Hierarchical Modeling of Polymer Nanocomposites: From Ab-initio, to Atomistic up to Coarse-grained Simulations

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Outline

- **Introduction:** General Overview of Polymer Surfaces/Interfaces. Confined systems. Characteristic Length-Time Scales.

- **Multi-scale Particle Approaches:** Ab-initio (DFT), Microscopic (atomistic) and Mesoscopic (coarse-grained) simulations.

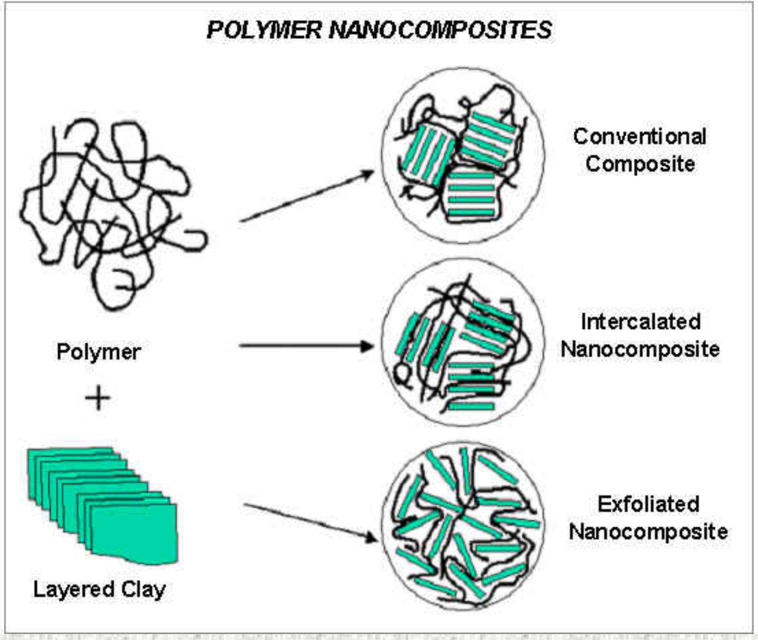
☐ **Applications:**

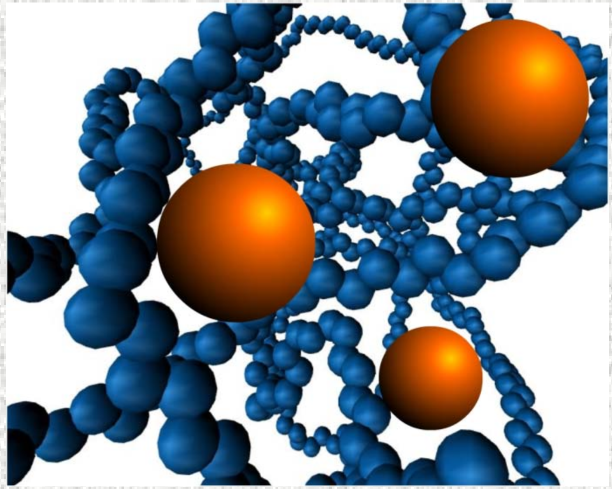
  - ✓ Polymer/Metal hybrid systems.

  - ✓ Polymer/Graphene interfaces.

- **Conclusions – Open Questions.**

INTRODUCTION - MOTIVATION





- ❑ Hybrid **Polymer/solid nanocomposites:** particles are used to enhance/modify the properties of the entire system:
  - ➢ Thermodynamics
  - ➢ Mechanical properties
  - ➢ Dynamical/rheological behavior
  - ➢ … etc.

INTRODUCTION

THEORIES & COMPUTER SIMULATIONS:

-- probe microscopic structural features

-- organization of the adsorbed groups

-- dynamics at the interface

-- study in the molecular level

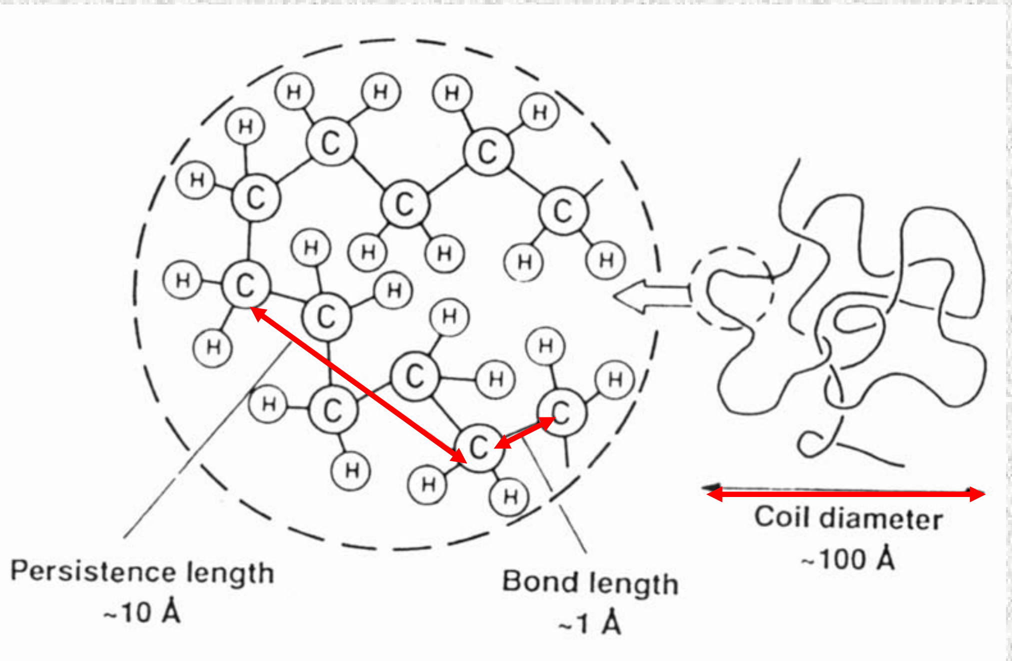
- ❑ **Obtain information about the spatial dependence of:**
  - ➢ **the short-time (local) dynamics**
  - ➢ **the long-time self diffusion coefficient**
- ❑ **Structure – Properties relations**

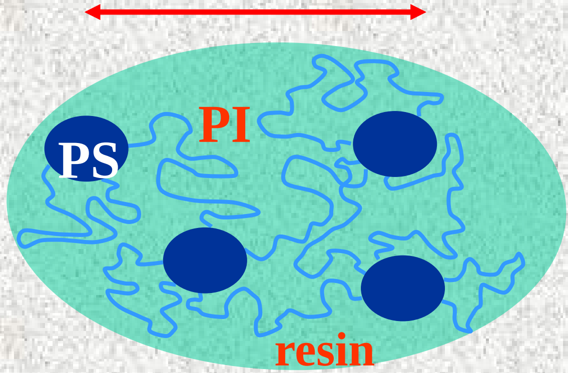
❑ **Example - Open question: what is the extend of the surface effect on the lateral motion (diffusion) of the polymer chains?**

-- Experimentally: from 3-4 R_G [Lin et al. 1997] **to 25 R_G** [Frank et al. 1996]

Time – Length Scales Involved in Polymer Composite Systems

- **Bond** length ~ 1 Å (10^{-10} m)
- **Kuhn** length or persistence length) ~ 10 Å
- **Radius of gyration** ~ 100 Å
- Phase separated polymers ~ 1 µm (10^{-6} m)

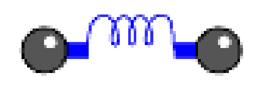




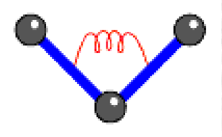
- **Polymer/solid interface** length scales ~ ?

Time – Length Scales Involved in Polymer Composite Systems

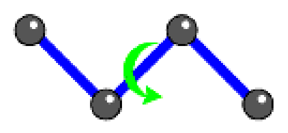
- **Bond vibrations: ~ 10^{-15} sec**



- **Angle rotations: ~ 10^{-13} sec**

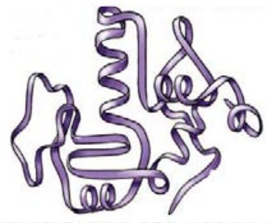


- **Dihedral rotations: ~ 10^{-11} sec**



- **Segmental relaxation: 10^{-9} - 10^{-12} sec**

- **Maximum relaxation time of a chain, τ_1: ~ 1 sec (in $T < T_m$)**



- **Polymer/solid interface characteristic relaxation times: ?**

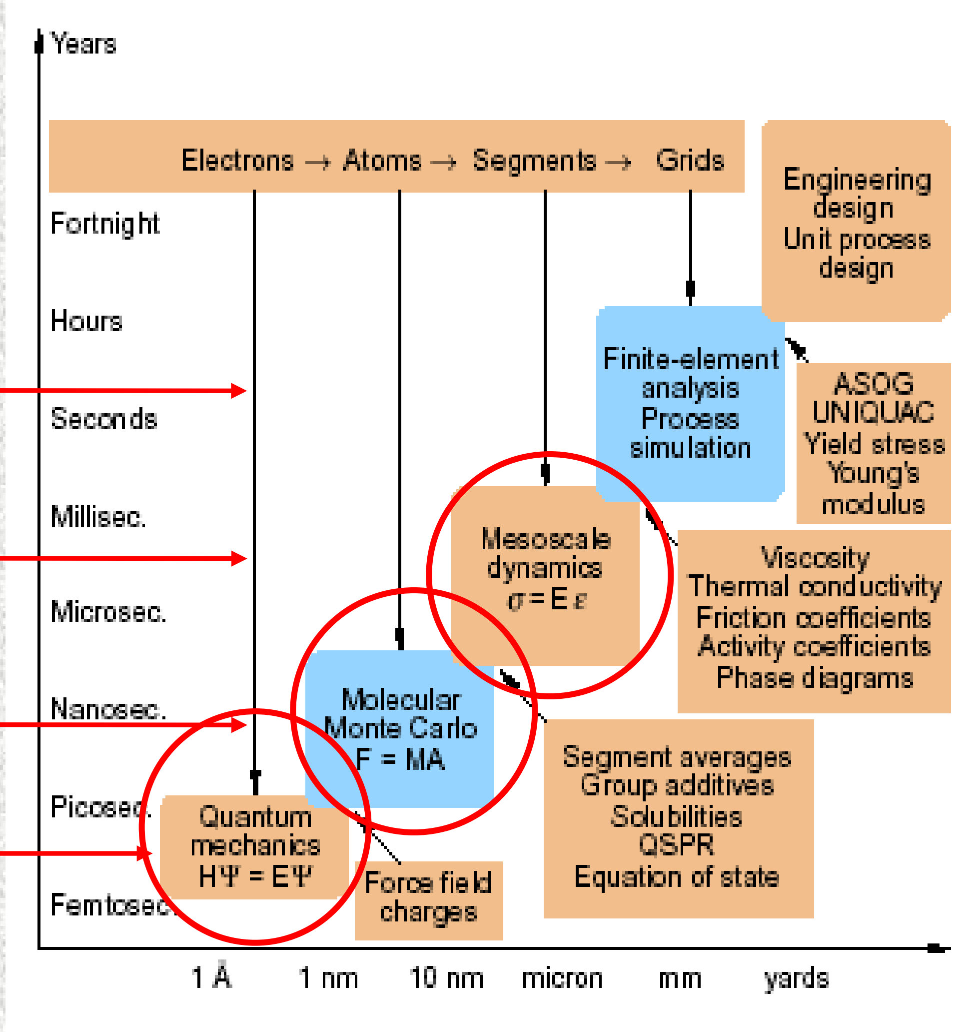
Hierarchical Modeling of Molecular Materials

D) description in macroscopic - continuum level

C) description in mesoscopic (coarse-grained) level

B) description in microscopic (atomistic) level

A) description in quantum level



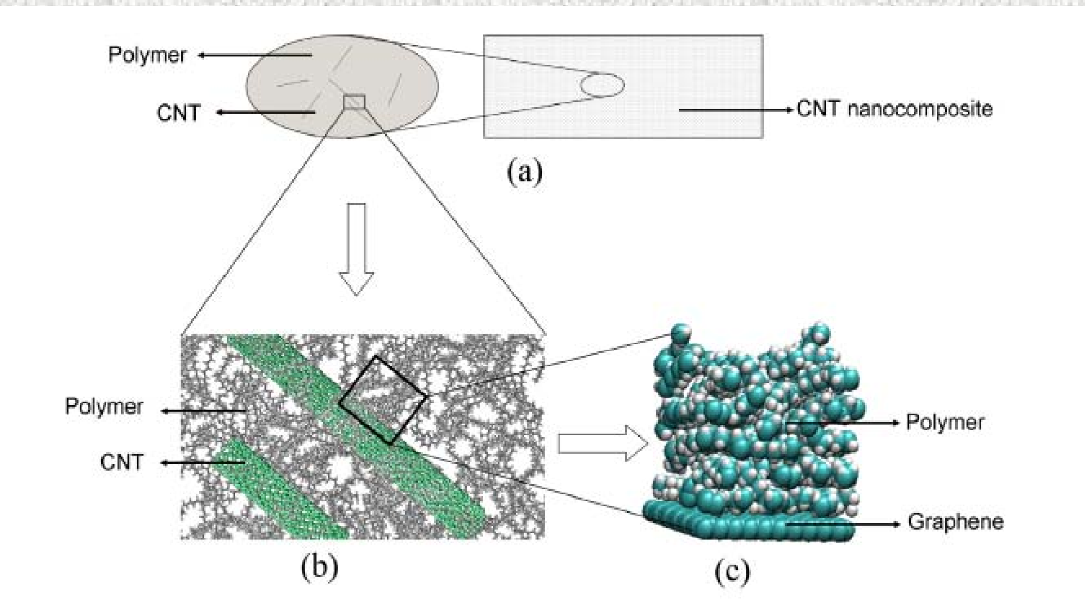
❑ Main goal: **Built rigorous "bridges" between different simulation levels.**

Quantitative prediction of properties of hybrid complex systems.

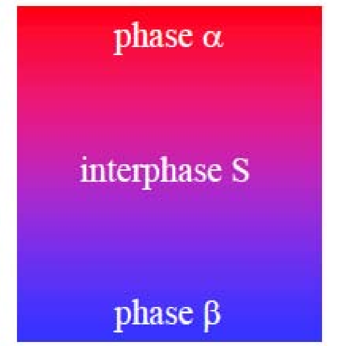
INTRODUCTION

- **Physics-based Multi-scale modeling: key factor for the design and the optimization of composite materials.**

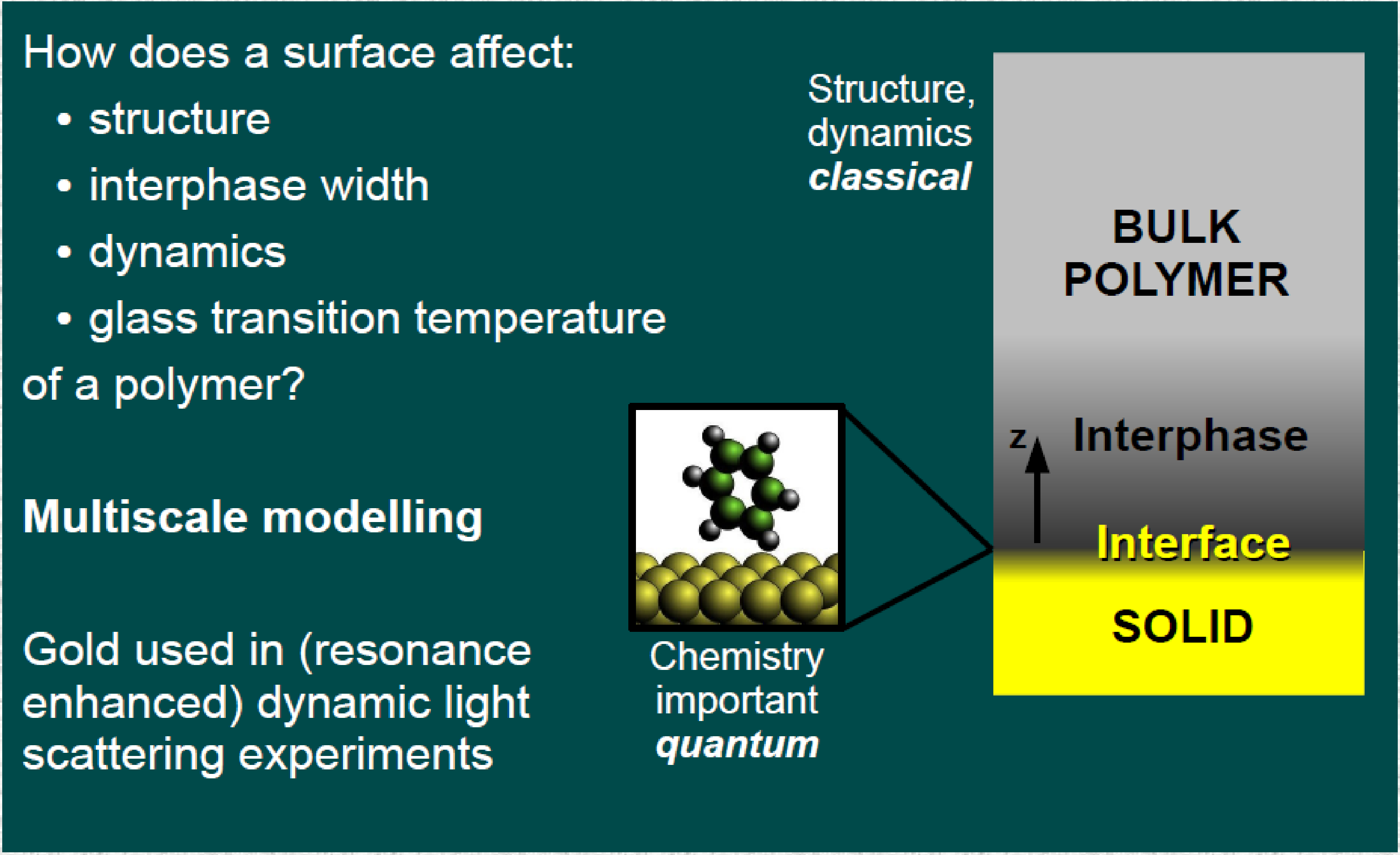
- **Model System: Polymer/solid interfaces.**



- Interface: junction between two homogeneous bulk phases
- A region of finite thickness due to finite range of intermolecular forces (interface - interphase)



Application - Modeling of Polymer Interfacial Systems: Polymer/Metal Interfaces



How does a surface affect:

- structure
- interphase width
- dynamics
- glass transition temperature

of a polymer?

