Transferability of Coarse Grained Models: Multiscale Simulations of Liquid Crystalline Phase Transitions

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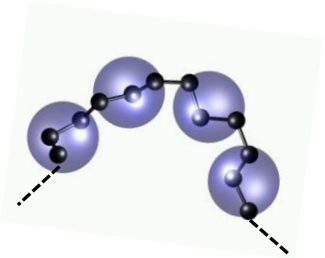
Systematic coarse graining

Mapping scheme: $\mathbf{R} = \mathbf{M}\mathbf{r}$



Possible aim of systematic coarse graining:
consistent sampling of phase space on the atomistic and CG level

$$P^{at}(\mathbf{r}) = Z_{at}^{-1} \exp[-\beta U^{at}(\mathbf{r})]$$

mapped to CG coordinates ➪ $P^{at}(\mathbf{R}) = \langle \delta(\mathbf{M}\mathbf{r} - \mathbf{R}) \rangle$

possible consistency criterion: =

$$P^{CG}(\mathbf{R}) = Z_{CG}^{-1} \exp[-\beta U^{CG}(\mathbf{R})]$$

➪ “theoretical” solution: Boltzmann inversion

$$U_{PMF}^{CG}(\mathbf{R}) = -k_B T \ln P^{at}(\mathbf{R}) + const$$

Systematic coarse graining

$$U_{PMF}^{CG}(\mathbf{R}) = \sum_{i,j} U_2(r_{ij}) + \sum_{i,j,k} U_3(r_{ij}, r_{jk}, r_{ik}) + \cdots + const$$

$$\approx \sum_{i,j} V_{\text{eff}}(r_{ij}) + const$$

Approximating the PMF:

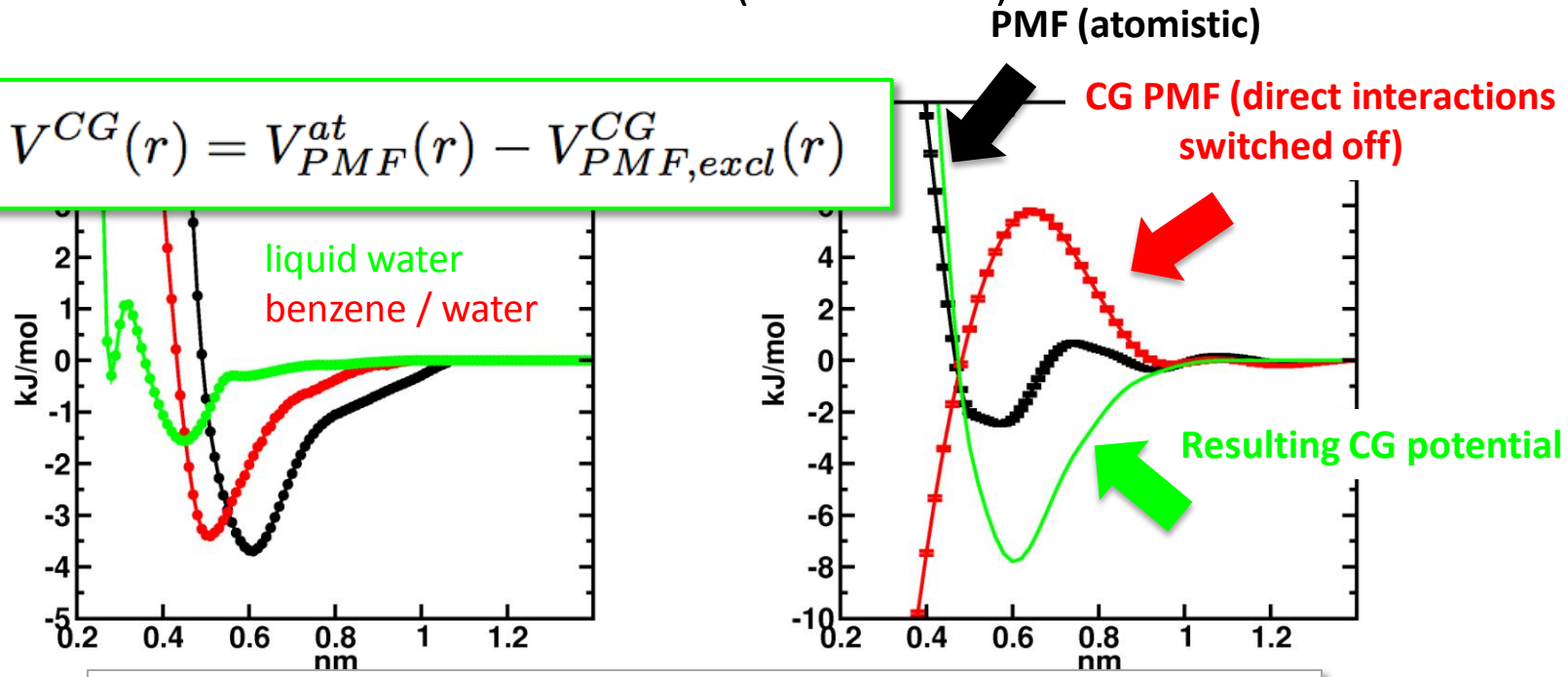
- choice of types of interactions (pair potentials …)
- choice of parametrization target
  - pair correlation functions, i.e. pair PMFs, “Henderson solution”
  - mean forces, multidimensional PMFs
  - relative entropy
  - routes relying on thermodynamic cycles (“subtracting” pair PMFs, CRW)

