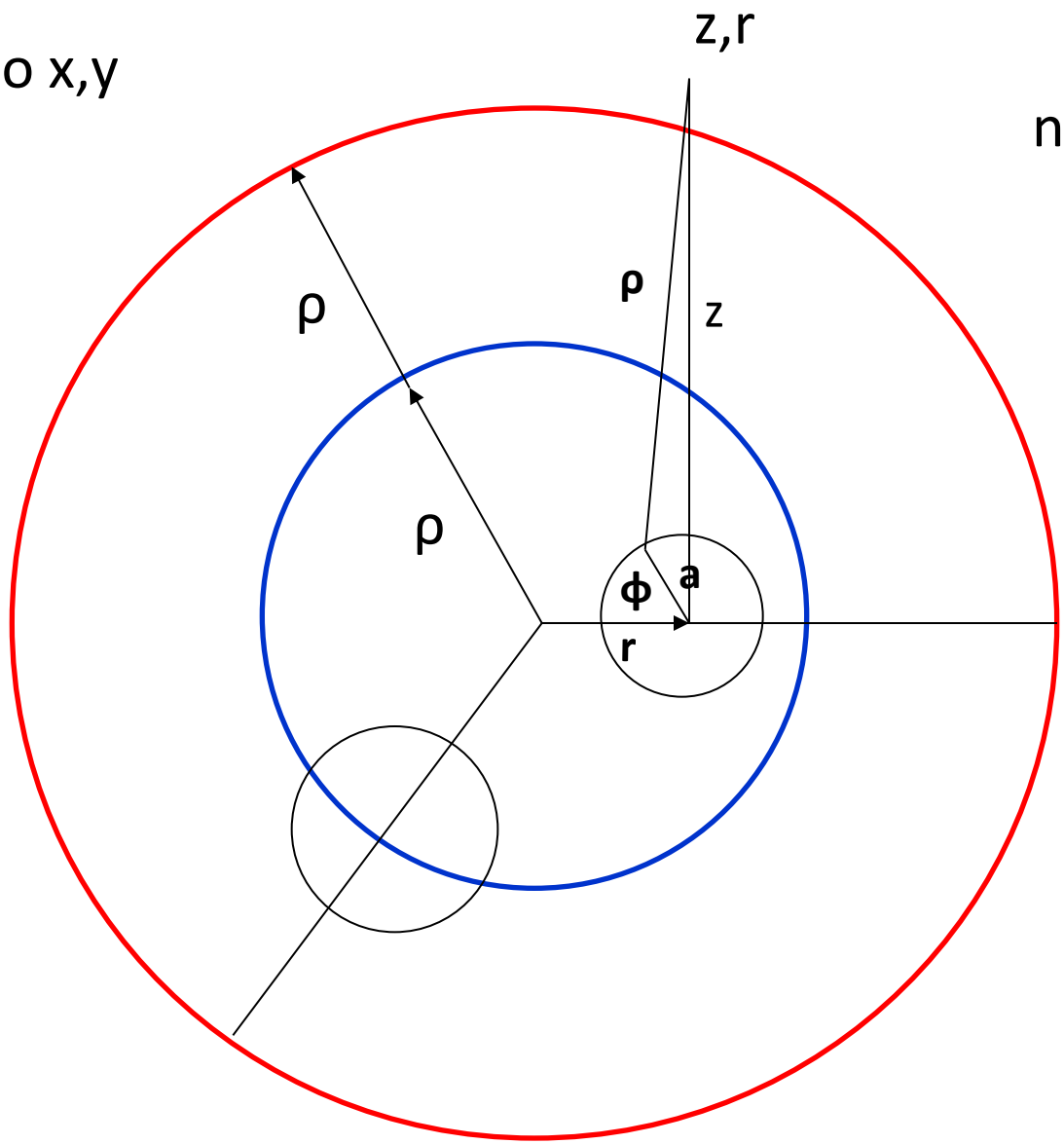
ρ = ακτίνα δίσκων

Εξαιρεταίος χώρος **K(z,r)**





Επίπεδο x,y

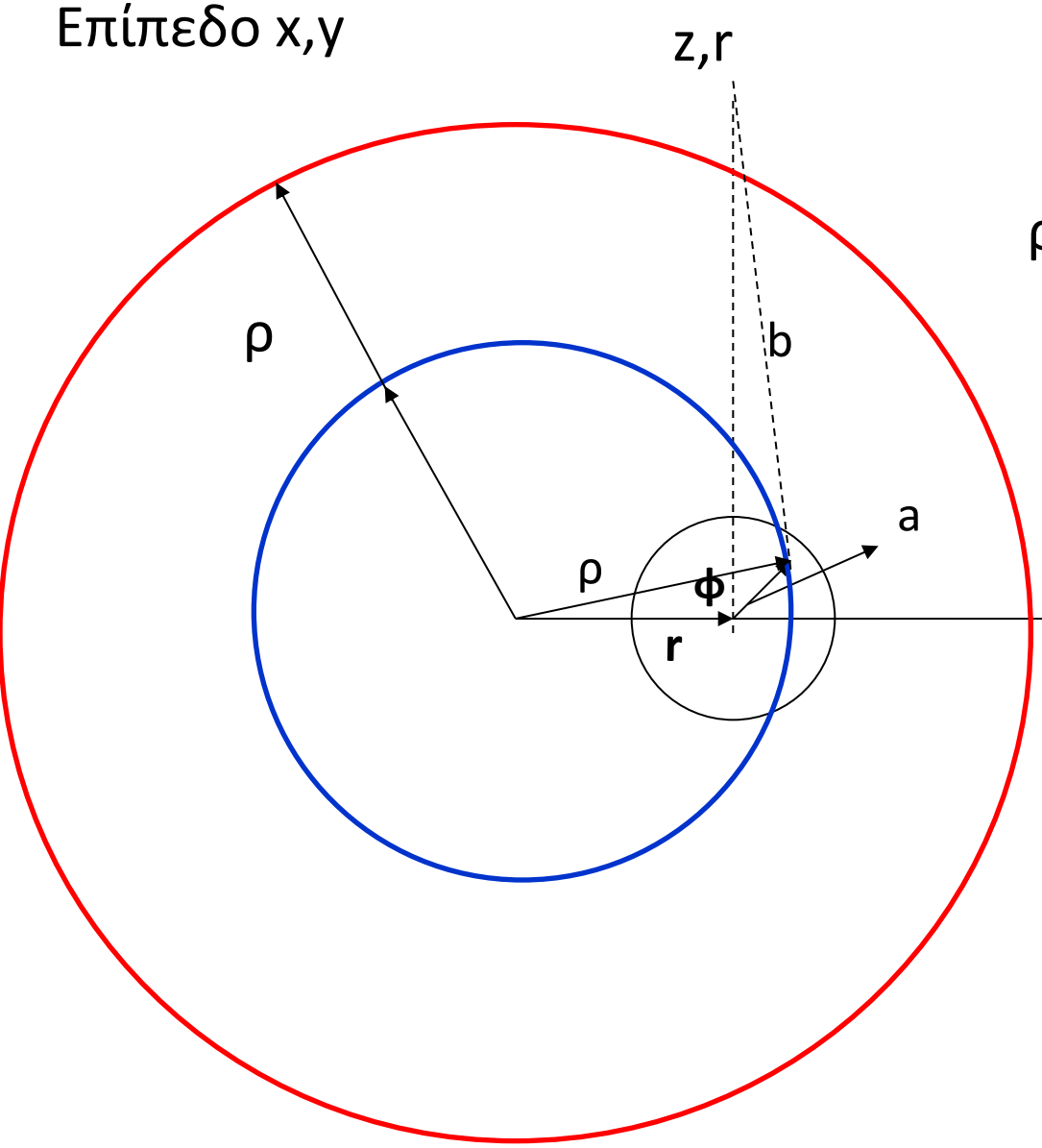


n(θ,ϕ)

$\rho^2 = a^2 + z^2$

$\mathrm{Sin}[\theta] = z/\rho$

Επίπεδο x,y



n(θ,ϕ)

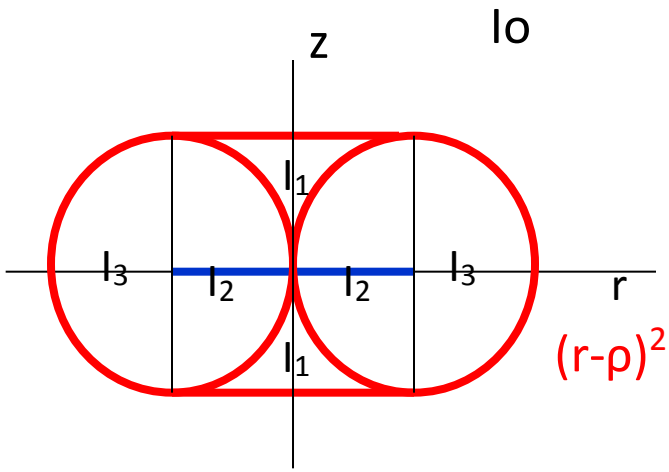
$\rho^2 = a^2 + r^2 - 2arCos[\varphi]$

$b^2 = a^2 + z^2$

Για b=ρ ϕ=ϕc

Sin[θ]=z/ρ για ϕ<ϕc

Sin[θ]=z/b για ϕ>ϕc ,



Ολοκλήρωση των r,z,θ,ϕ

$(r-\rho)^2 + z^2 = \rho^2$

$I = Io + I_1 + I_2 + I_3$

Τα I τετραπλα ολοκληρώματα

Όρια

$z : -z_\tau , z_\tau$

$r : 0 , r_\tau$

θ: 0 , ArcSin[z/ρ] για $\phi<\phi_c$

0 , ArcSin[b/z] για $\phi>\phi_c$