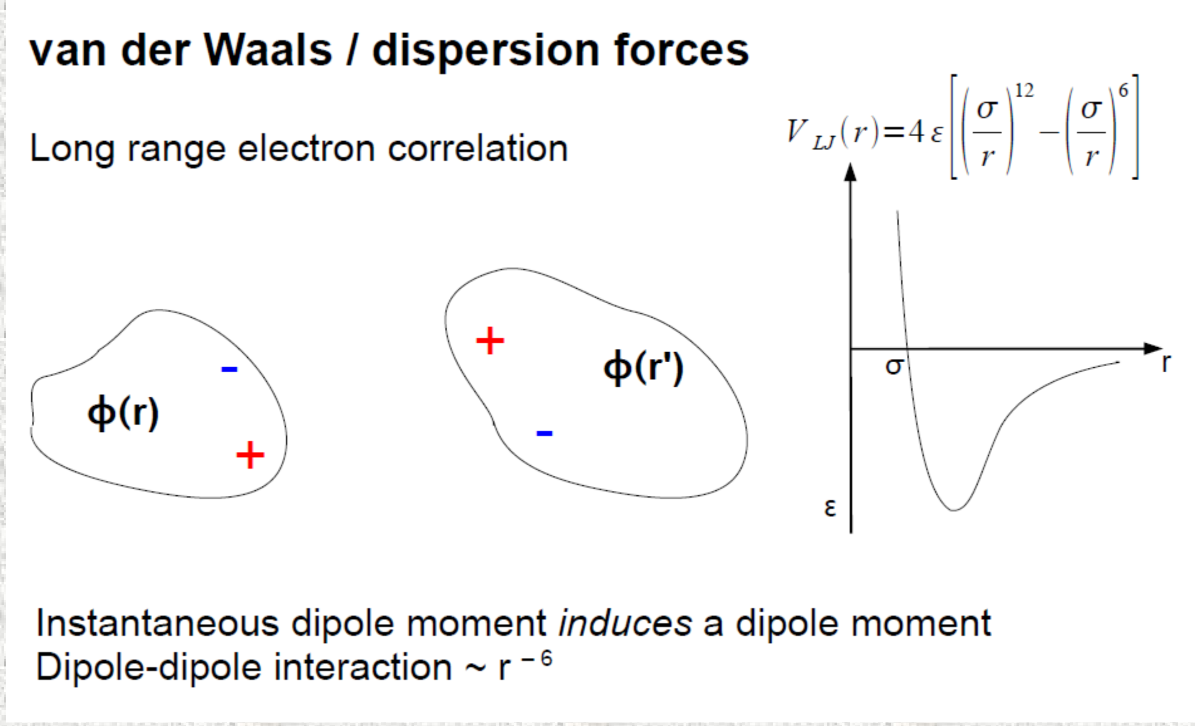
Multiscale modelling

Gold used in (resonance enhanced) dynamic light scattering experiments

➢ **Questions:** **(1) Can we calculate analytically metal / molecule (dispersion) interaction ?**

Application - Modeling of Polymer Interfacial Systems: Polymer/Metal Interfaces

- (2) Is a LJ type of potential a good approximation ?



van der Waals / dispersion forces

Long range electron correlation

$$V_{LJ}(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

Instantaneous dipole moment *induces* a dipole moment

Dipole-dipole interaction ~ r^{-6}

- **Answers:**

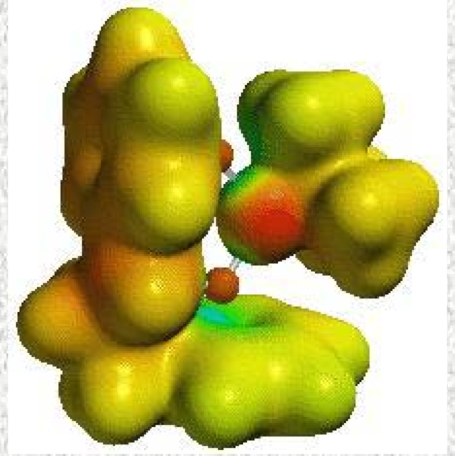
- **(1) Molecule/Metal interaction cannot be estimated analytically.**

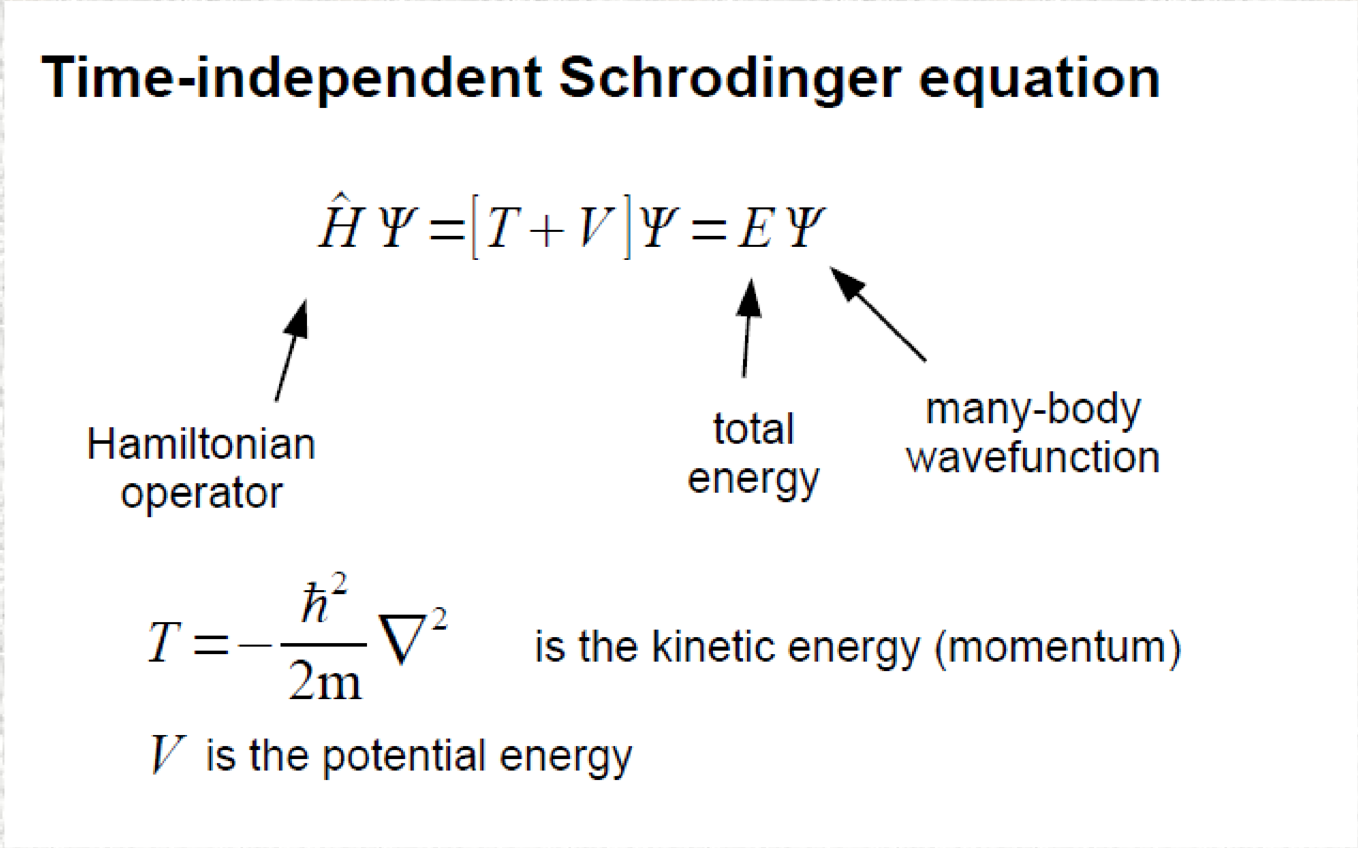
- **(2) We do not know if LJ potential is a good approximation.**

- **Idea: Use DFT calculations of a single molecule adsorbed onto the metal surface.**

Modeling Complex Hybrid Systems: (A) Ab-initio Calculations

- ☐ **Description of the system in the most detailed (quantum) level.**





Time-independent Schrodinger equation

$$\hat{H}\Psi = [T + V]\Psi = E\Psi$$

$$T = -\frac{\hbar^2}{2m}\nabla^2$$ is the kinetic energy (momentum)

V is the potential energy

✓ **Difficult to solve Schrodinger's equation for many-body system:**

Density Functional Theory: Hohenberg – Kohn – Sham

- Electronic wavefunction → electron density $\rho(r)=\sum_{i=1}^{N}\left|\phi_i^2(r)\right|$

- Solve N independent Kohn Sham equations iteratively:

$$\left[T_s+V_s\right]\phi_i=\varepsilon_i\phi_i$$

$$V_s=\frac{1}{2}\int\frac{\rho(r')}{\left|r-r'\right|}d^3r'+V_{XC}(r)+V_{ext}$$

Coulomb energy

Exchange and Correlation

External potential due to nuclei

- Exchange and Correlation is the main approximation in DFT.

- For more information see for example: Electronic Structure by R.M. Martin

Multi-scale Modeling of Complex Systems: Density Functional Theory

❑ Exchange and Correlation Functional

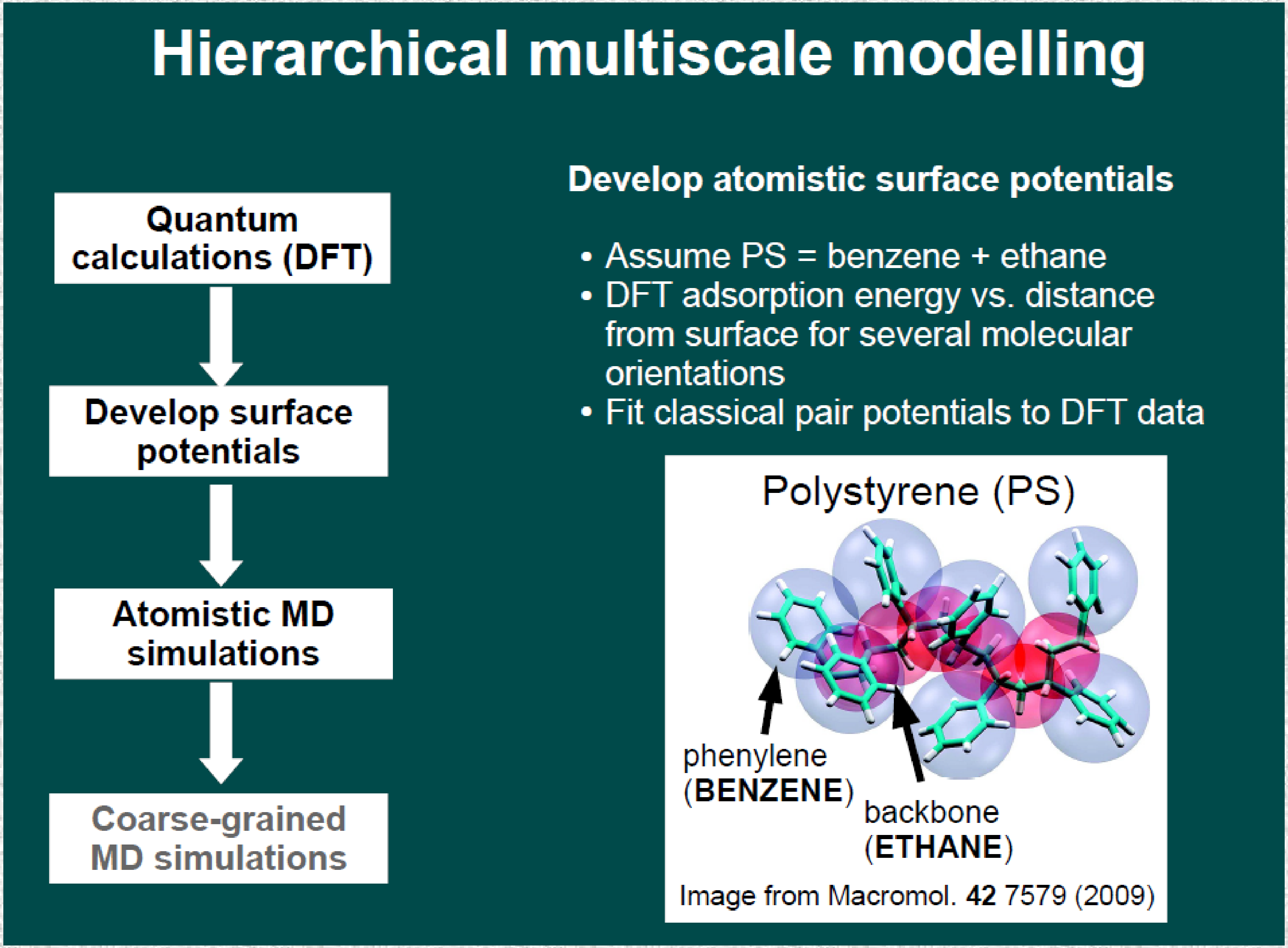
- **Local density approximation (LDA):**
  Based on "jelium"(homogeneous electron gas)

- **Generalized gradient approximation (GGA):**
  Includes a gradient term in the electron density
  Several GGA functionals, e.g. PW91, PBE, revPBE

- **Hybrid:**
  Combination of Hartree-Fock and DFT XC functional
  → empirical coupling parameter
  Several functionals, e.g. BLYP, B3LYP

- **van der Waals:**
  Long range correlation not in standard DFT

Application: 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)

phenylene (**BENZENE**)

backbone (**ETHANE**)

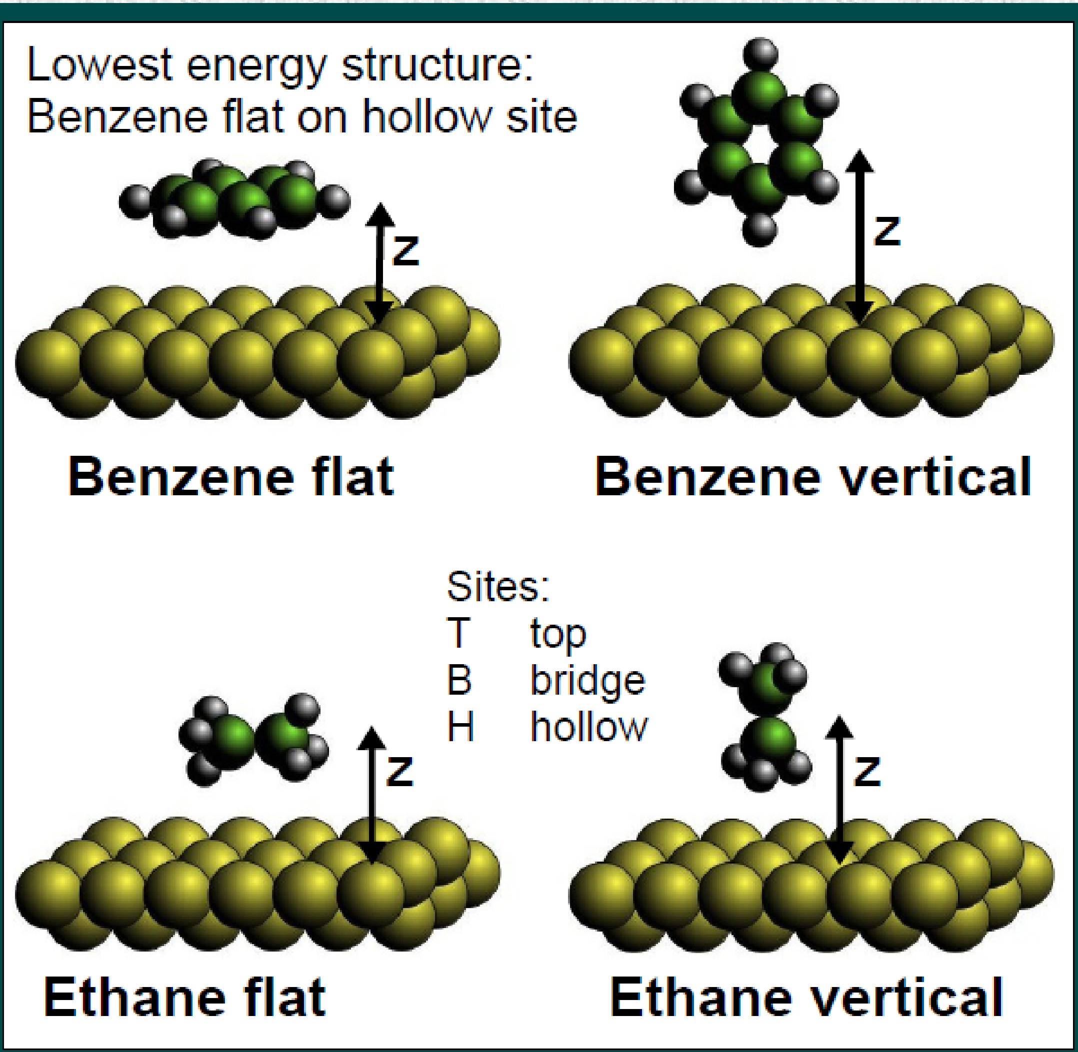
Image from Macromol. **42** 7579 (2009)

[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



Lowest energy structure:
Benzene flat on hollow site

Benzene flat

Benzene vertical

Sites:

T	top
B	bridge
H	hollow

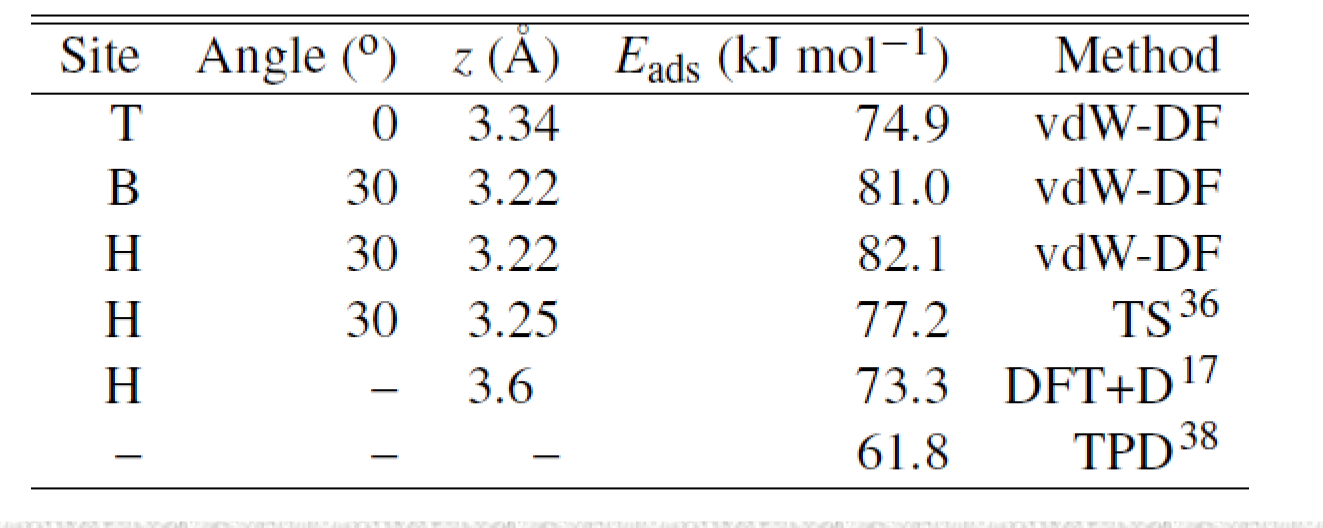
Ethane flat

Ethane vertical

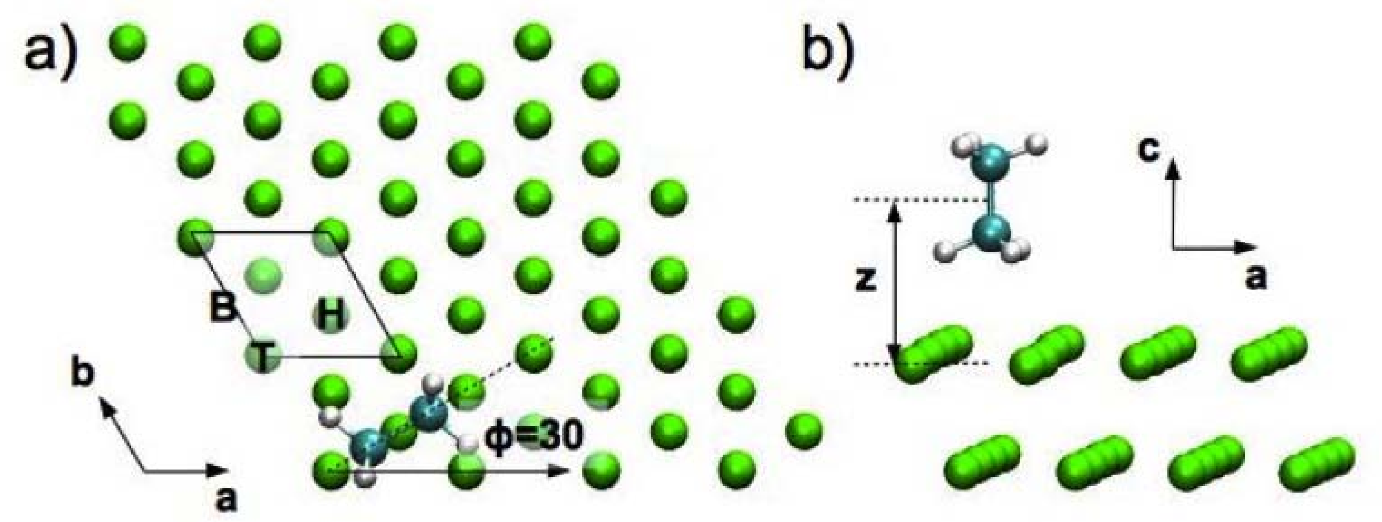
[1] Dion PRL **92** (2004)
[2] Gulans PRB **79** (2009)
[3] Johnston JPCC **115** (2011)
[4] McNellis PRB **80** (2009)
[5] Tonigold JCP **132** (2010)
[6] Syomin JPC 105 (2001)

Benzene/Au systems: Density Functional Theory

☐ **Adsorption sites, angles, distances and energy for a single benzene, ethane molecule:**



Site	Angle (º)	z (Å)	E_{ads} (kJ mol^{-1})	Method
T	0	3.34	74.9	vdW-DF
B	30	3.22	81.0	vdW-DF
H	30	3.22	82.1	vdW-DF
H	30	3.25	77.2	TS[36]
H	–	3.6	73.3	DFT+D[17]
–	–	–	61.8	TPD[38]



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 “built a bridge” between ab-initio and classical simulations.

Important question: How do we parameterize DFT data (energies) in order to obtain an accurate microscopic (atomistic) interaction potential?

$$E_{ads}^{DFT}$$

❑ 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 pair classical non-bonded potential (usually Lennard-Jones type).

❑ Require: Optimization over many parameter space, i.e. a highly complex numerical problem.

Polymer/Metal Interfaces: Parameterization of DFT Calculations

[K. Johnston and VH, J. Phys. Chem. C, 115, 1407 (2011)]

☐ <u>Idea</u>: Use a Simulated Annealing code.

✓ Parameters of the non-bonded interaction are chosen in order to minimize a cost function.

✓ 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.