CG (dilute) solute/solute interactions

Low solute concentration:

- solvent/solvent and solute/solvent interactions predetermined
  e.g. from iterative Boltzmann inversion
- solute/solute PMF (e.g. from umbrella sampling): parameterization target
- remove environment contribution (no iteration)

$$V^{CG}(r) = V^{at}_{PMF}(r) - V^{CG}_{PMF,excl}(r)$$



- strong emphasis on solute-solute association strength

PCCP, 11 (2009), 2077

Systematic coarse graining

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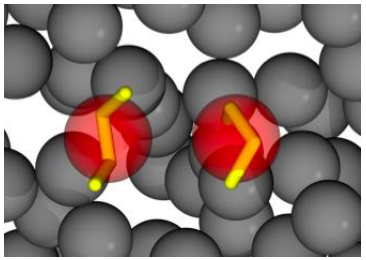
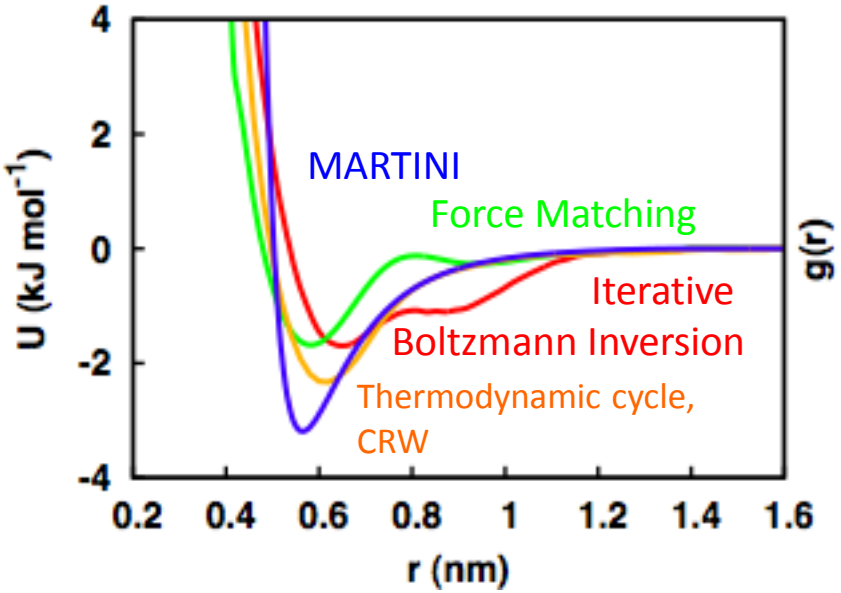
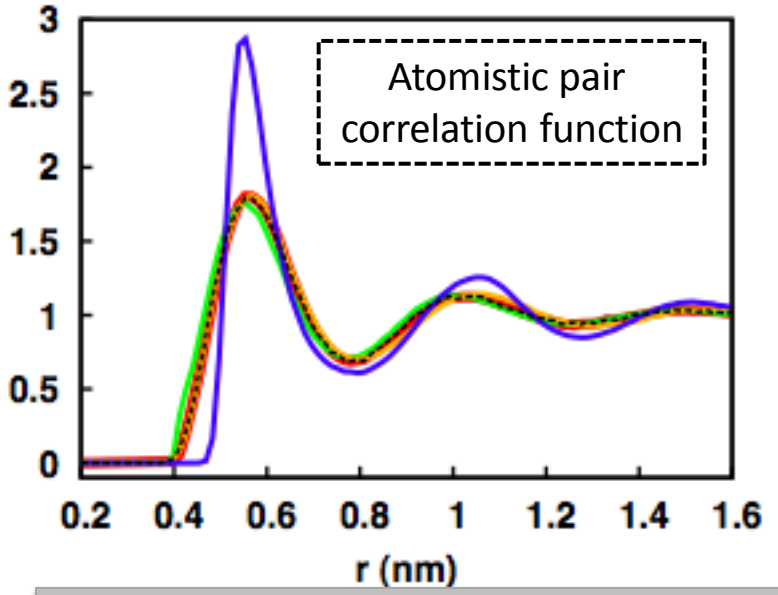
Challenge: representability and transferability



Systematic coarse graining

Example: liquid butane





the “one” Henderson pair potential

⇔

multiple solutions that yield a “decent” structural representation

Representation	ΔG;(kJ/mol)
AA, Gromos 53a5	-13.6 +/- 0.7
CG, IB	-11.3 +/- 0.7
CG, FM	-7.1 +/- 0.5
CG, MARTINI*	-11.6 +/- 1.6
CG, SB	-10.3 +/- 1.0

AJ Rzepiela, M Louhivuori, CP, SJ Marrink, *PCCP* **2011**

Representability and transferability

We have seen that systematic CG approaches inevitably suffer from approximations leading to *representability* and *transferability* problems.