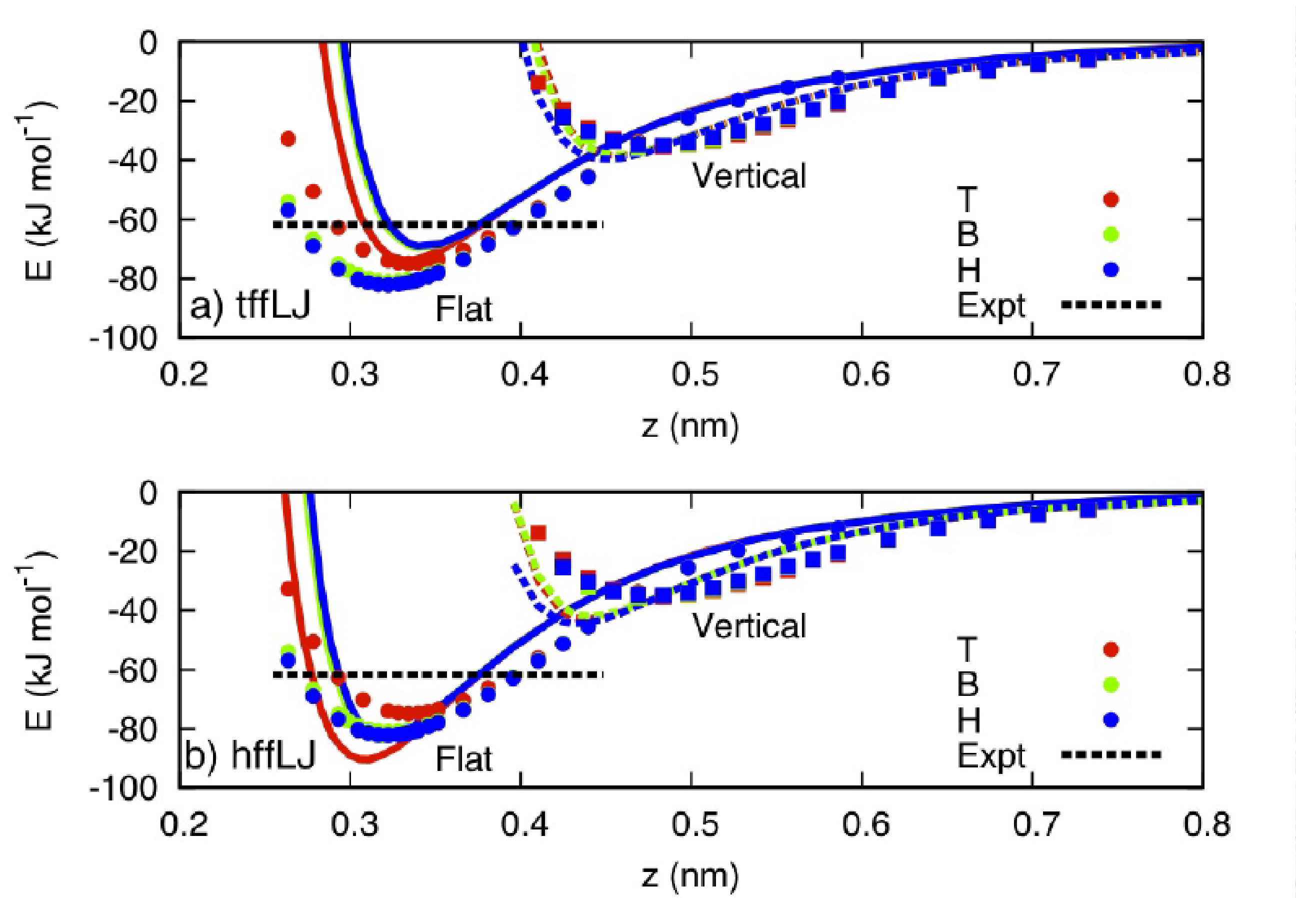
-- n_k: number of molecule-surface distances (z_j) for each conformation.

-- $W(i,z_j)$: statistical weights.

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

- **Benzene/Au interaction - use a typical LJ atomistic potential:**

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

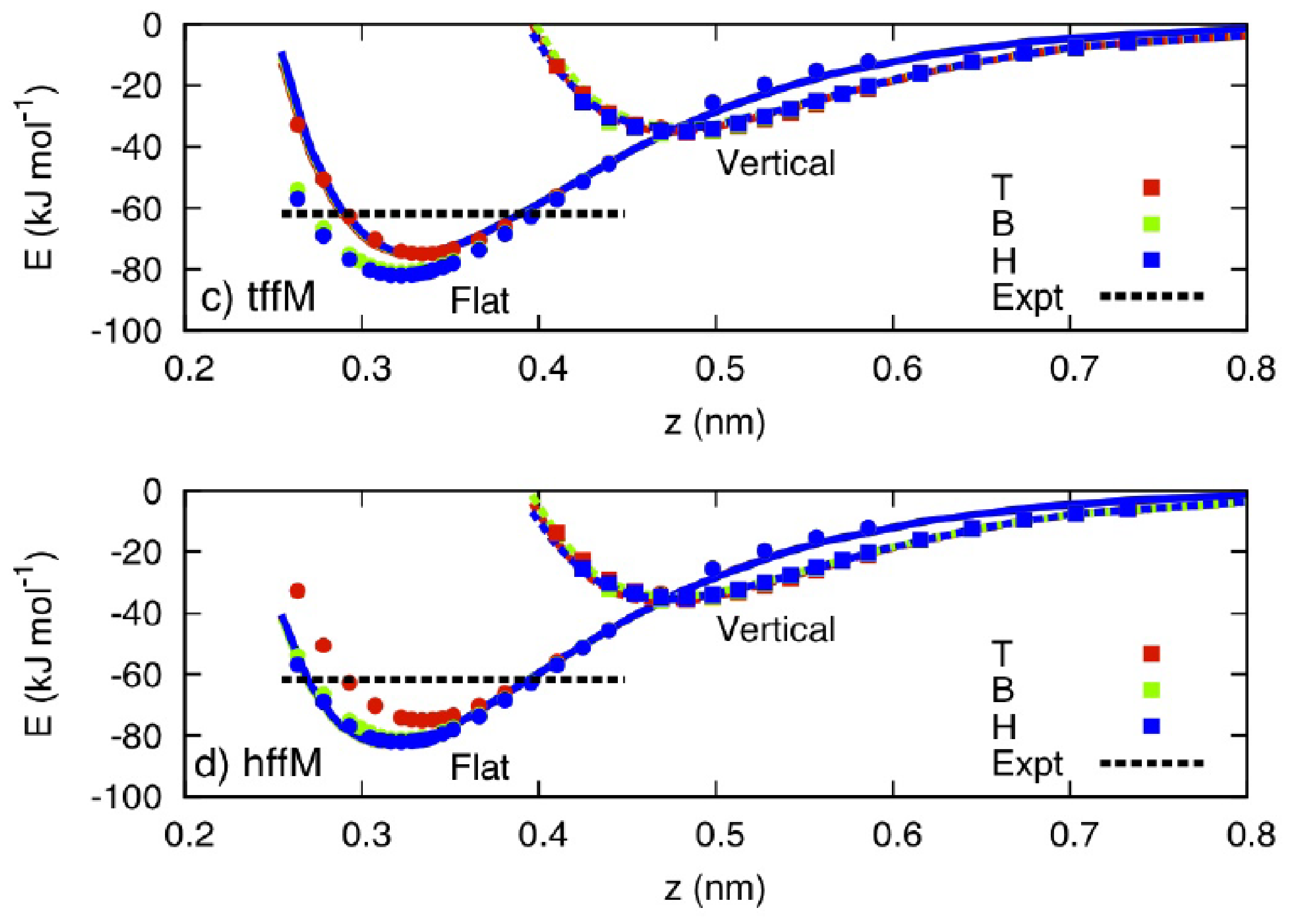


☐ **LJ Potential (lines) is NOT a good choice for a proper description of molecule/metal DFT interaction potential (symbols).**

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

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

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

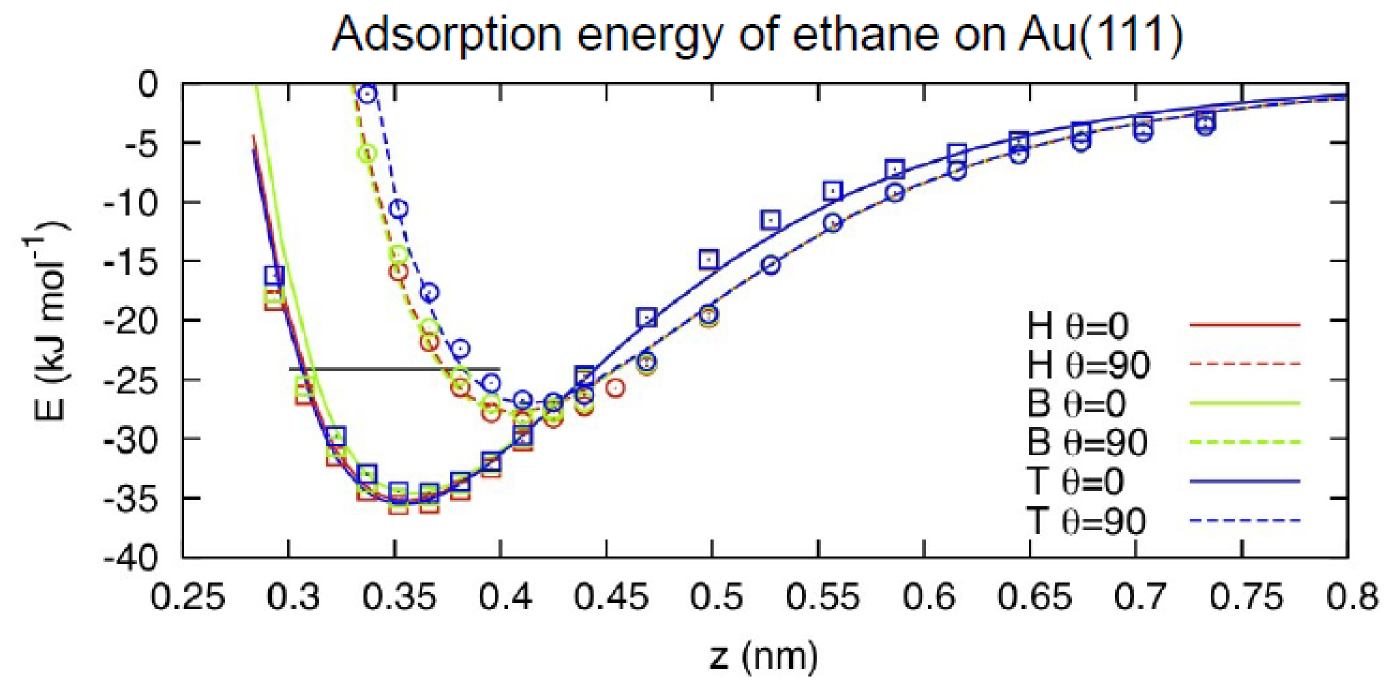


Very good agreement between DFT and Atomistic data at all distances!

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

- **Ethylene/Au interaction - Morse potential:** $V_{LJ}(r_{ij}) = \varepsilon_{ij}\left[\exp\left(-2\alpha_{ij}\left(r_{ij} - r_{0,ij}\right)\right) - 2\exp\left(-\alpha_{ij}\left(r_{ij} - r_{0,ij}\right)\right)\right]$

Adsorption energy vs distance for various sites/orientations



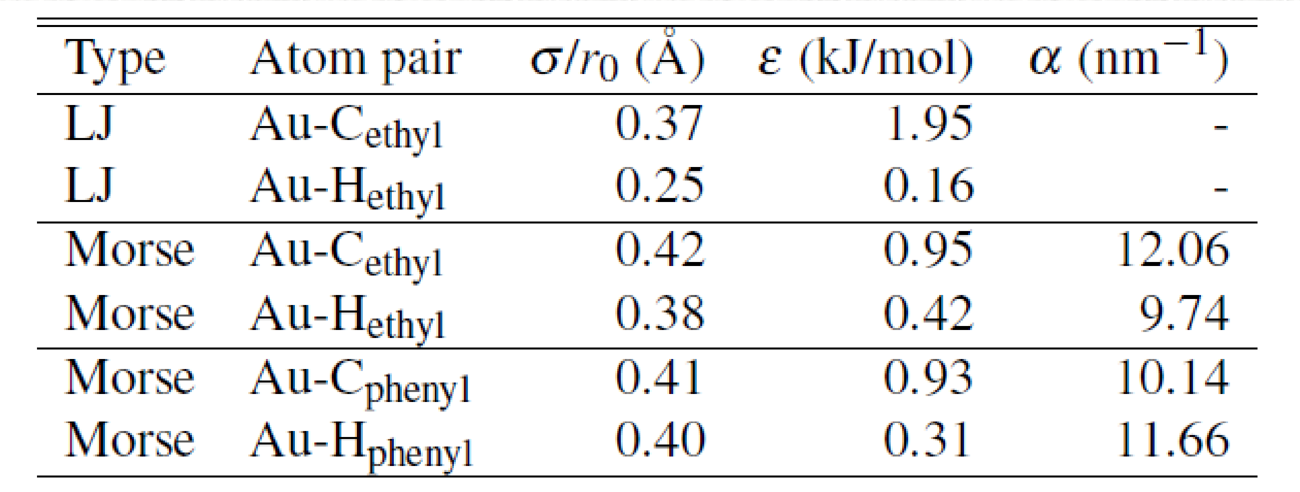
- vdW dominated interaction
- Adsorption much weaker than benzene
- Morse potential is good fit to DFT data

Polymer/Metal Interfaces: New Atomistic Force Field

- **Results**: **New atomistic force field for PS/Au systems using Morse potential.**

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

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



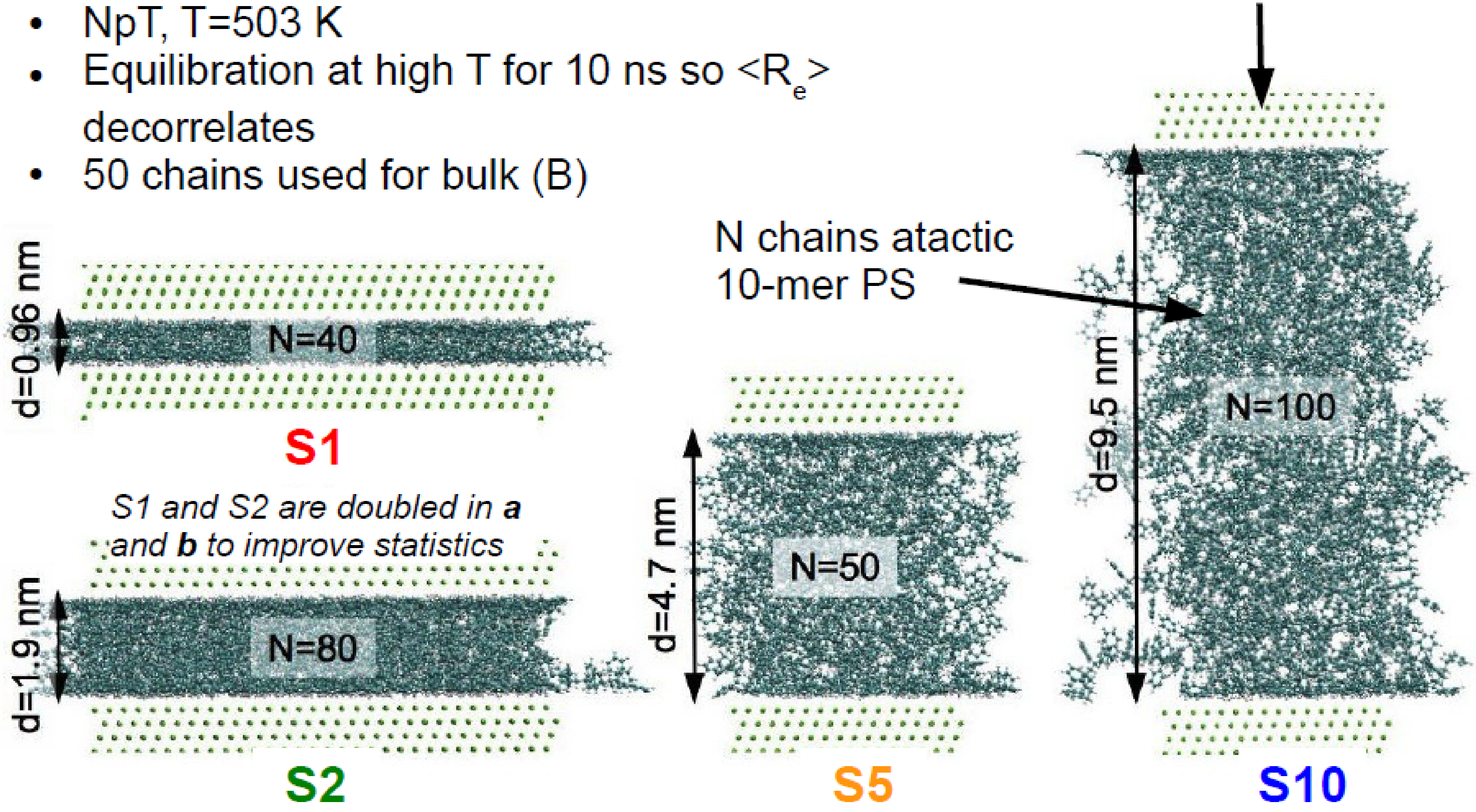
Type	Atom pair	σ/r_0 (Å)	ε (kJ/mol)	α (nm^{-1})
LJ	Au-C$_{\text{ethyl}}$	0.37	1.95	-
LJ	Au-H$_{\text{ethyl}}$	0.25	0.16	-
Morse	Au-C$_{\text{ethyl}}$	0.42	0.95	12.06
Morse	Au-H$_{\text{ethyl}}$	0.38	0.42	9.74
Morse	Au-C$_{\text{phenyl}}$	0.41	0.93	10.14
Morse	Au-H$_{\text{phenyl}}$	0.40	0.31	11.66

☐ **Excellent agreement between DFT and atomistic data, using a Morse potential, at all distances, adsorption sites and orientations.**

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)

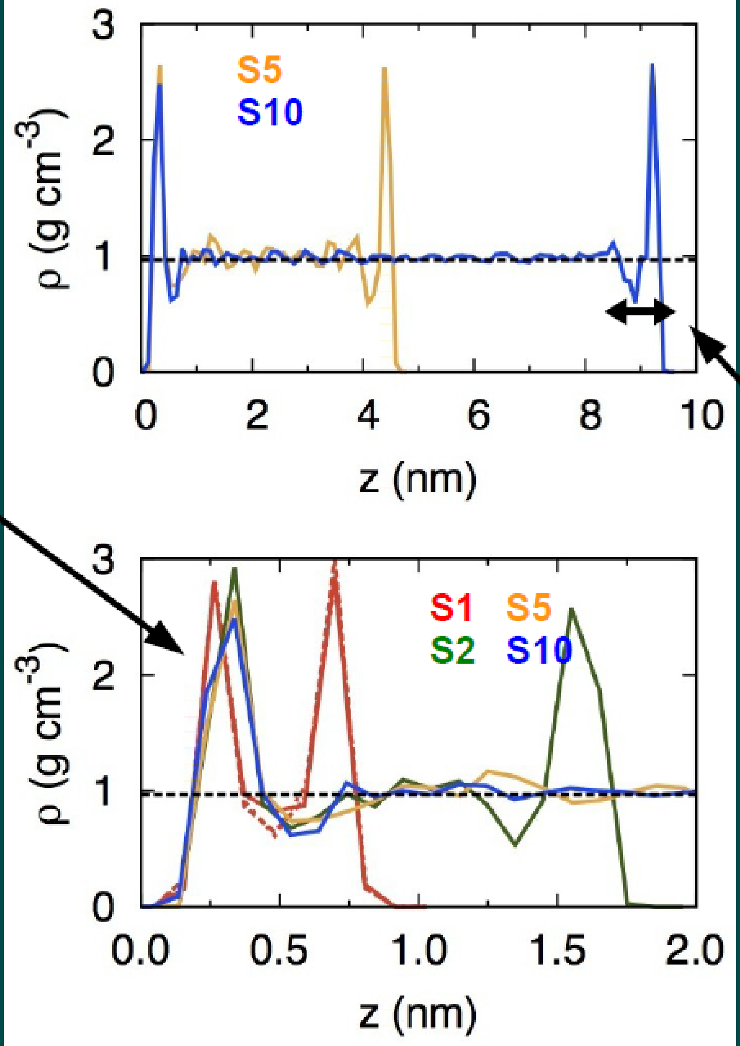
7 layer Au slab
Fixed positions



S1 and S2 are doubled in ***a*** *and* ***b*** *to improve statistics*

Hybrid Polystyrene/Au Systems: Density - Structure

Density profiles



Single peak at surface (adsorption layer)

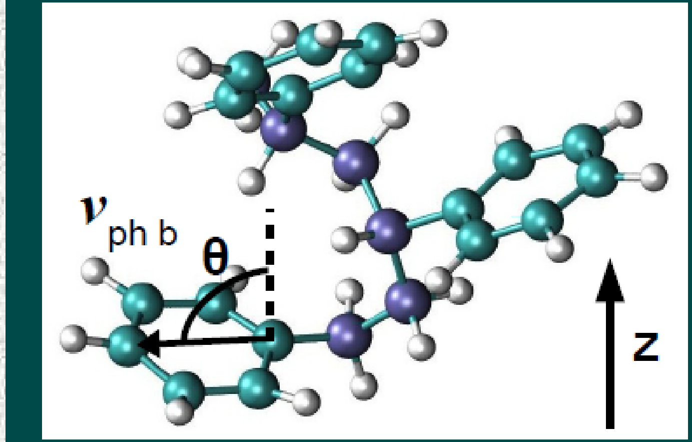
Film reaches bulk density ≈1.5 nm from surface