How can we deal with a change of state point?

Example 1: concentration transferability

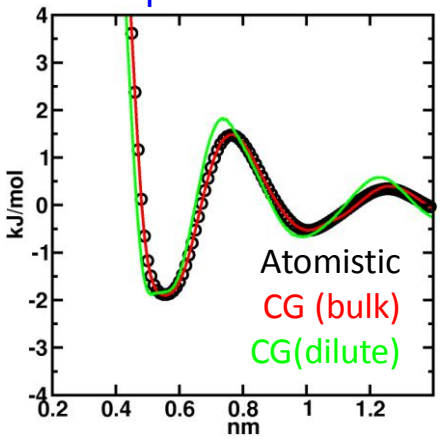
Example 2: transferability across a phase transition

Example 1: Concentration transferability

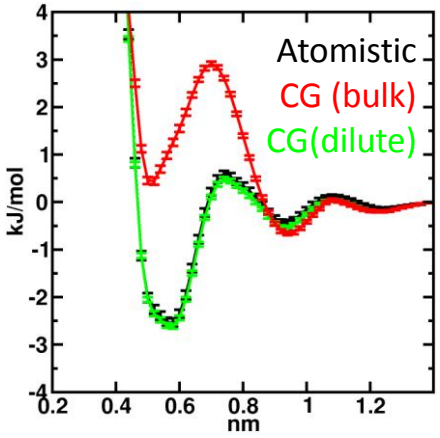
Hydrophobic molecules in aqueous solution (**explicit CG water model**)

Benzene- benzene pair PMF

Liquid benzene



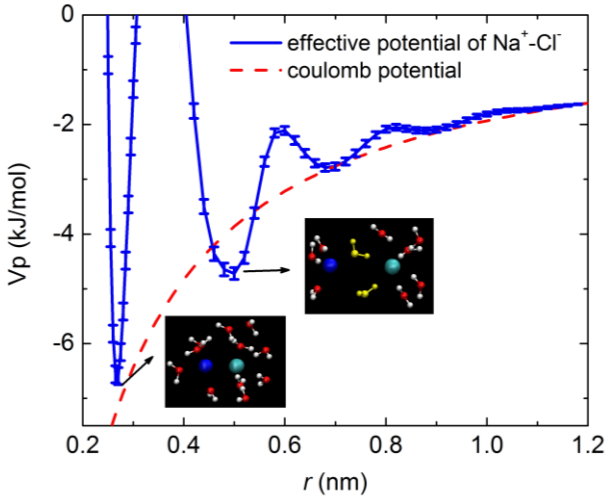
Dilute aqueous benzene solution



A. Villa, CP, N. van der Vegt *JCTC* **2010**

Implicit-solvent aqueous electrolytes

Ion- ion pair PMF



$$V_{total}(r,c) = V_{short}(r) + V_{coul}(r,c) = V_{short}(r) + \frac{q_1 q_2}{4\pi\,\varepsilon_0 \varepsilon_E(c) r}$$

Ion specific

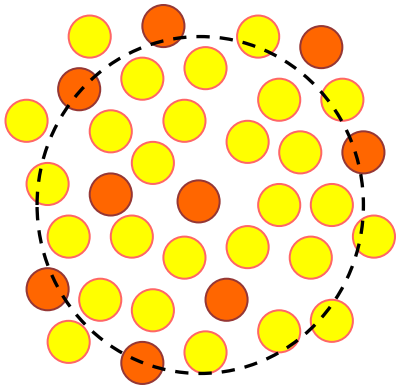
transferable

JW Shen, C. Li, N. van der Vegt, CP, *JCTC* **2011**

➪ models reproduce association strength (@ infinite dilution) and pair structure **over a range of concentrations**

Example 1: Concentration transferability

⇨Kirkwood Buff analysis: link structure / solution thermodynamics



KB integral:

$$G_{ij} = \int_0^R \left[g_{ij}(r) - 1\right] 4\pi r^2 dr$$

Excess coordination number:

$$\Delta N_{ij} = \rho_j \int_0^R \left[g_{ij}(r) - 1\right] 4\pi r^2 dr$$

Preferential solvation parameter:

$$\Delta_{BW} = G_{BB} + G_{WW} - 2G_{BW}$$

⇨Δ_{BW} : deviation of local solution composition from global one

⇨ link between solution structure and thermodynamics

chemical potential

$$\left(\frac{\partial \mu_B}{\partial x_B}\right)_{P,T} = \frac{k_B T}{x_B(1 + \rho_B x_W \Delta_{BW})}$$

activity coefficient

$$\left(\frac{\partial \ln \gamma_B}{\partial \ln x_B}\right)_{P,T} = -\frac{\rho_W x_B \Delta_{BW}}{1 + \rho_W x_B \Delta_{BW}}$$

Example 1: Concentration transferability

⇨Kirkwood Buff analysis: CG benzene / water system

chemical potential

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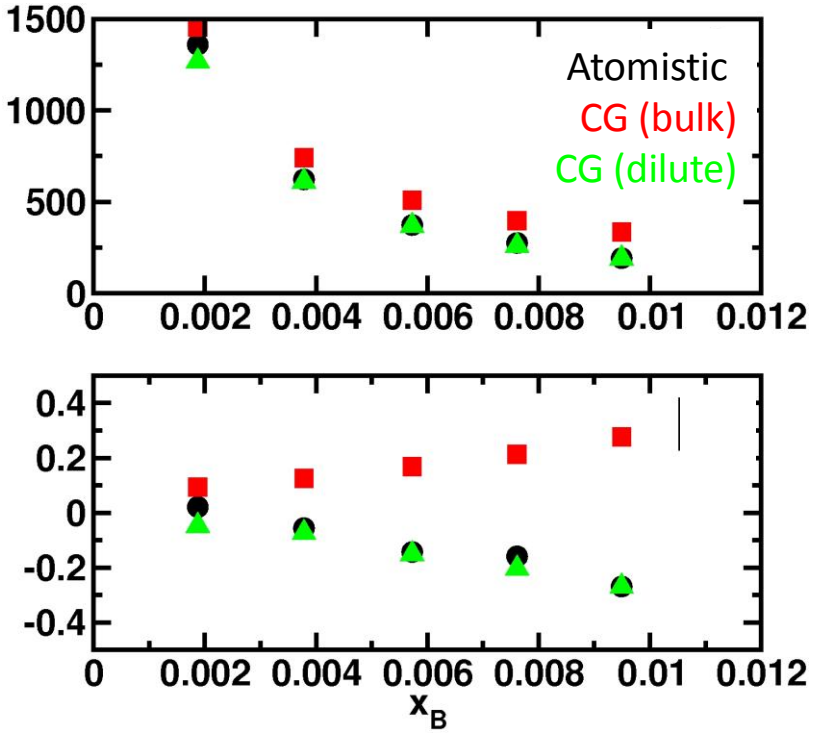
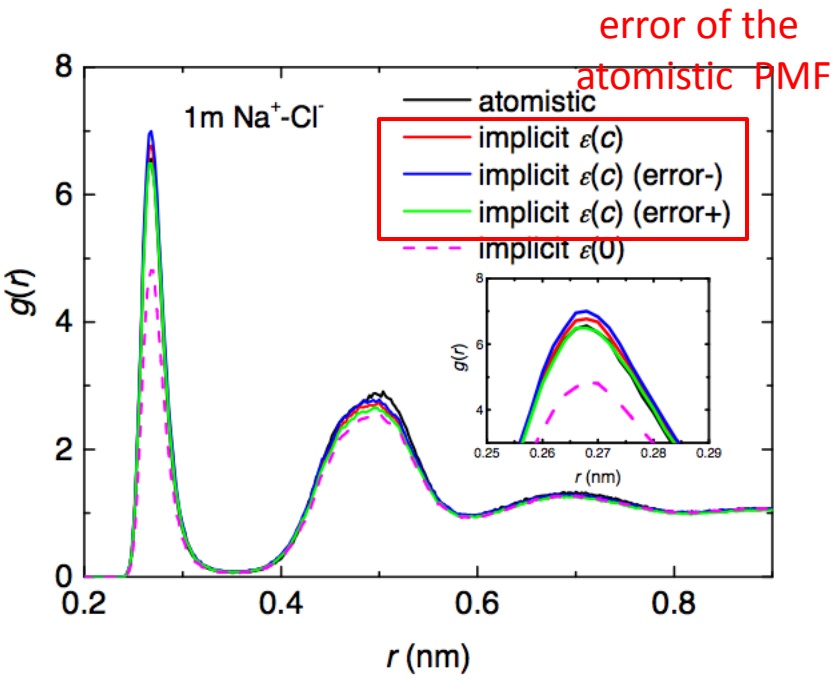
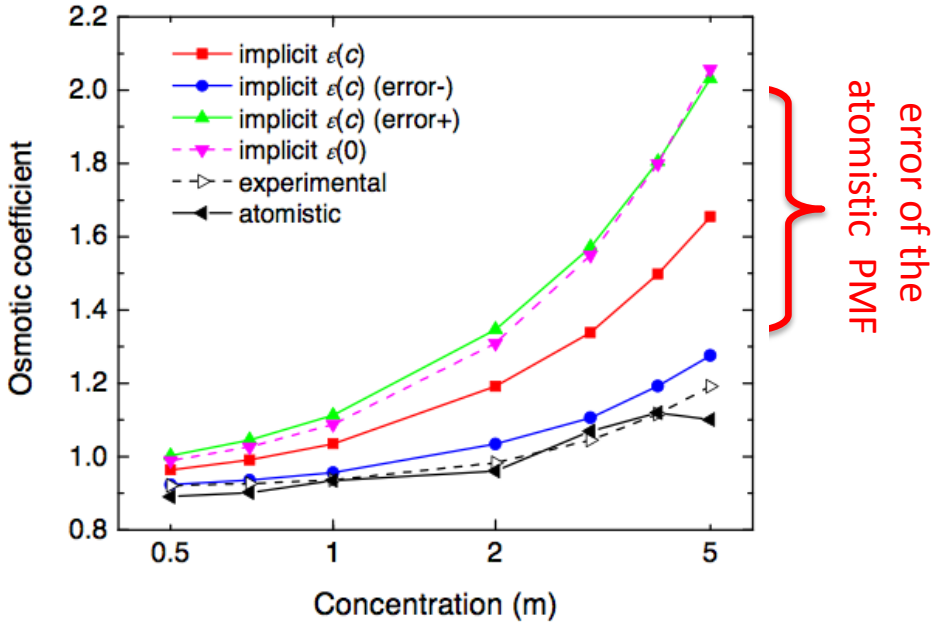