Hybrid Polystyrene/Au Systems: Structure

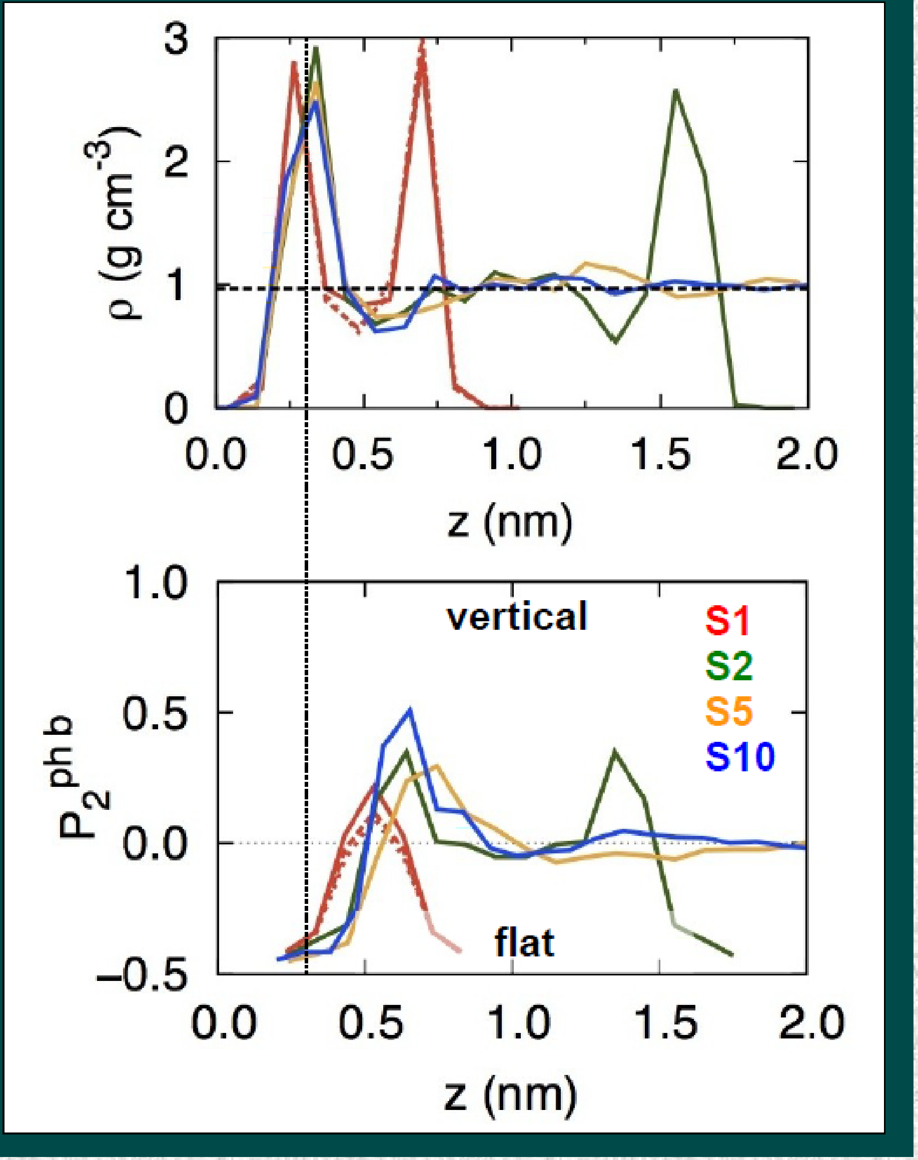
Structure – Orientation parameter P_2

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

```
= +1.0 perpendicular
  -0.5 parallel
```



Phenyl rings in adsorption layers align parallel to surface

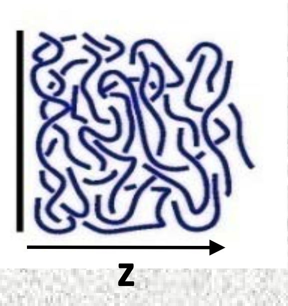


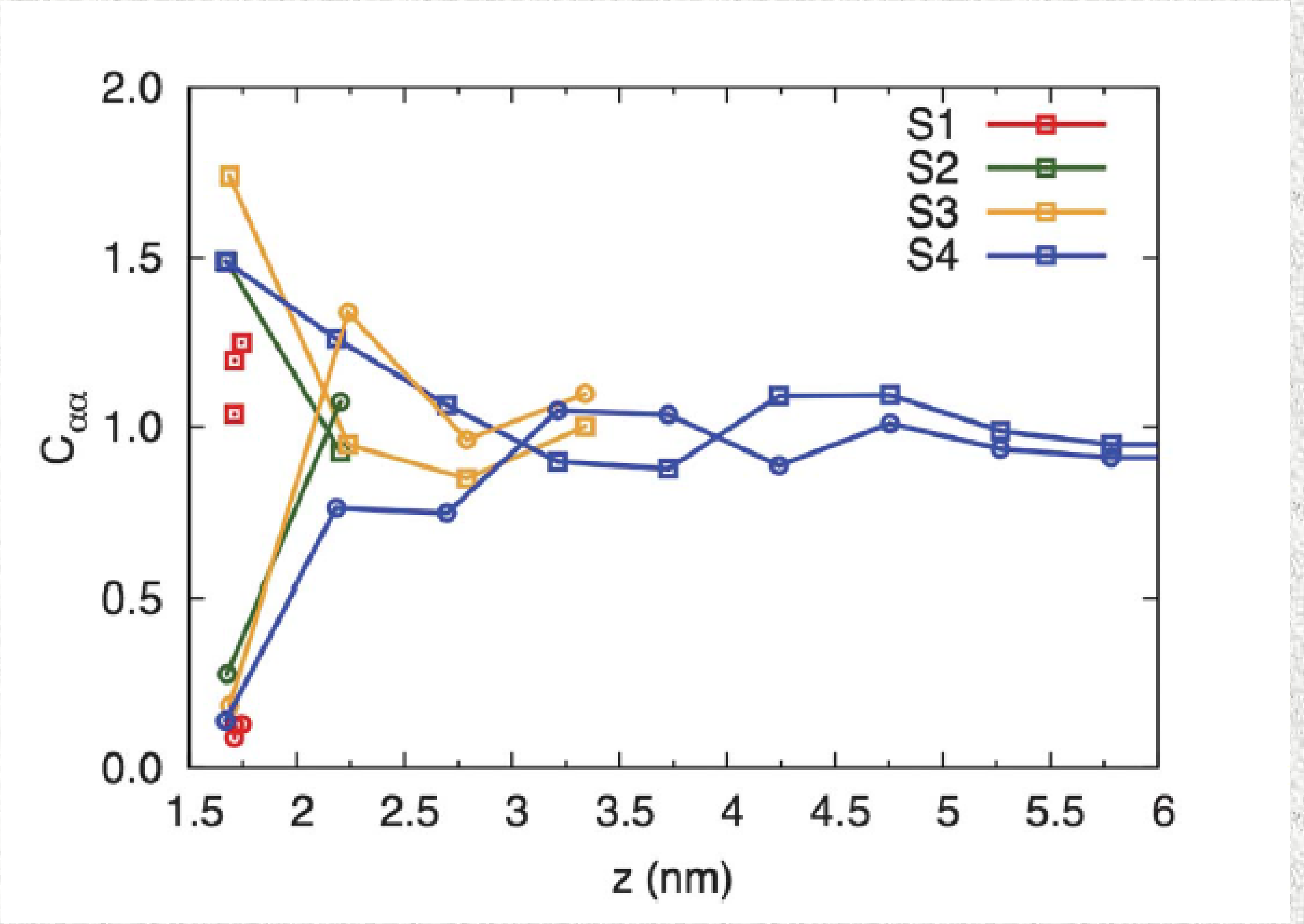
Polystyrene/Au Interfaces: Conformation Tensor

$$C_{\alpha\beta} = \frac{\langle R_\alpha \bullet R_\beta \rangle}{3\langle R^2 \rangle_{eq}}$$

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

- **Bulk: $C_{xx}=C_{yy}=C_{zz}=1$**

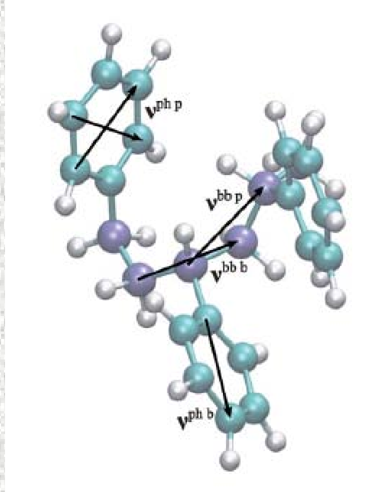


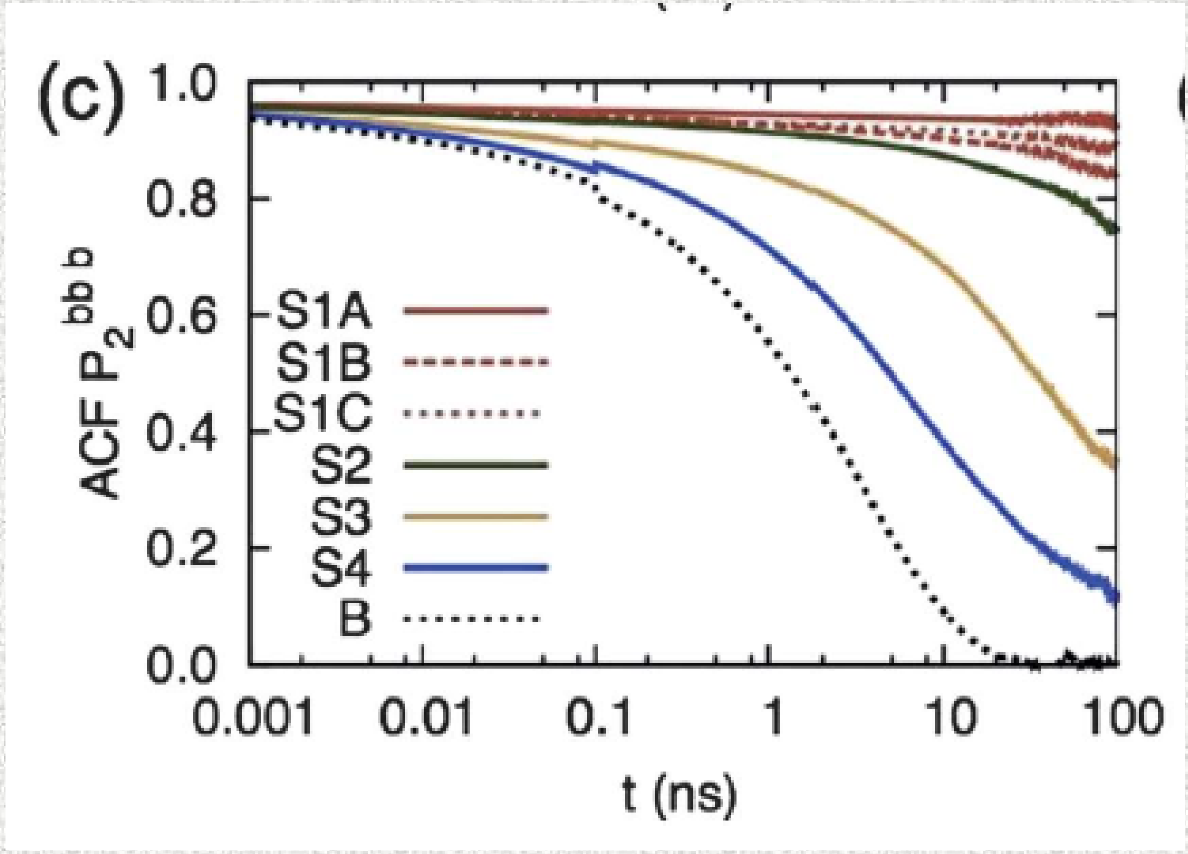


- **(squares) $(C_{xx} + C_{yy})/2 > 1$ for distances < 3 nm from the Au substrate**
- **(circles) $C_{zz} < 1$ for distances < 3-4 nm from the Au substrate**

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

❑ Local dynamics of different vectors along the monomer





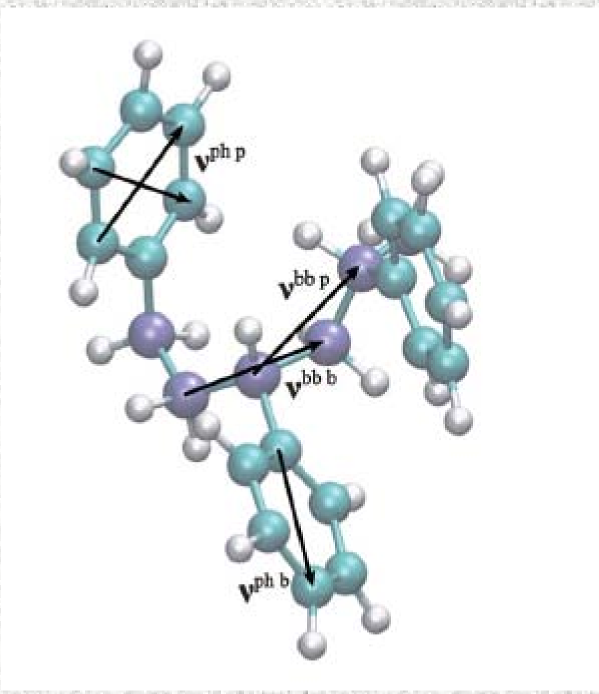
$$P_2(t)=\frac{1}{2}\left(3\left\langle\cos^2(\theta(t))\right\rangle-1\right)$$

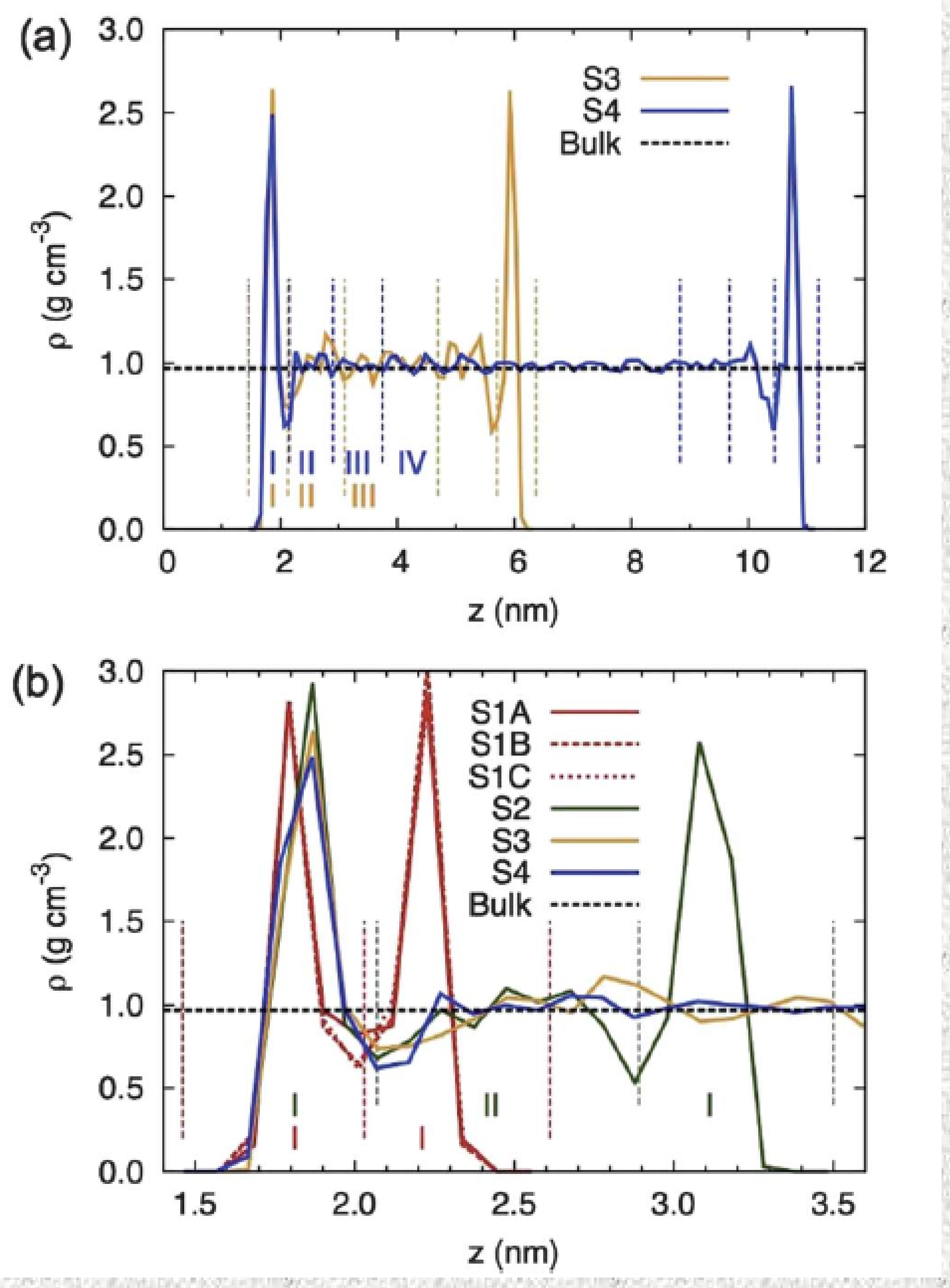
❑ $P_2(t)$ can be fitted with stretched exponential functions:

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

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

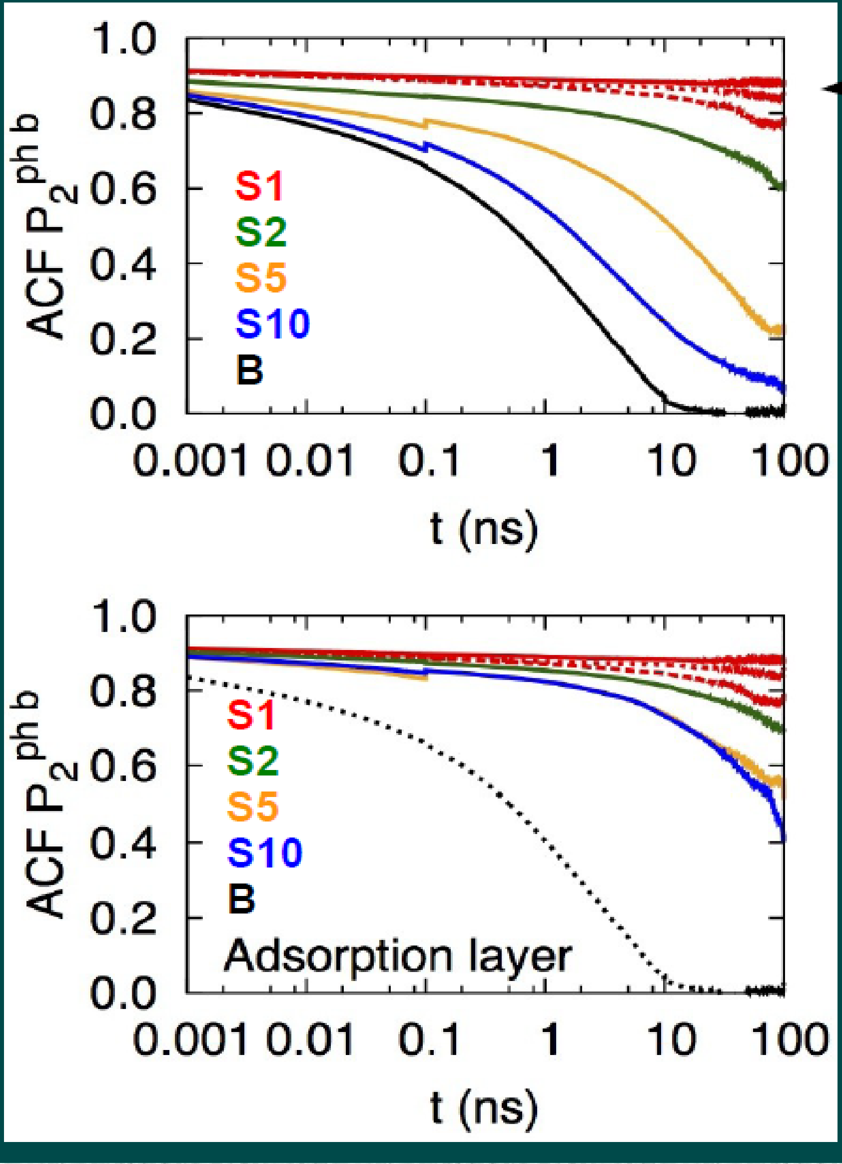
- **Define adsorption layers I - IV**





Hybrid Polystyrene/Au Systems: Local Dynamics

Dynamics – Time autocorrelation function for P2



S1 films almost frozen

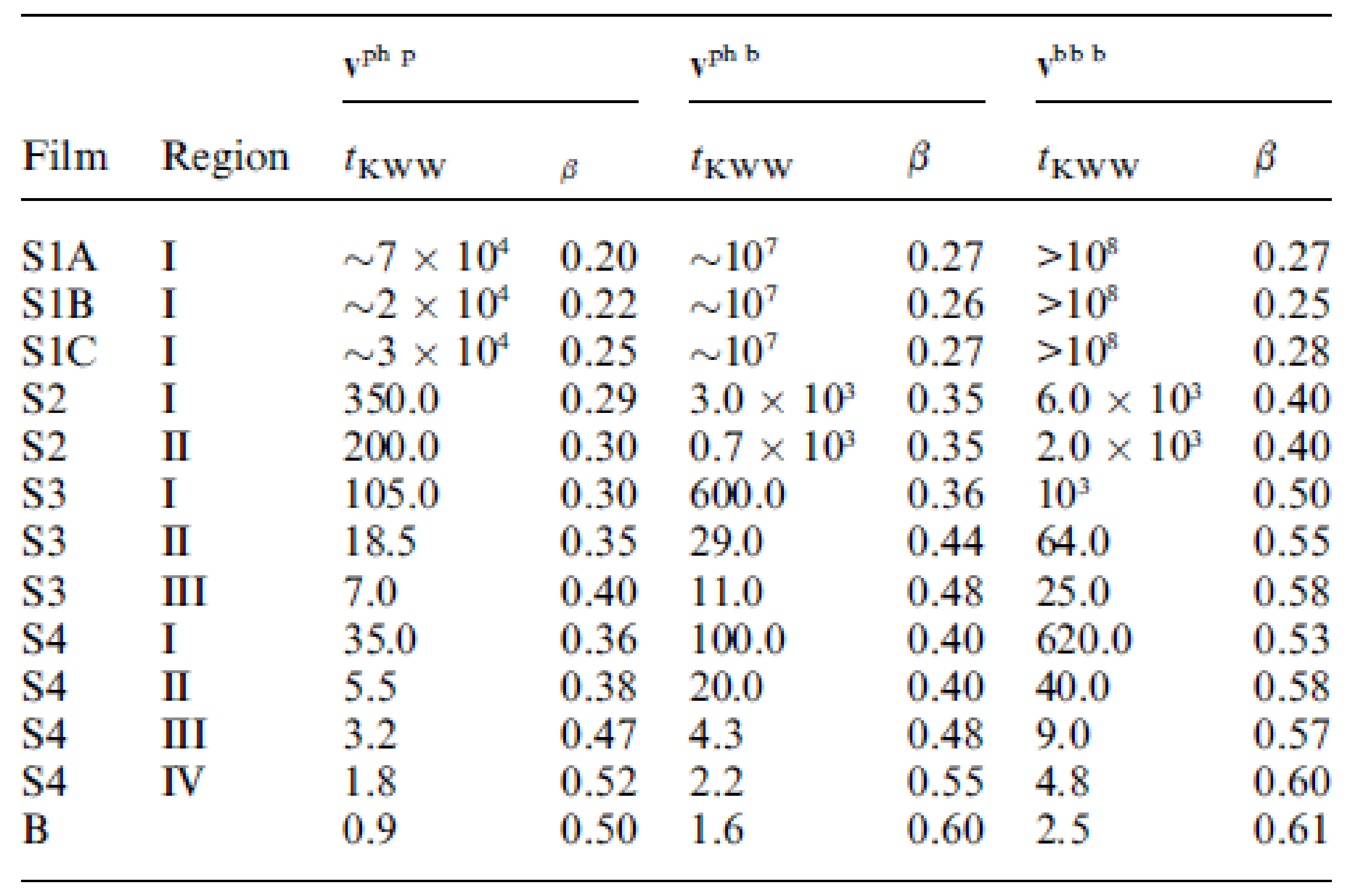
Confinement increases decorrelation time