- CG (dilute): concentration transferable (up to demixing)
- hydrophobic association cast into solute/solute interactions
- pairwise additive up to demixing

Example 1: Concentration transferability

⇨Kirkwood Buff analysis: implicit-solvent electrolyte





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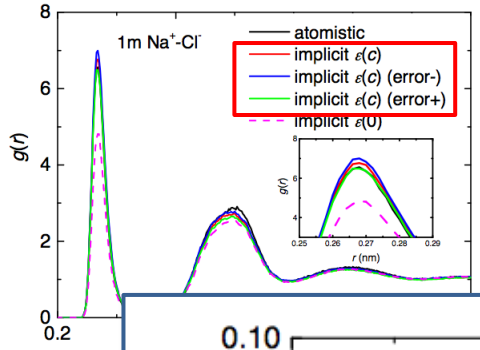
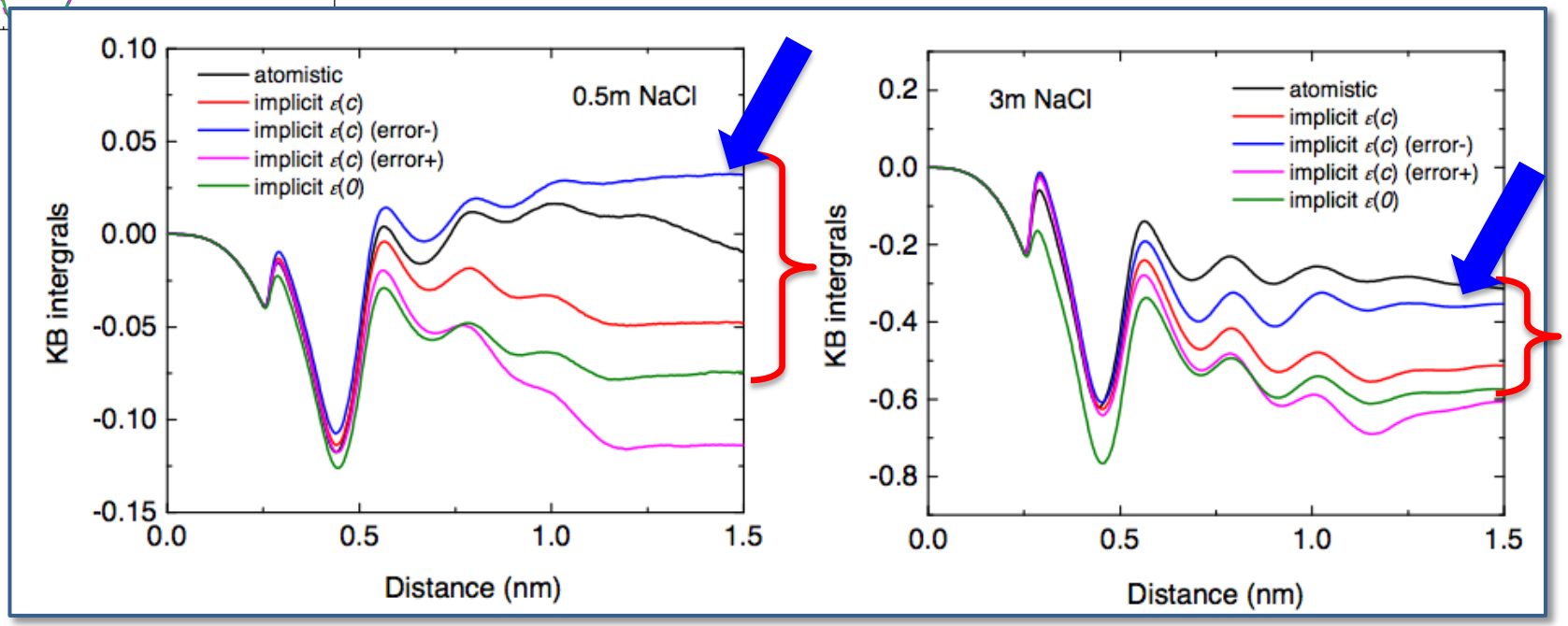


error of the atomistic PMF

$$\Rightarrow G_{ij} = \int_0^R \left[g_{ij}(r) - 1\right] 4\pi r^2 dr,$$



Example 1: Concentration transferability

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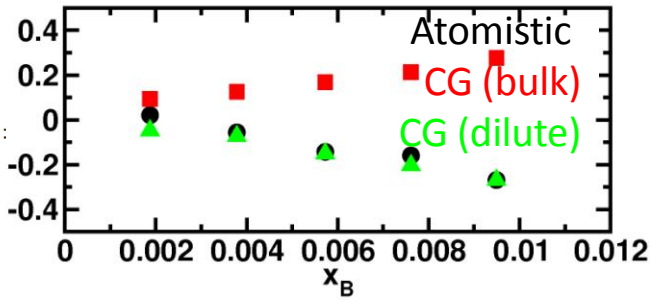
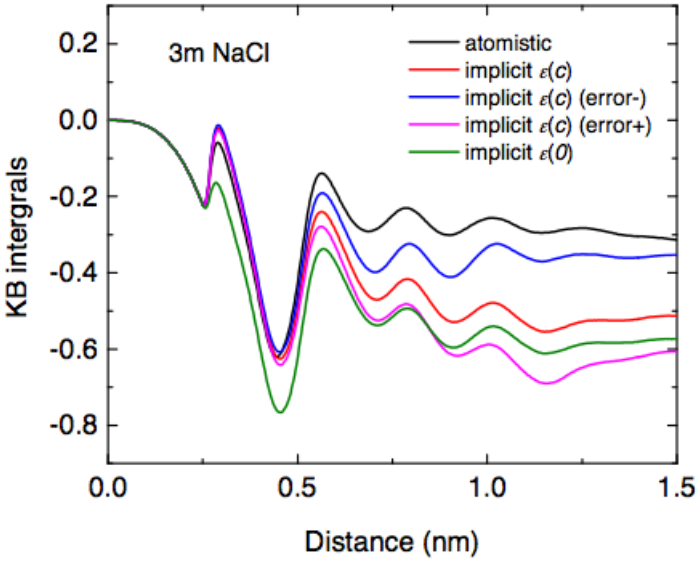
$$\left(\frac{\partial \ln \gamma_B}{\partial \ln x_B}\right)_{P,T}$$



A. Villa, CP, N. van der Vegt *JCTC* **2010**

Implicit-solvent aqueous *electrolytes*



JW Shen, C. Li, N. van der Vegt, CP, *JCTC* **2011**

➪ KB analysis useful to understand (and improve, see Ganguly et al 2012) concentration transferability

Representability and transferability

We have seen that systematic CG approaches inevitably suffer from approximations leading to *representability* and *transferability* problems.