Dynamics slowest in adsorption layer

Similar trend in mean square displacements

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

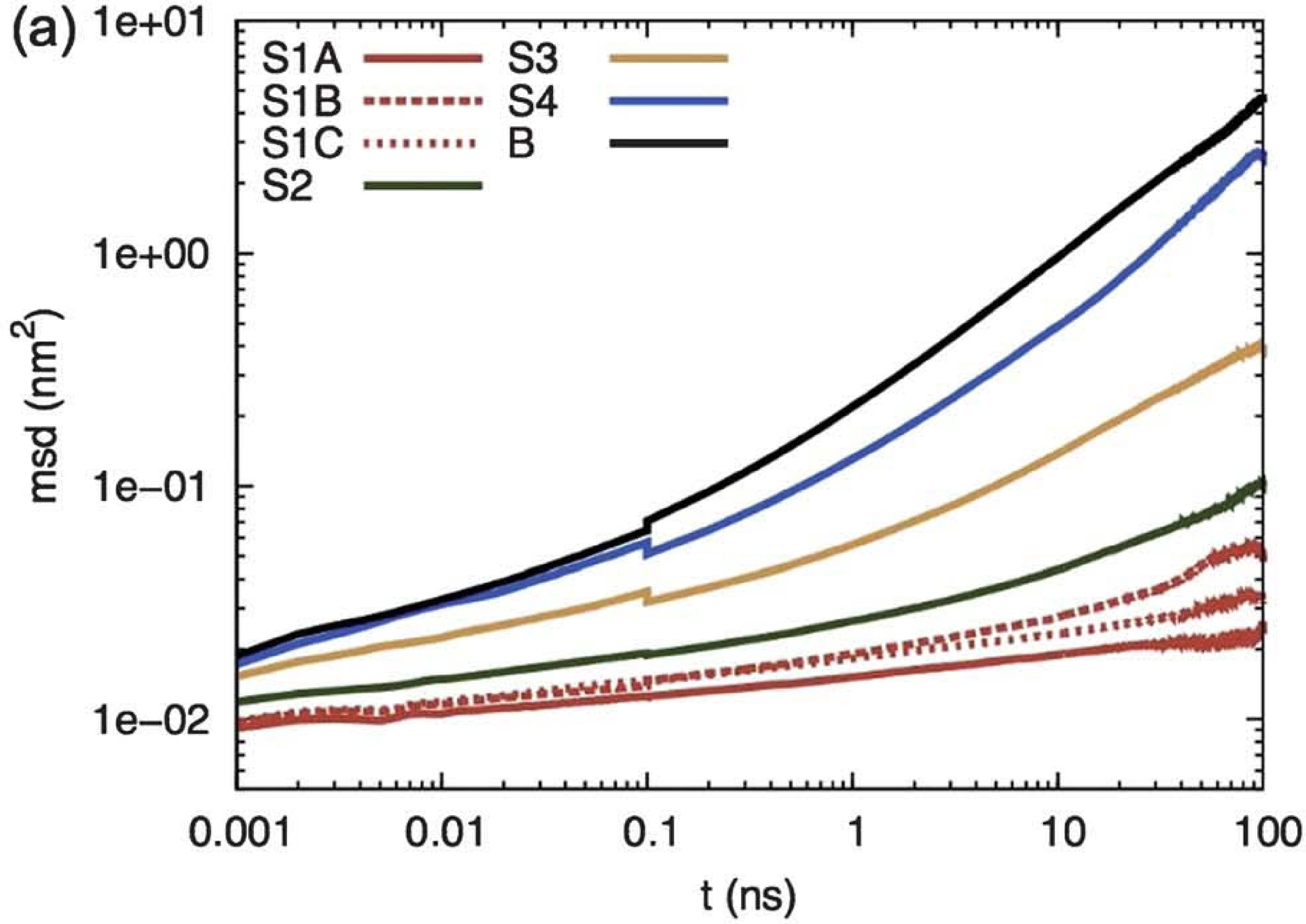
- **Segmental relaxation times (ns) and stretching exponents of PS molecules for different adsorption layers.**



Film	Region	$\nu^{ph\ p}$		$\nu^{ph\ b}$		$\nu^{bb\ b}$	
		t_{KWW}	β	t_{KWW}	β	t_{KWW}	β
S1A	I	$\sim 7 \times 10^4$	0.20	$\sim 10^7$	0.27	$>10^8$	0.27
S1B	I	$\sim 2 \times 10^4$	0.22	$\sim 10^7$	0.26	$>10^8$	0.25
S1C	I	$\sim 3 \times 10^4$	0.25	$\sim 10^7$	0.27	$>10^8$	0.28
S2	I	350.0	0.29	3.0×10^3	0.35	6.0×10^3	0.40
S2	II	200.0	0.30	0.7×10^3	0.35	2.0×10^3	0.40
S3	I	105.0	0.30	600.0	0.36	10^3	0.50
S3	II	18.5	0.35	29.0	0.44	64.0	0.55
S3	III	7.0	0.40	11.0	0.48	25.0	0.58
S4	I	35.0	0.36	100.0	0.40	620.0	0.53
S4	II	5.5	0.38	20.0	0.40	40.0	0.58
S4	III	3.2	0.47	4.3	0.48	9.0	0.57
S4	IV	1.8	0.52	2.2	0.55	4.8	0.60
B		0.9	0.50	1.6	0.60	2.5	0.61

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

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

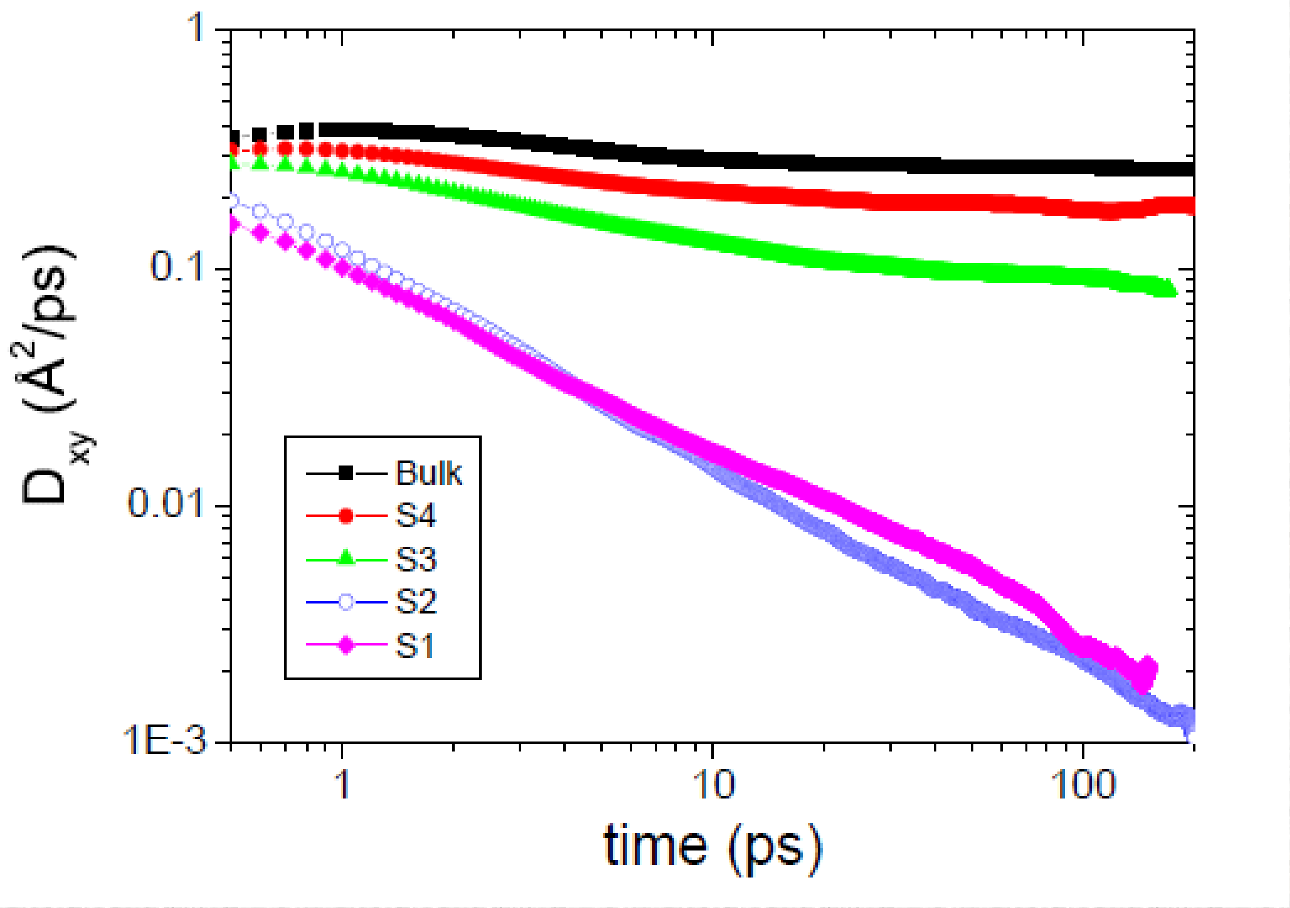


- ❑ Strongly confined systems : practically frozen.

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

- ☐ **Define effective diffusivity in the xy plane:**

$$D \equiv D(z,t) = \frac{\left\langle \left(R_{cm}(t) - R_{cm}(0) \right)^2 \right\rangle}{6t}$$



Current Work: (C) Realistic Polymer Nanocomposites

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

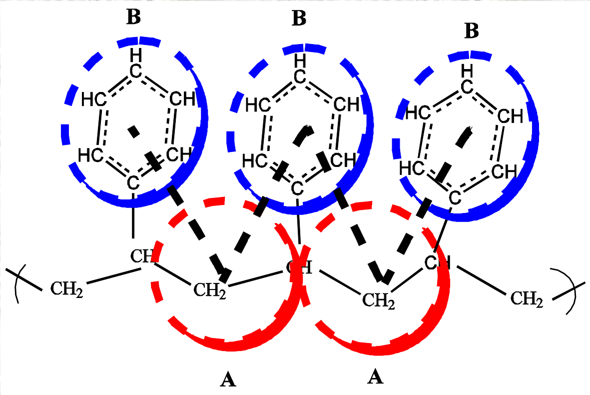
- Full study of realistic nanocomposites requires modeling of huge systems.

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.

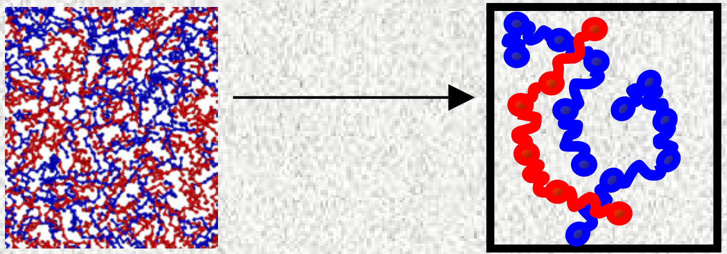
$\sigma_A = 4.25$ Å, $\sigma_B = 5.10$ Å

- 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.

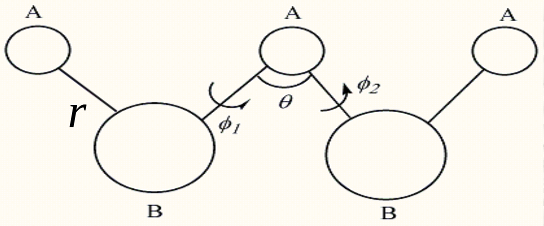
Re-introduction (back-mapping) of the atomistic detail if needed.

DEVELOP THE EFFECTIVE MESOSCOPIC CG POLYMER FORCE FIELD

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

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

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

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

- **Assumption:**

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

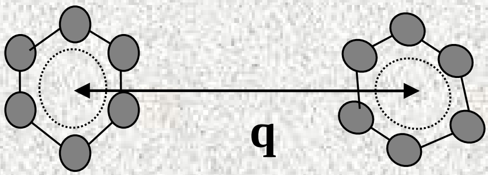
- **Finally:**

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

NONBONDED INTERACTION PARAMETERS: REVERSIBLE WORK

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

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



<u>Reversible work method</u> [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:**

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

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

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

NONBONDED INTERACTION PARAMETERS: REVERSIBLE WORK

- **Calculate "reversible work" using a numerical method (eg. MC or MD).**

- **Assumptions:**

(A) Neglect many-body effect. Exact for the gas phase.

(B) Chain effect is not described. In our case CG particles belong to a macromolecule.

Solution: Use of conditional reversible work
[Fritz et al, 2009]

- **Main idea: Use instead two very short chains and keep constant the distance between the center-of-mass of only the two target CG (e.g. 1, 2) particles.**

(A) Calculate the PMF including all atomistic interactions, $V_{PMF}^{1-2}(\mathbf{q},T)$

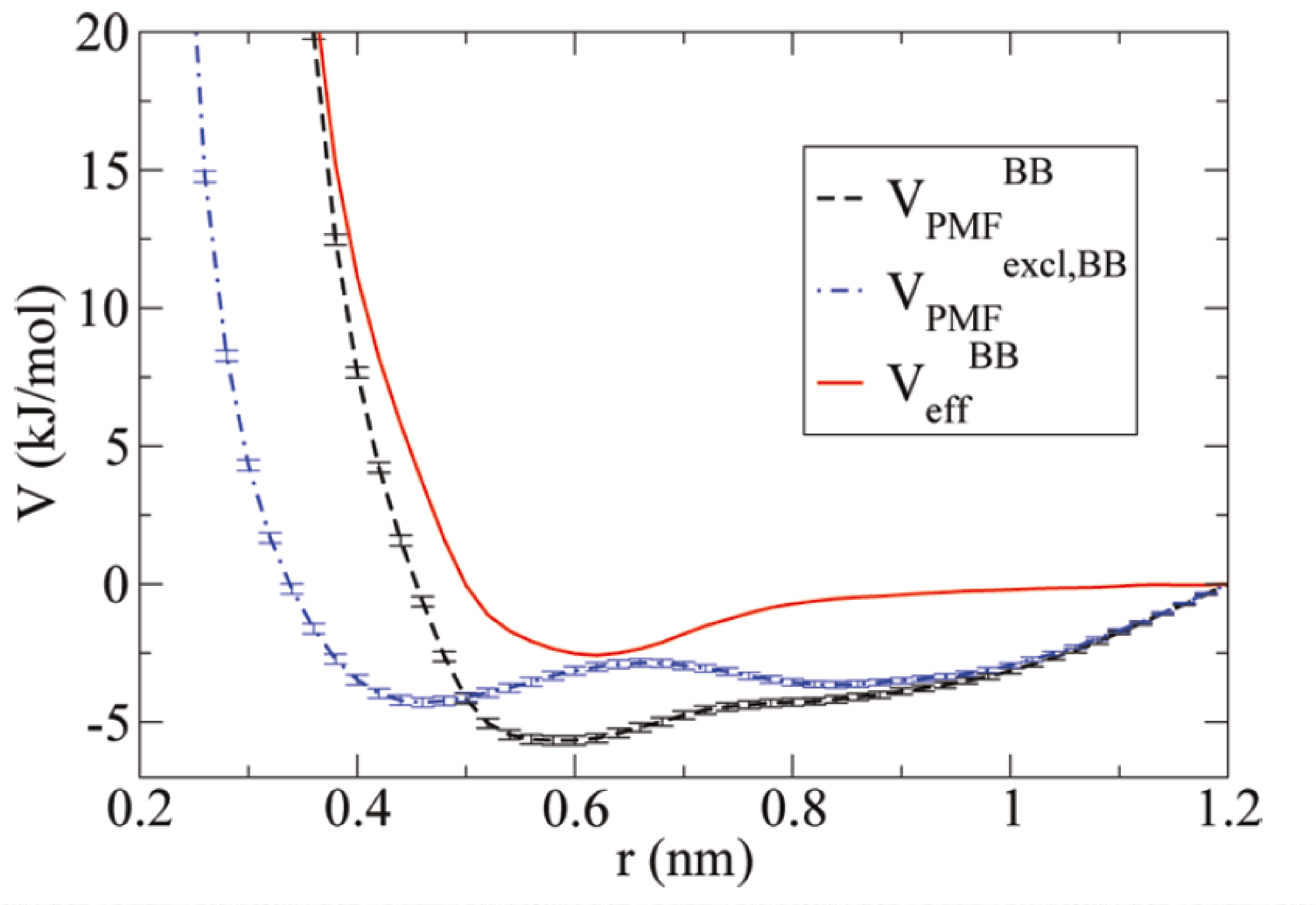
(B) Calculate the PMF with all atomistic interactions excluding the A-B ones. $V_{PMF}^{1-2,Excl}(\mathbf{q},T)$

- ❑ **Effective CG interaction is:**

$$U_{nb}^{CG,1-2}(\mathbf{q},T) = V_{PMF}^{1-2}(\mathbf{q},T) - V_{PMF}^{1-2,Excl}(\mathbf{q},T)$$

CG NONBONDED EFFECTIVE INTERACTION POTENTIAL

- CG effective potential calculated by the reversible work method using short chains.



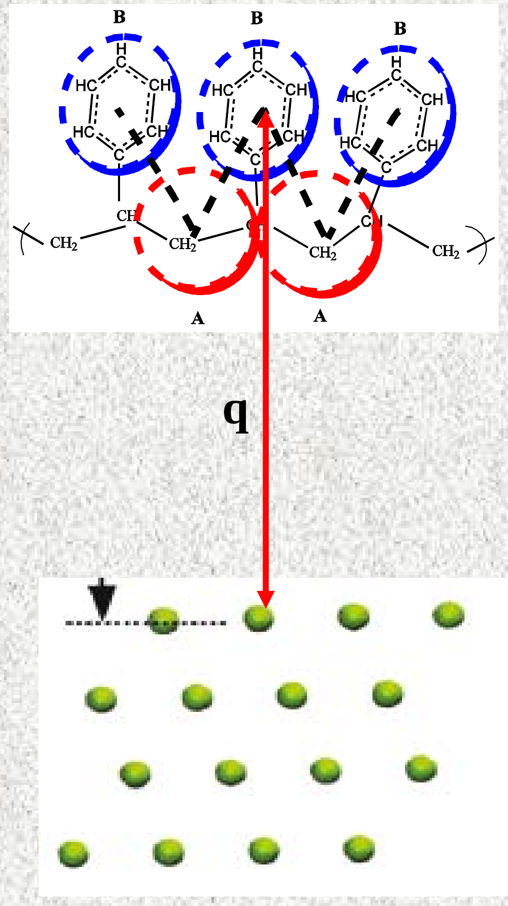
Polymer/Metal Interfaces: Coarse-Grained Model

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

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

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

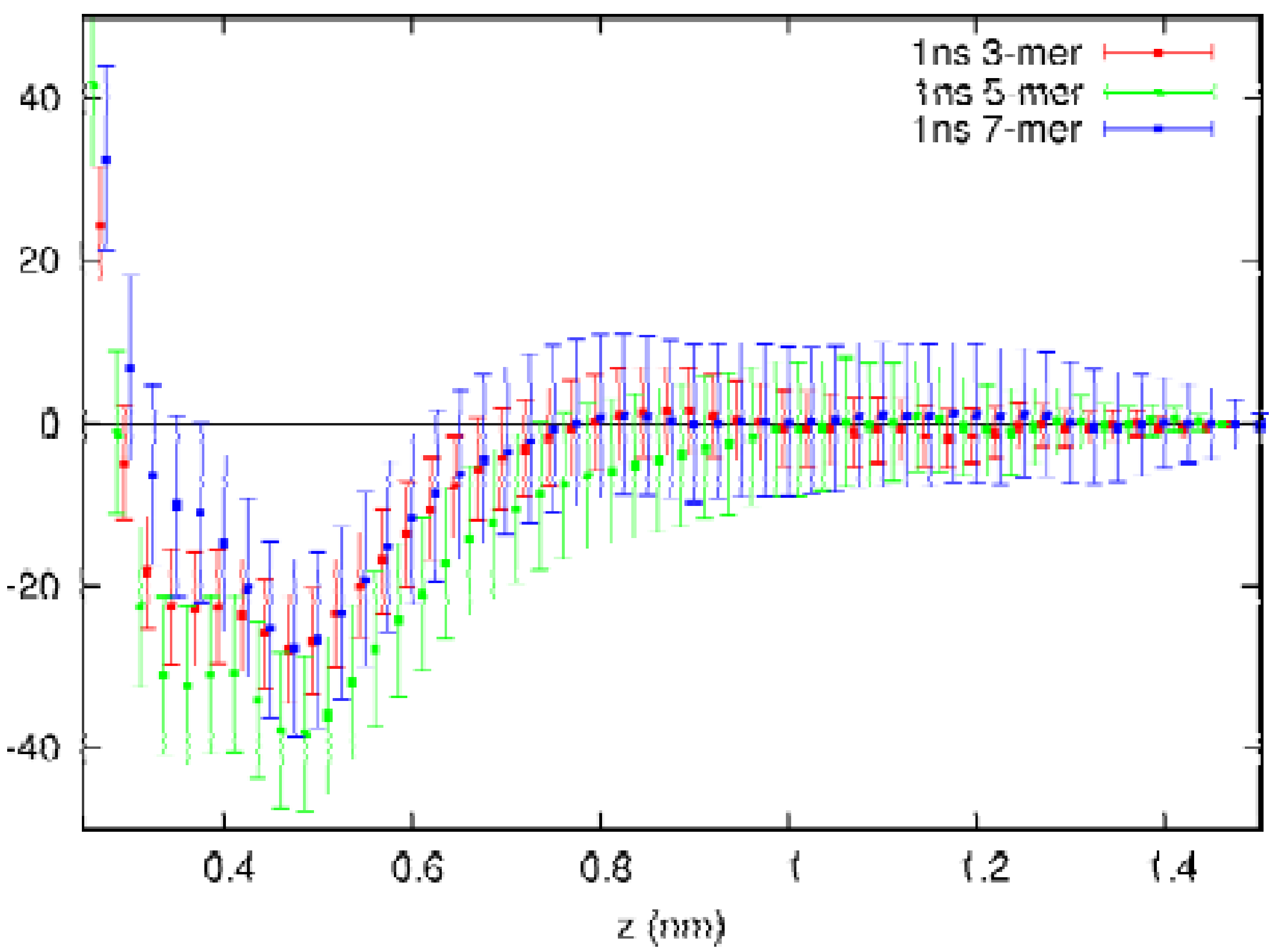
$$\boxed{U^{CG}_{superatom/surface}(\mathbf{q})}$$



Polymer/Metal Interfaces: Coarse-Grained Model

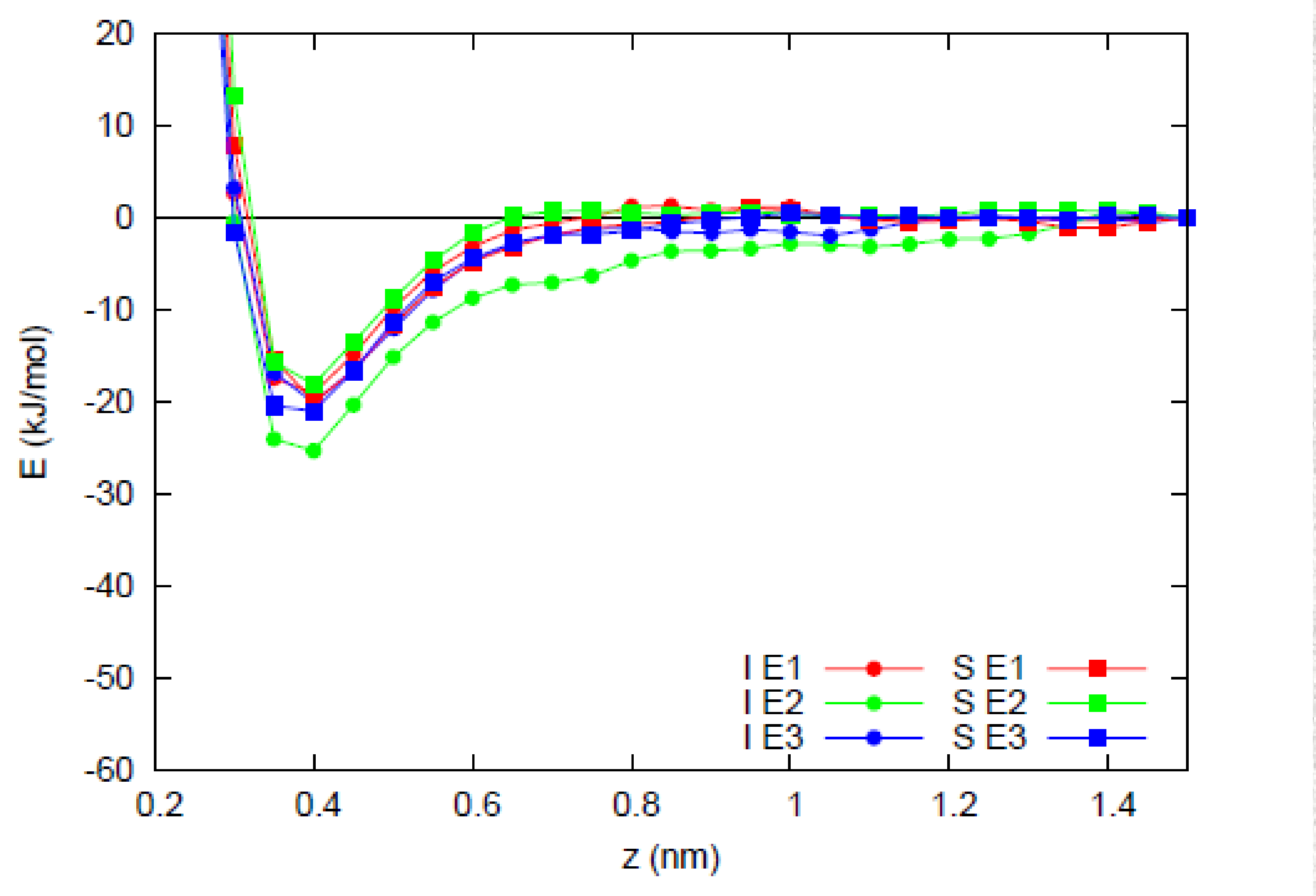
- ❑ **Effect of chain length: Interaction potential for phenyl ("P") bead**

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



Polymer/Metal Interfaces: Coarse-Grained Effective Interaction

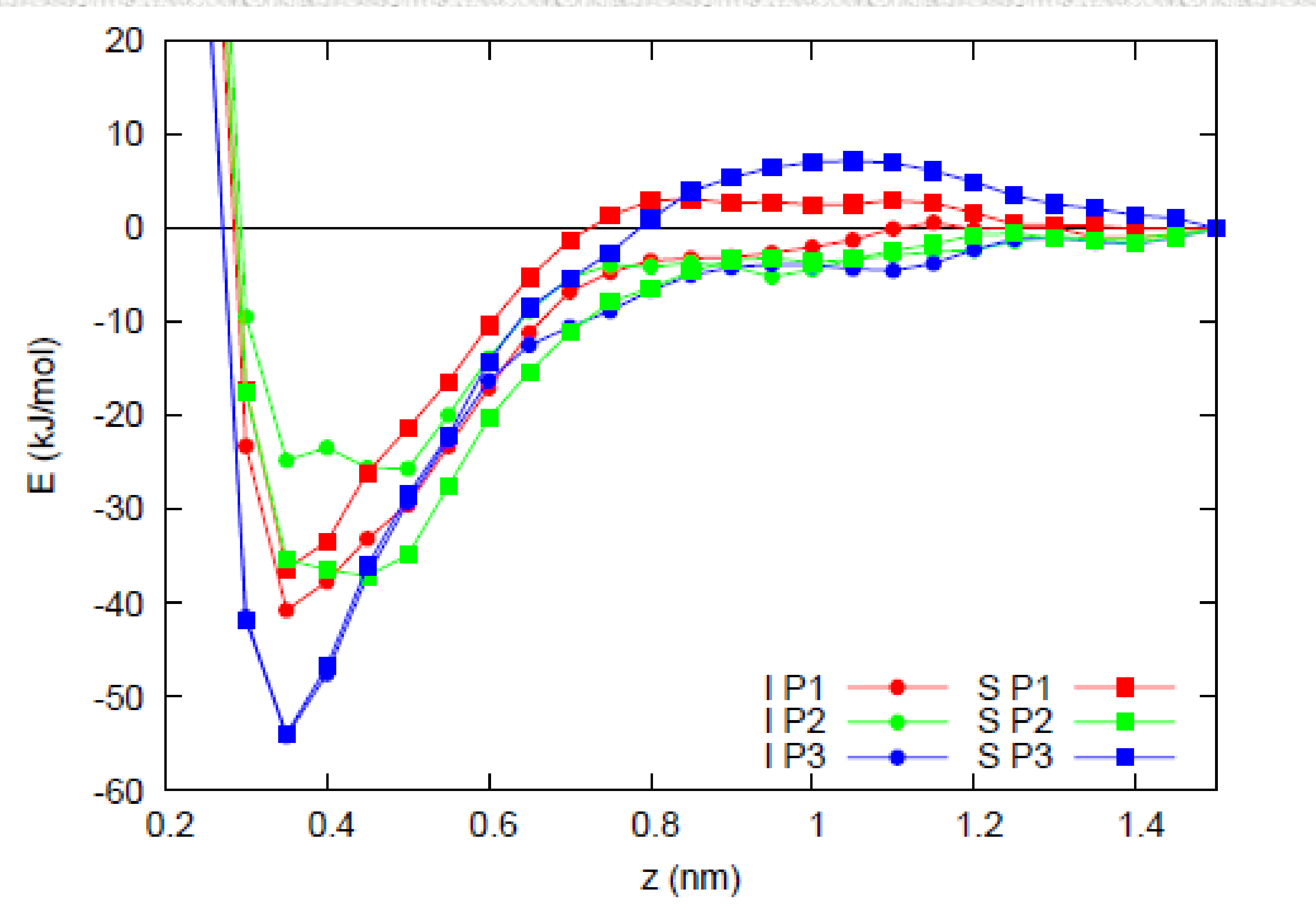
- Effect of chain tacticity and position along the chain: Ethylene (“E”) bead



- Central backbone, “E”, beads are strongly adsorbed on the surface (?)

Polymer/Metal Interfaces: Coarse-Grained Effective Interaction

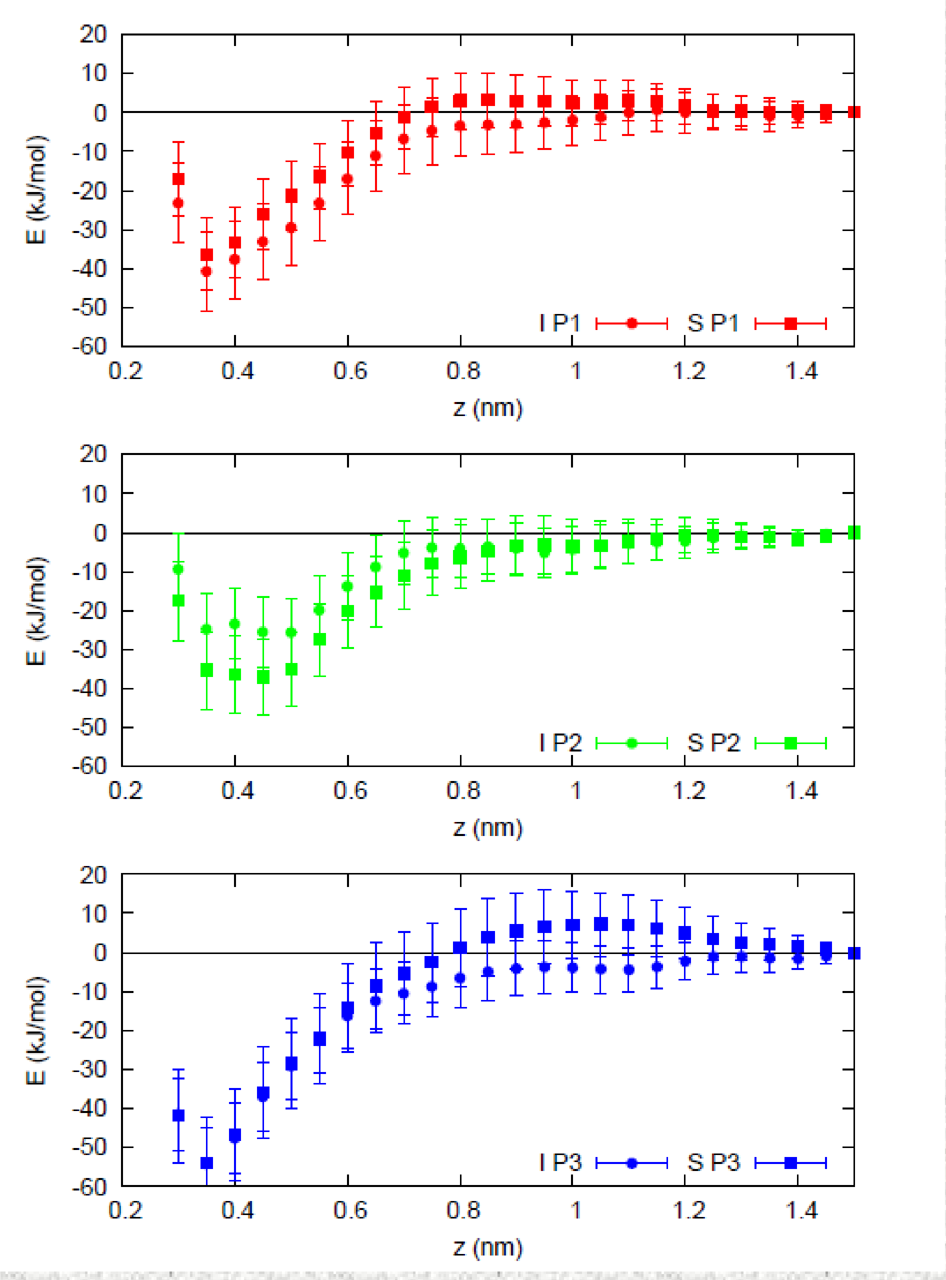
- ❑ **Effect of chain tacticity and position along the chain: Phenyl ("P") bead**



- ❑ **End phenyl (side) "P", beads are strongly adsorbed on the surface (?)**

Polymer/Metal Interfaces: Coarse-Grained Effective Interaction

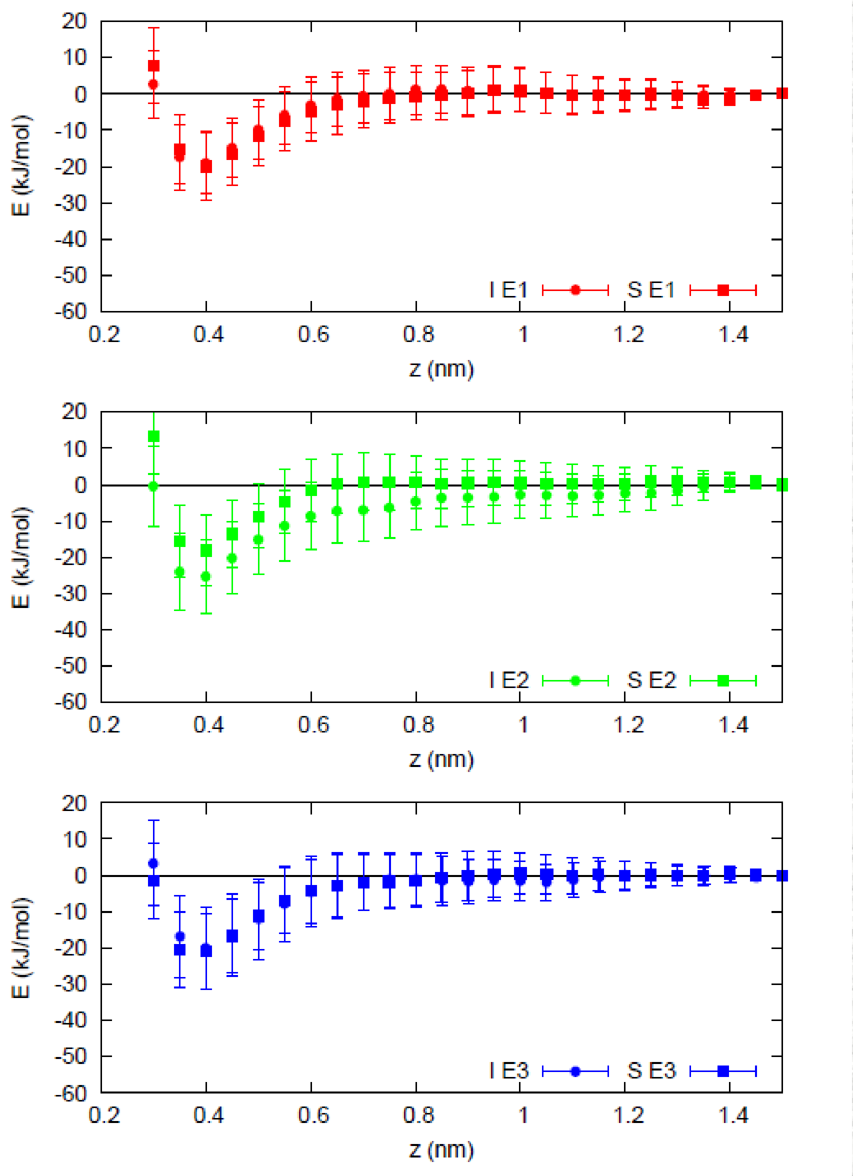
- ☐ **Effect of chain tacticity and position along the chain: Ethylene ("E") bead**



- ☐ **Central backbone, "E", beads are strongly adsorbed on the surface (?)**

Polymer/Metal Interfaces: Coarse-Grained Effective Interaction

- ☐ Effect of chain **tacticity** and **position along the chain**: Phenyl (“P”) bead



- ☐ Central backbone, “E”, beads are strongly adsorbed on the surface (?)

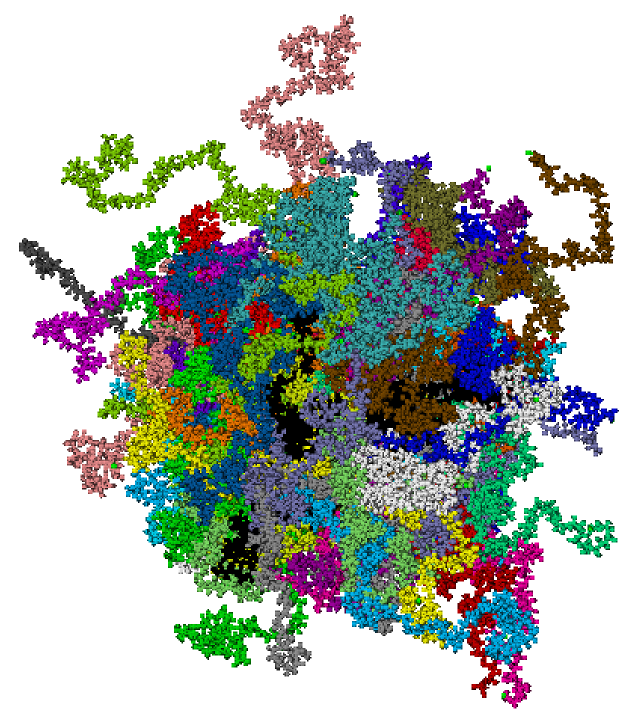
Current work: CG Simulations of PS/Au Hybrid Systems

❑ Example: Equilibrium Polymer Melts

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

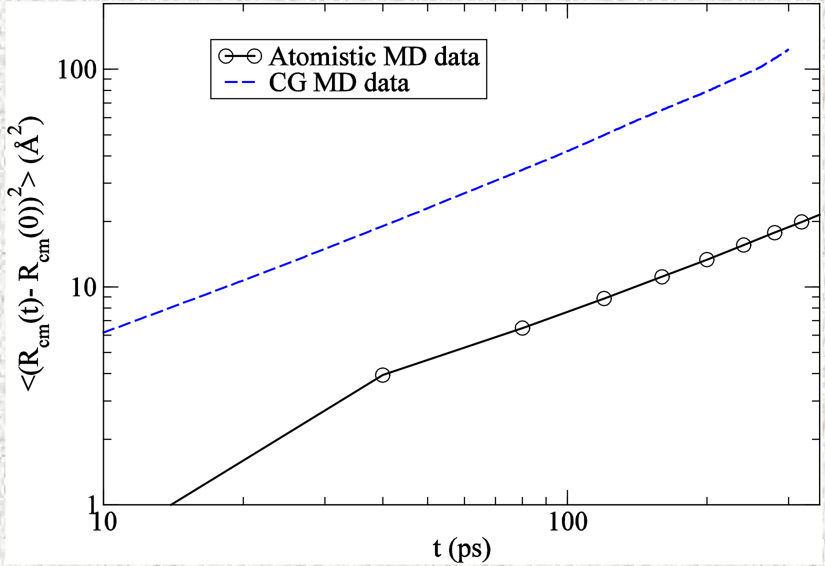
$$\boxed{m_i \frac{\partial^2 \mathbf{q}_i}{\partial t^2} = -\frac{\partial U^{CG}}{\partial \mathbf{q}_i} - \Gamma \frac{\partial \mathbf{q}_i}{\partial t} + W_i(t)}$$

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

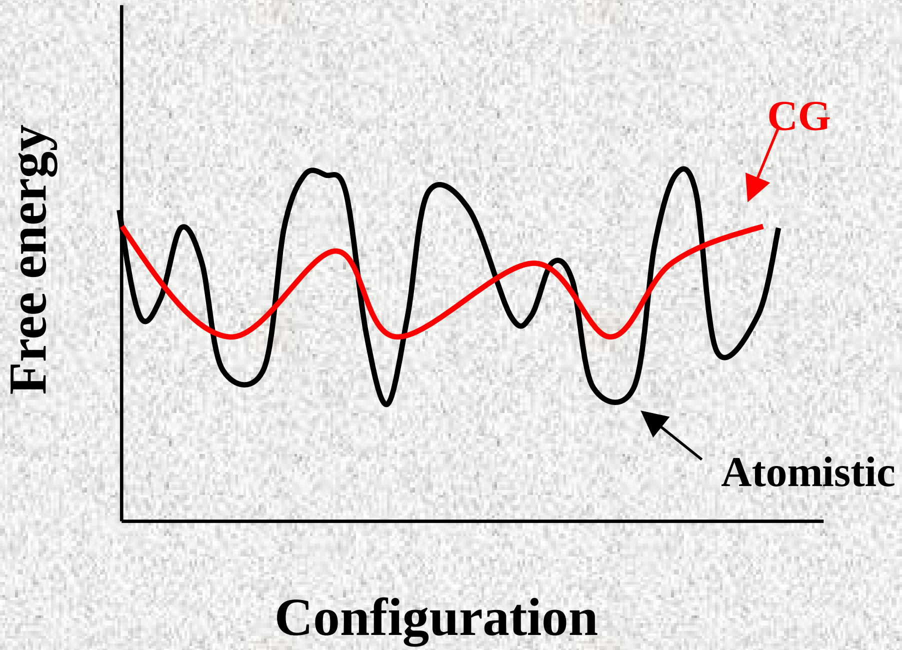


CG POLYMER DYNAMICS IS FASTER

PS, 1kDa, T=463K



Free Energy Landscape



-- CG effective interactions are *softer* than the real-atomistic ones due to lost degrees of freedom (lost forces).

➡ $\zeta_{AT} > \zeta_{CG}$ $D_{AT} < D_{CG}$

POLYMER DYNAMICS THROUGH CG SIMULATIONS

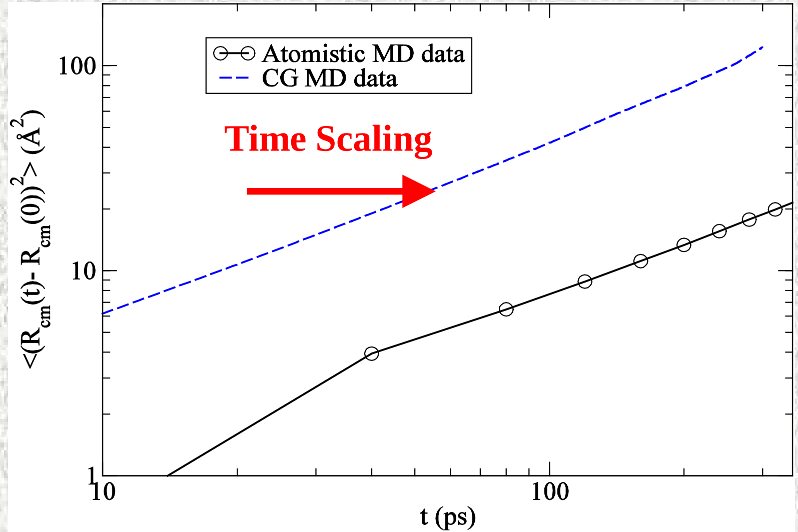
Quantitative Predictions - Proposed Semi-empirical Method:

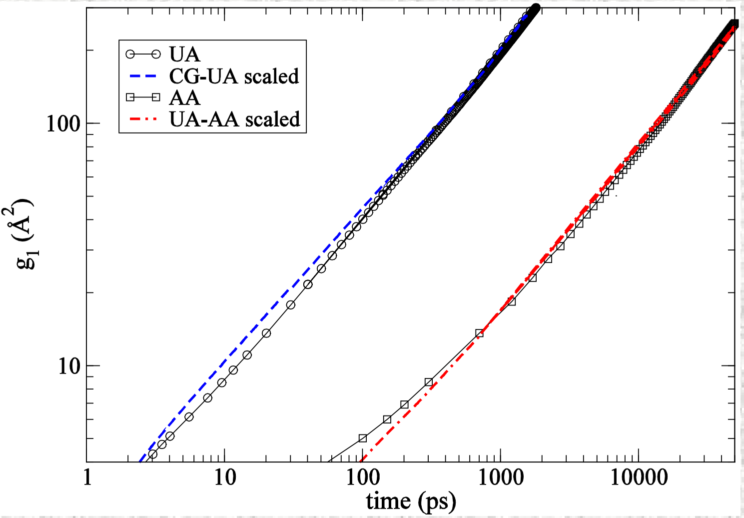
➢ **find the proper time in the CG description by scaling the raw data in time.**

A. Perform long microscopic (atomistic) simulations in a reference system.

B. Time mapping at that <u>specific state point</u>: calculate *S* for this system!

$$S = \tau_x \equiv \frac{D_{CG}}{D_{AT}} = \frac{\zeta_{AT}}{\zeta_{CG}}$$



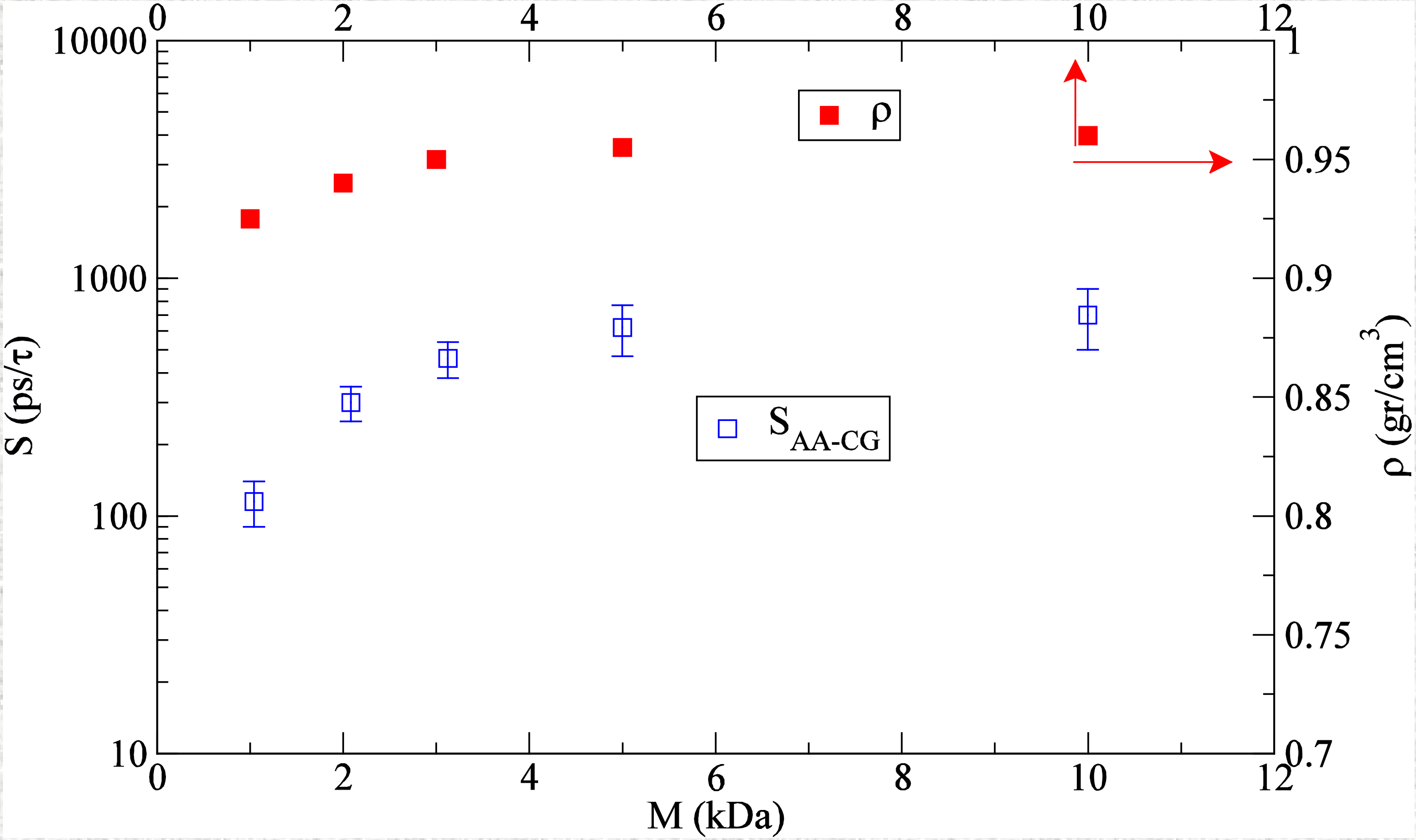


C. Check *transferability* of *S* for different systems, conditions (ρ, T, P, …).

APPLICATION: DYNAMICS OF LONG POLYSTYRENE MELTS

- **How does scaling parameter S depends on M, density?**

$$S \equiv \frac{D_{CG}}{D_{AT}} = \frac{\zeta_{AT}}{\zeta_{CG}}$$



[V. Harmandaris and K. Kremer, Soft Matter, 2012]

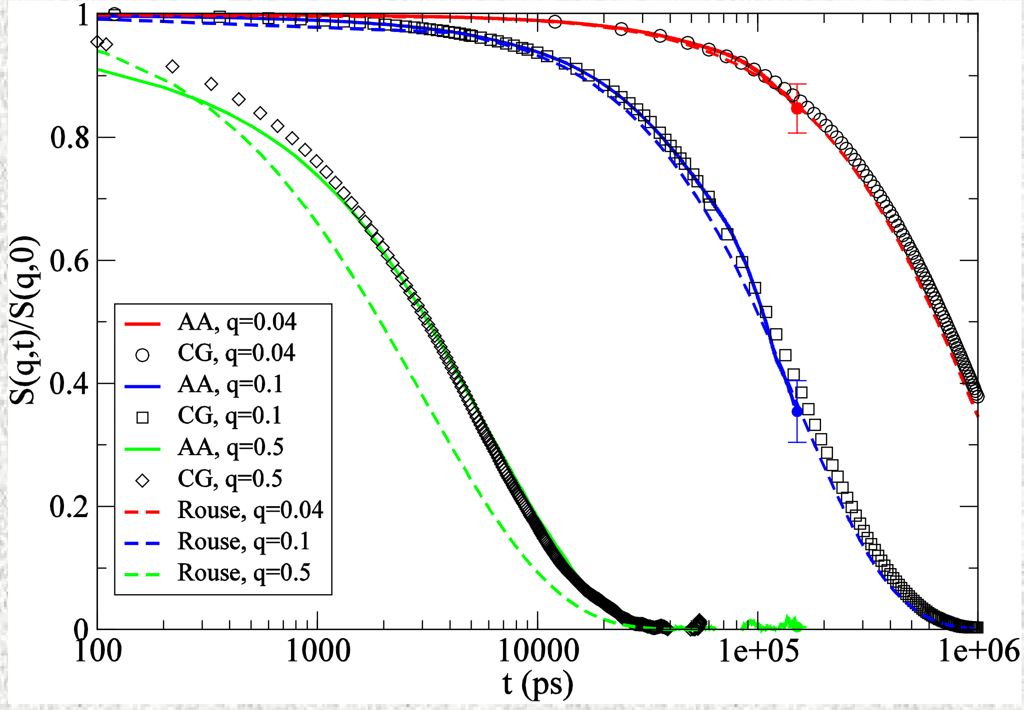
Local Dynamics: Single Chain Dynamic Structure Factor

[Harmandaris and Kremer, Macromolecules, 42, 791 (2009); Soft Matter 2009]

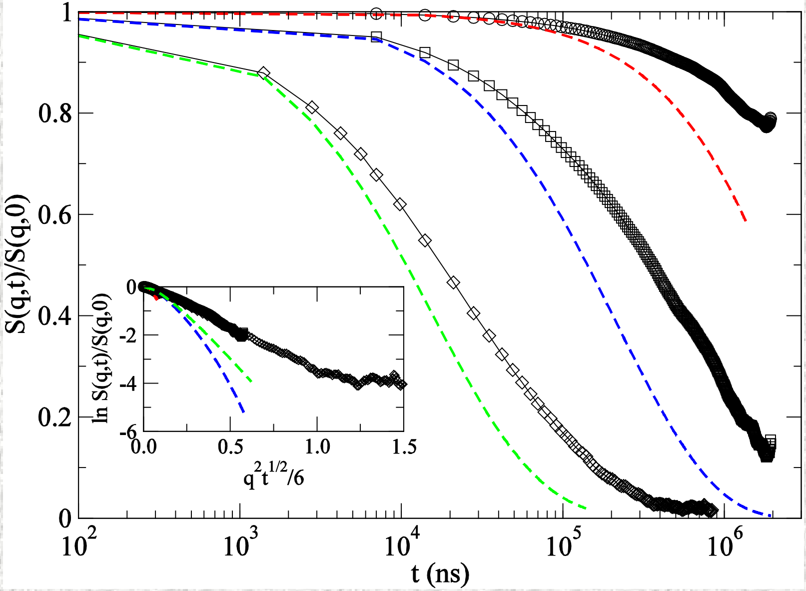
$$S(q,t)=\sum_{nm}\left\langle \sin\left[qR_{nm}(t)\right]/qR_{nm}(t)\right\rangle$$

$$R_{nm}(t)\equiv r_n(t)-r_m(0)$$

Short PS melt (M=1kDa)

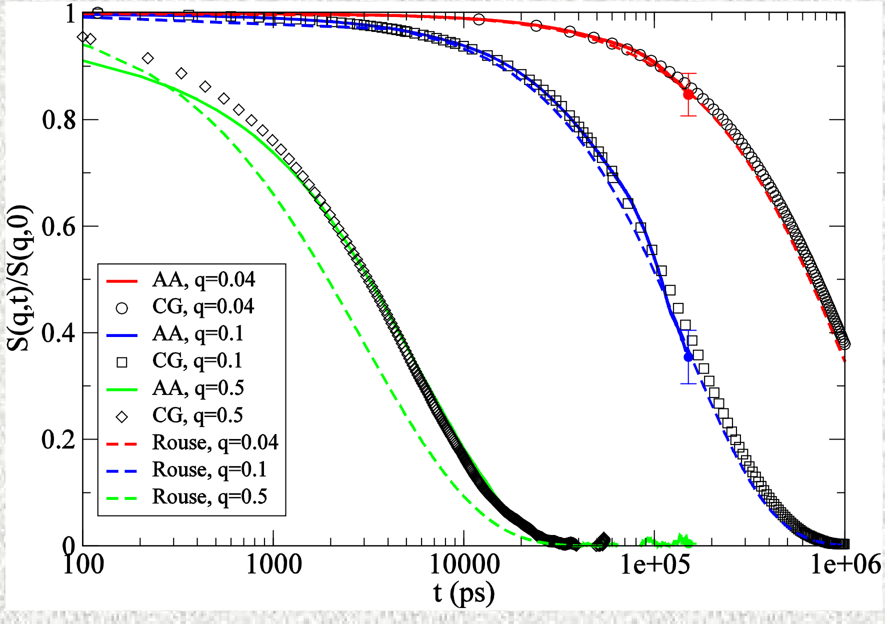


Entangled PS melt (M=50kDa)



Local Dynamics: Single Chain Dynamic Structure Factor

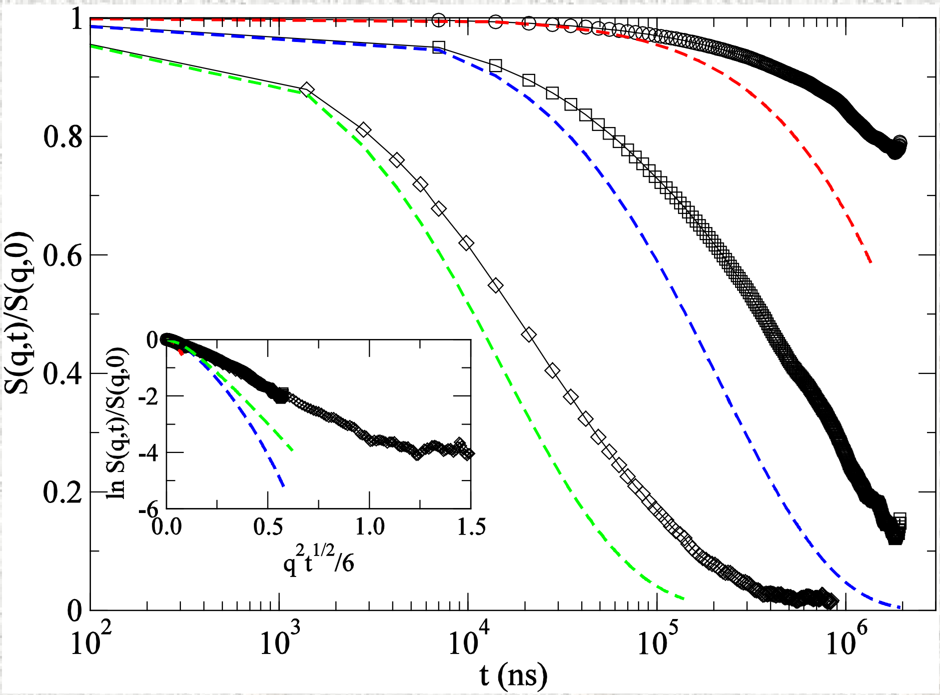
Short PS melt (M=1kDa)



$$S(q,t)=\sum_{nm}\left\langle \sin\left[qR_{nm}(t)\right]/\,qR_{nm}(t)\right\rangle$$

$$R_{nm}(t)\equiv r_n(t)-r_m(0)$$

Entangled PS melt (M=50kDa)



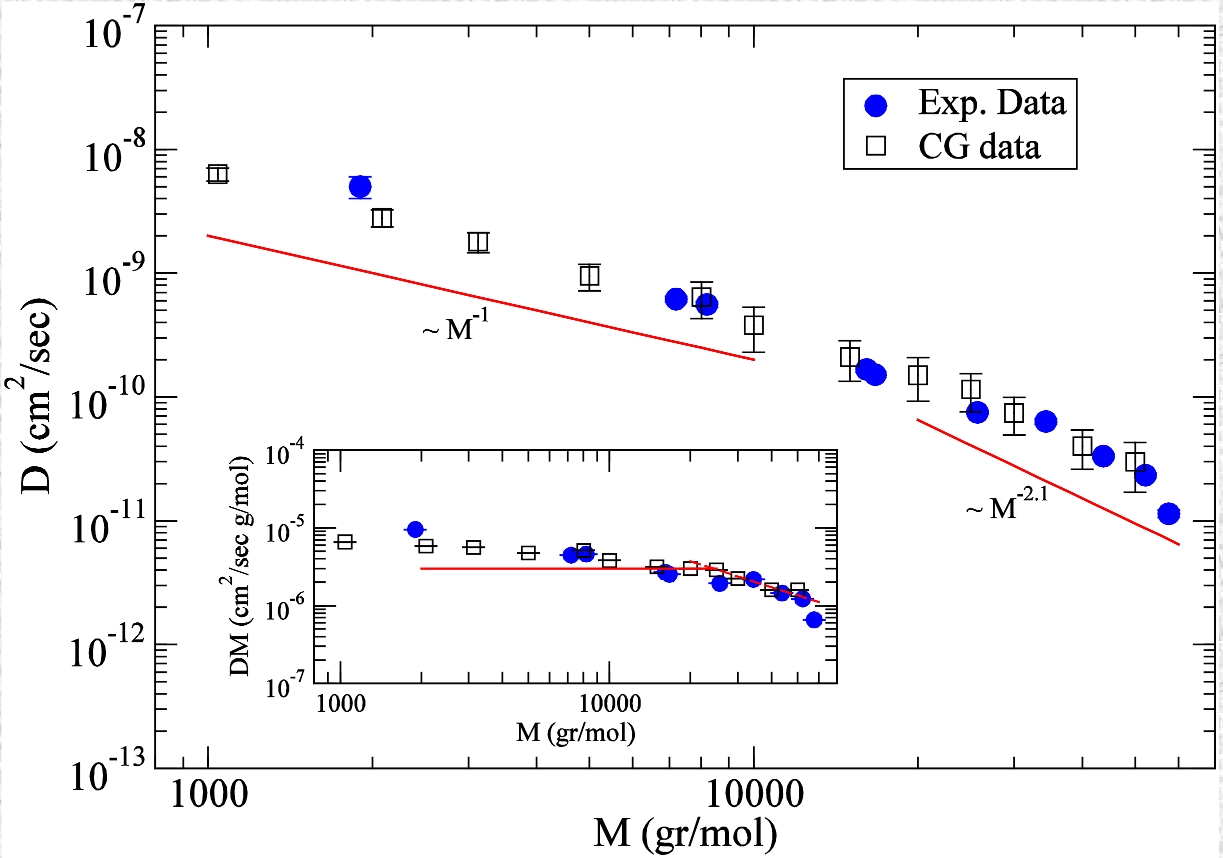
[V. Harmandaris and K. Kremer, Soft Matter, 2009]

CALCULATION OF M_e: Self Diffusion Coefficient

- **Crossover regime: from Rouse to reptation dynamics. Correct raw diffusion data for the chain end free volume effect.**

-- Rouse: D ~ M^{-1}

-- Reptation: D ~ M^{-2}



Crossover region:

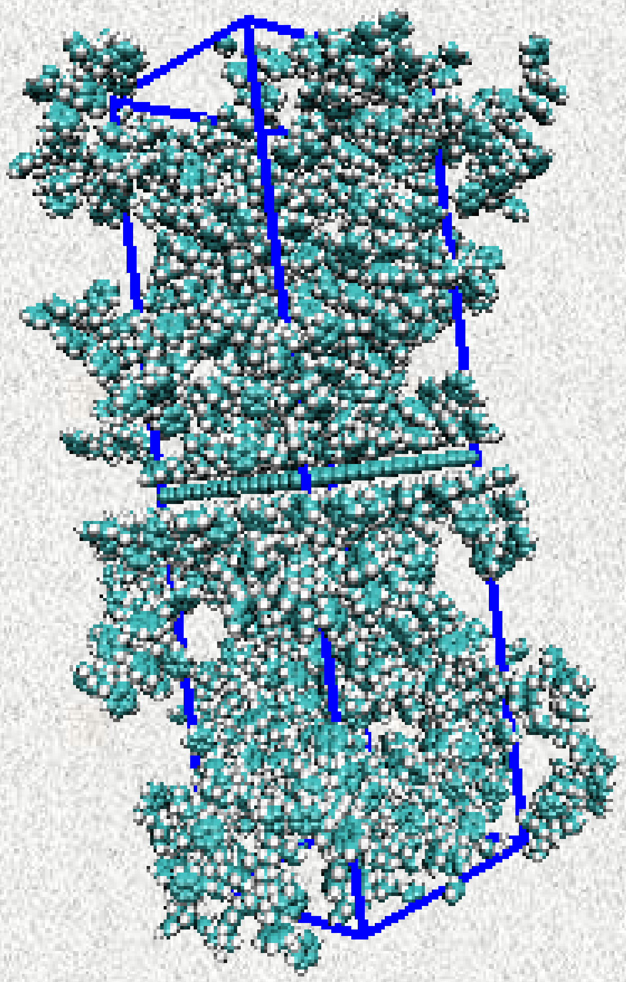
-- CG MD: M_e ~ 28.000-33.000 gr/mol

-- Exp.: M_e ~ 30.0000-35.000 gr/mol

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

Modeling of Polymer Nanocomposites: Polymer/Graphene Interfaces

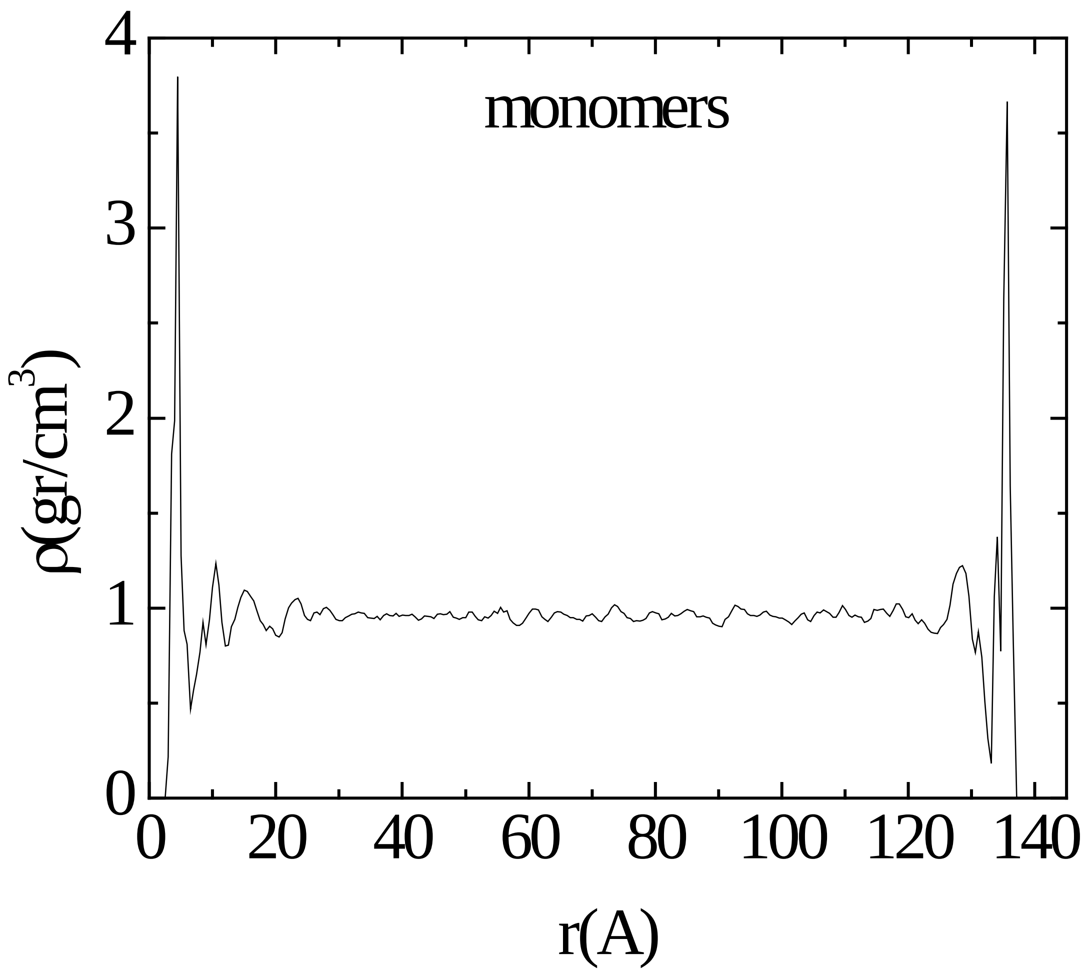
[T. Rissanou and VH, to be submitted]



Polystyrene/Graphene model systems

- ☐ Single layer solid phase.
- ☐ Polystyrene oligomers (10mer).
- ☐ Various Polymer/graphene systems.
- ☐ Film thickness: From 2 nm up to 12 nm.

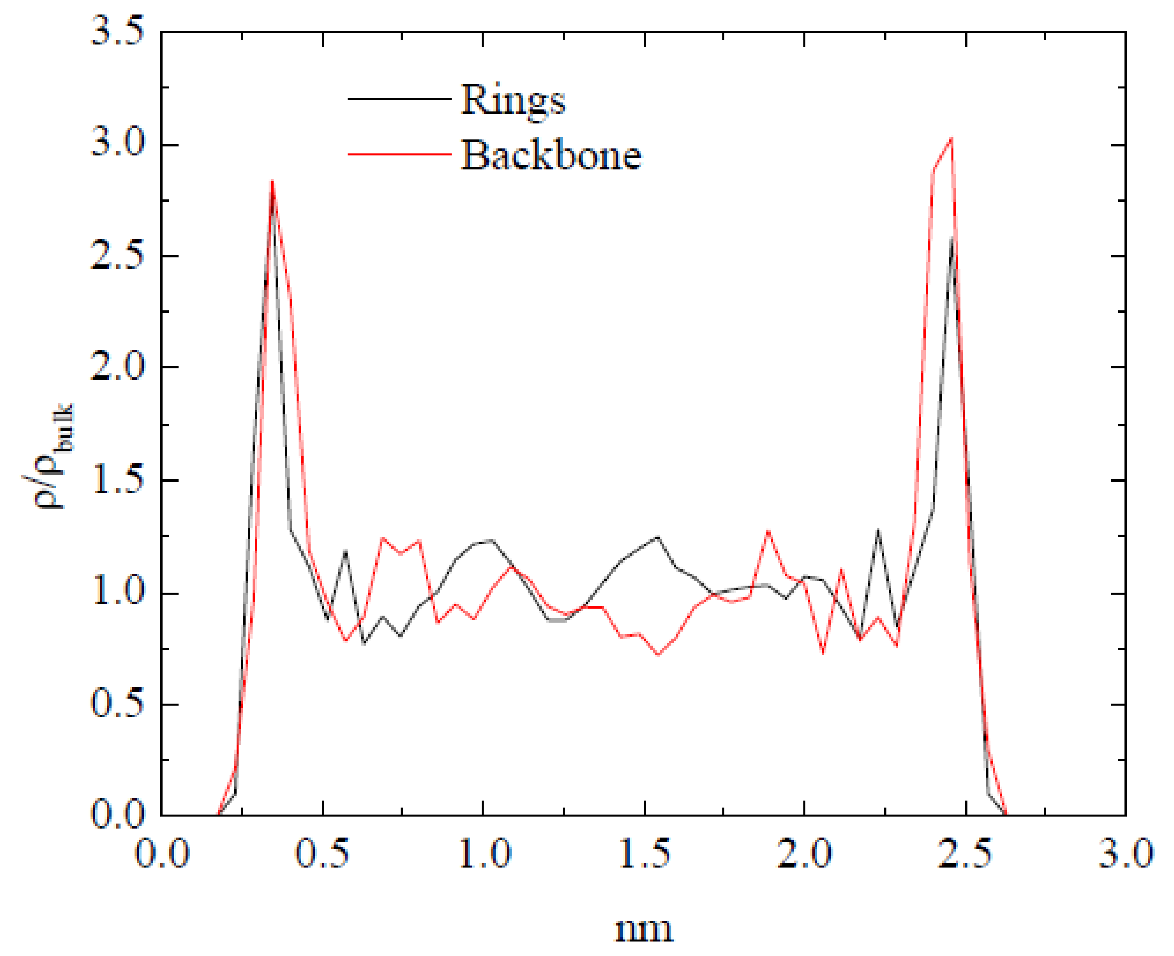
Polystyrene/Graphene Interfaces: Adhesion Strength



- ☐ **Typical oscillatory profile: Density reaches plateau (bulk) value after ~ 3 nm.**

Polystyrene/Graphene Interfaces: Adhesion Strength

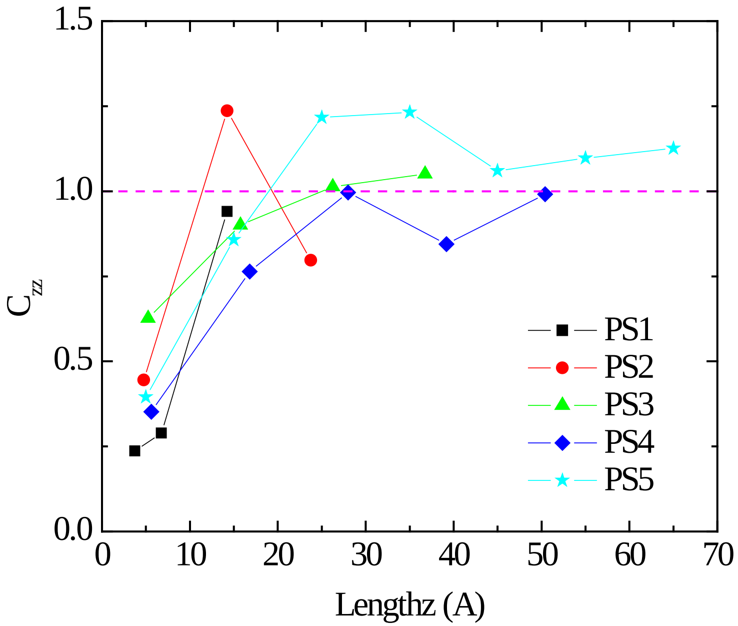
- **Density of rings, backbone in the interface:**

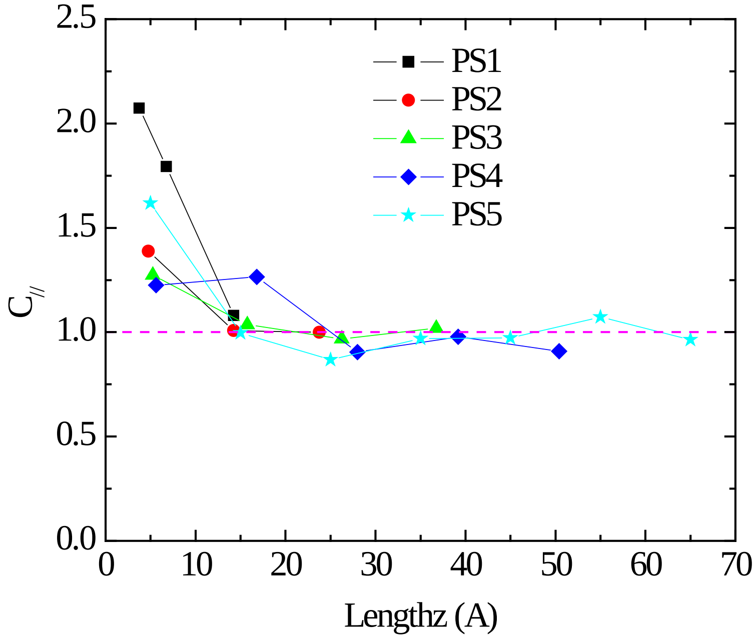


Polystyrene/Graphene Interfaces: Structural Properties

[T. Rissanou and VH, in preparation]

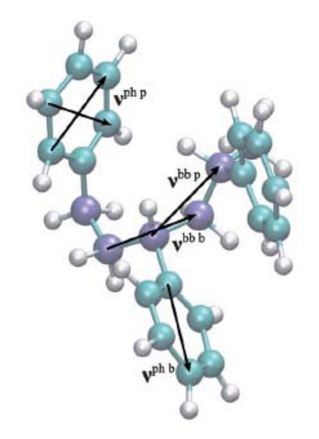
Conformation tensor $$c_{\alpha\beta} \equiv \frac{3\left\langle R_\alpha R_\beta \right\rangle}{\left\langle R^2 \right\rangle_{eq}}$$

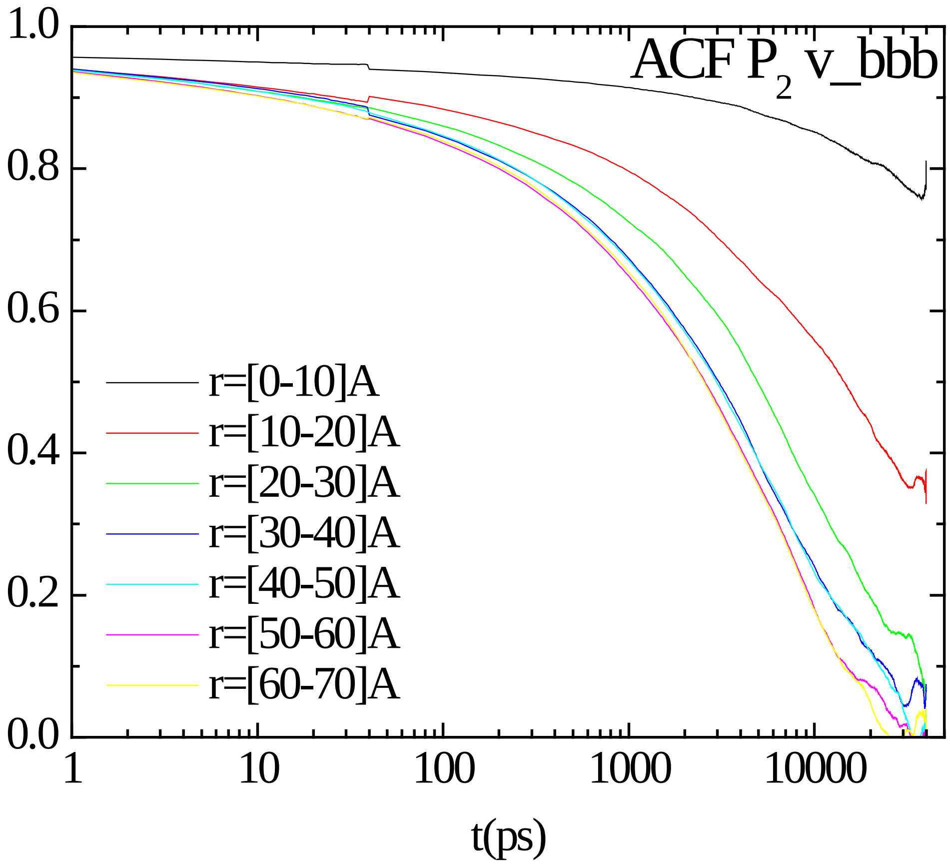




Polystyrene/Graphene Interfaces: Local Dynamics

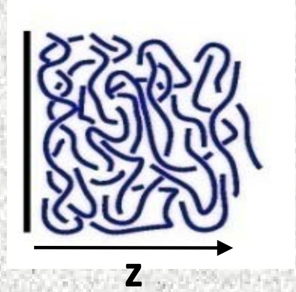
- ☐ **Local dynamics as a function of distance from the solid surface**

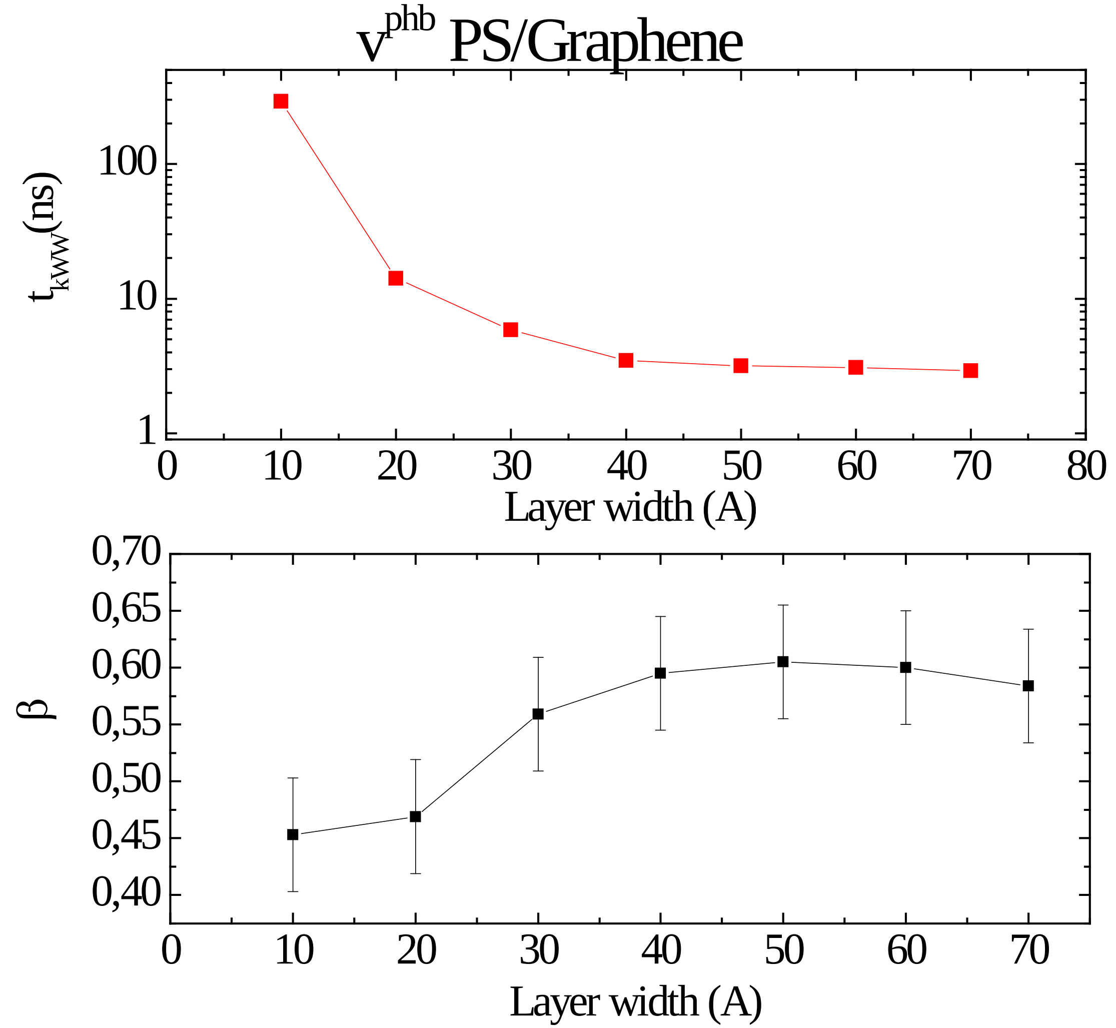




Polystyrene/Graphene Interfaces: Local Dynamics

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





- ❑ Dynamics is much slower close to the interface.
- ❑ Distribution of relaxation times is broader.

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.**

- **…**

ACKNOWLEDGMENTS

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ACMAC UOC [Greece]

Graphene Research Center, FORTH [Greece]