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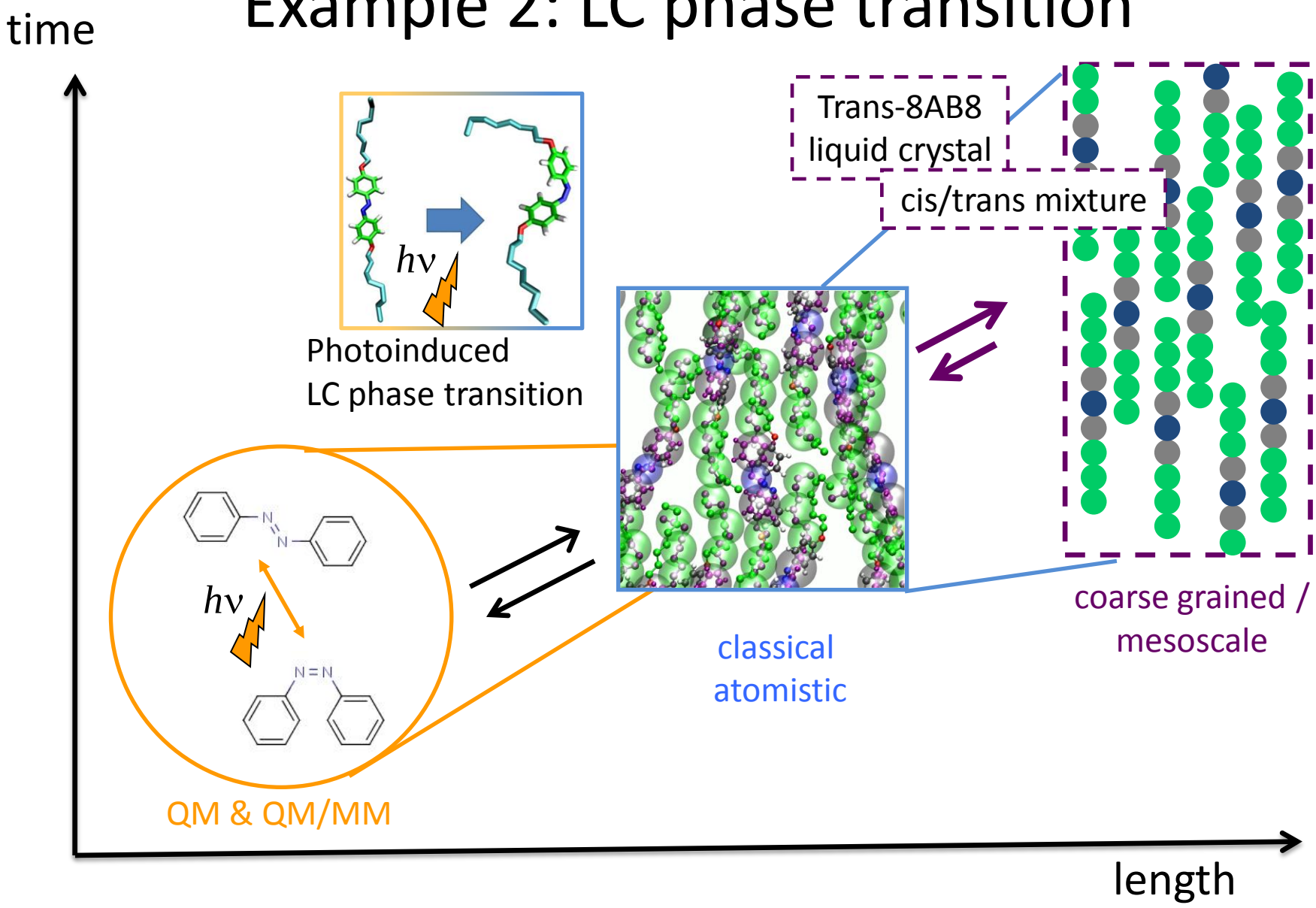
Example 1: concentration transferability

Example 2: transferability across a phase transition

Example 2: LC phase transition



M. Böckmann, D. Marx, CP, L. Delle Site, K. Kremer, N. Doltsinis, *PCCP*, **2011**

Example 2: LC phase transition

Aim: Construct CG model that:

Reproduces the atomistic (thermotropic) phase behavior

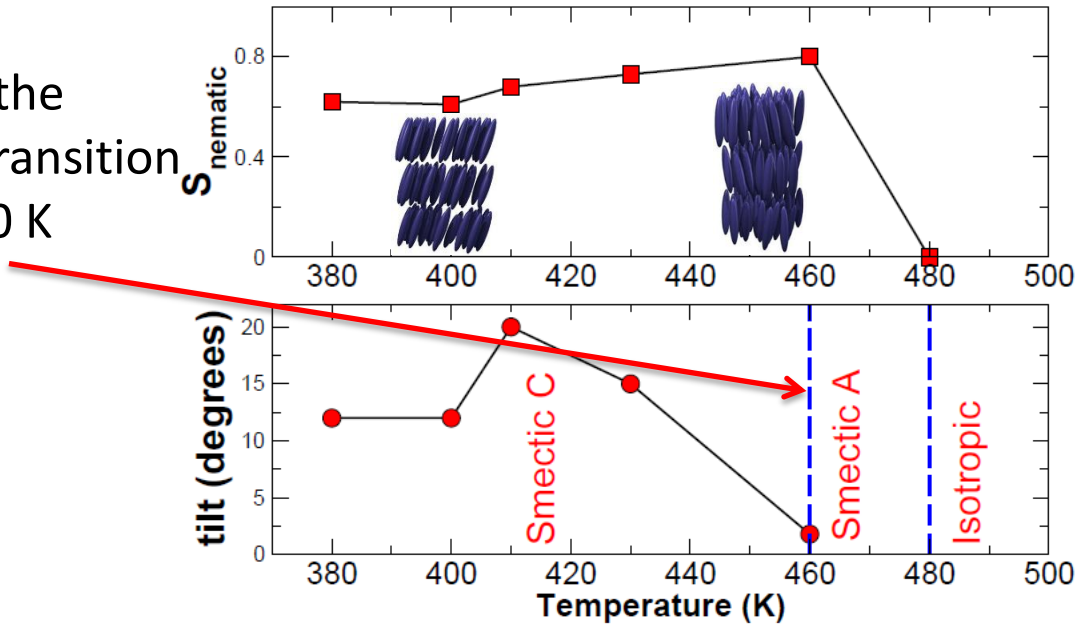
Reproduces atomistic structures (incl. box-aspect ratio/pressure anisotropy)

Target state point:

LC system just below the thermotropic phase transition

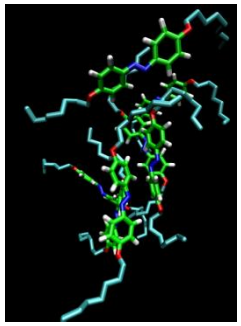
smectic system @ 460 K

➪ Find: suitable **isotropic reference** system

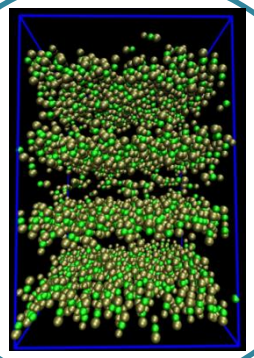


Example 2: LC phase transitions

Disordered @ 480 K

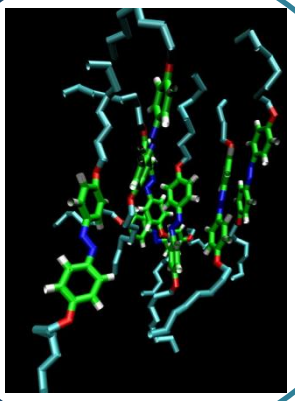


SmA @ 460 K



CG model should reproduce this transition !

Super-cooled fluid @ 460 K



CG model should reproduce structure

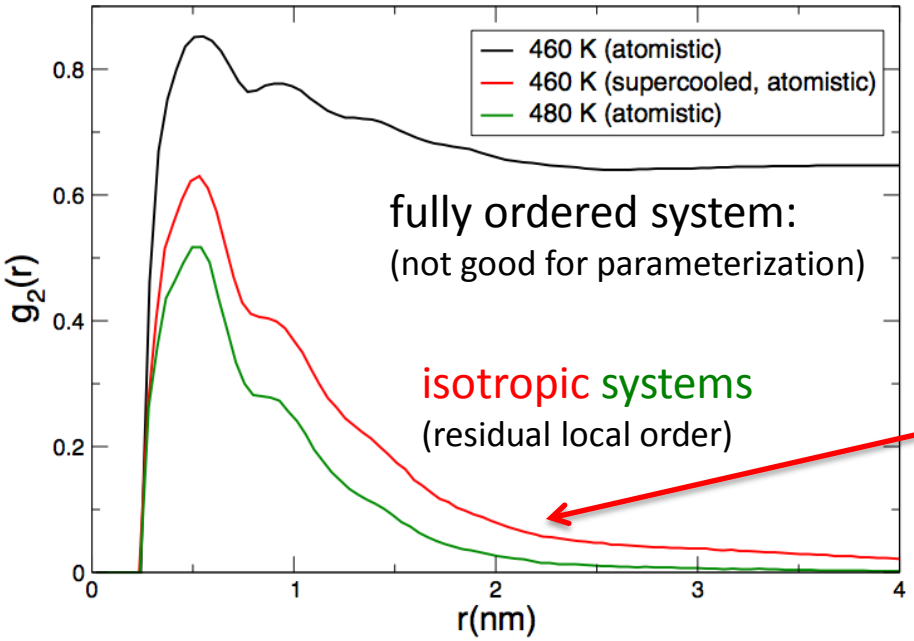
Parametrisation impossible here: (layering built into potentials)

overall isotropic

residual nematic order

Parametrise HERE !!

Example 2: LC phase transitions



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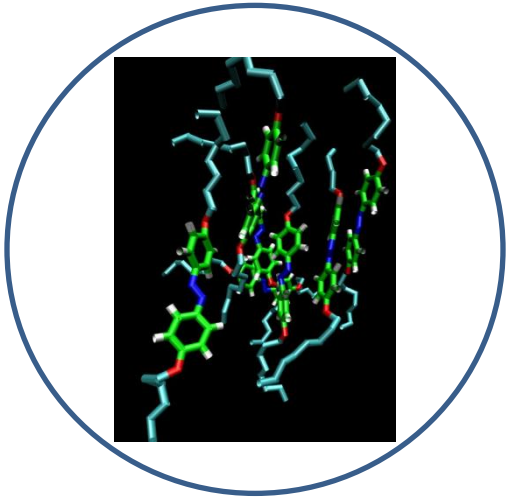
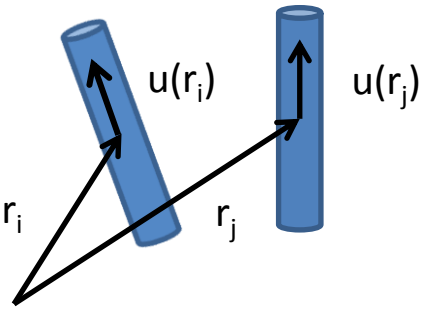
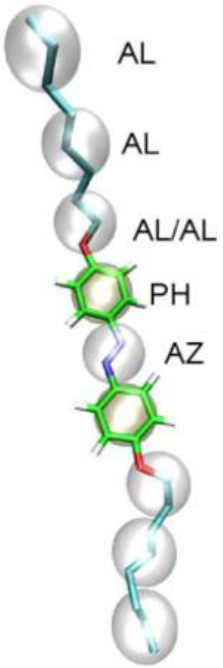


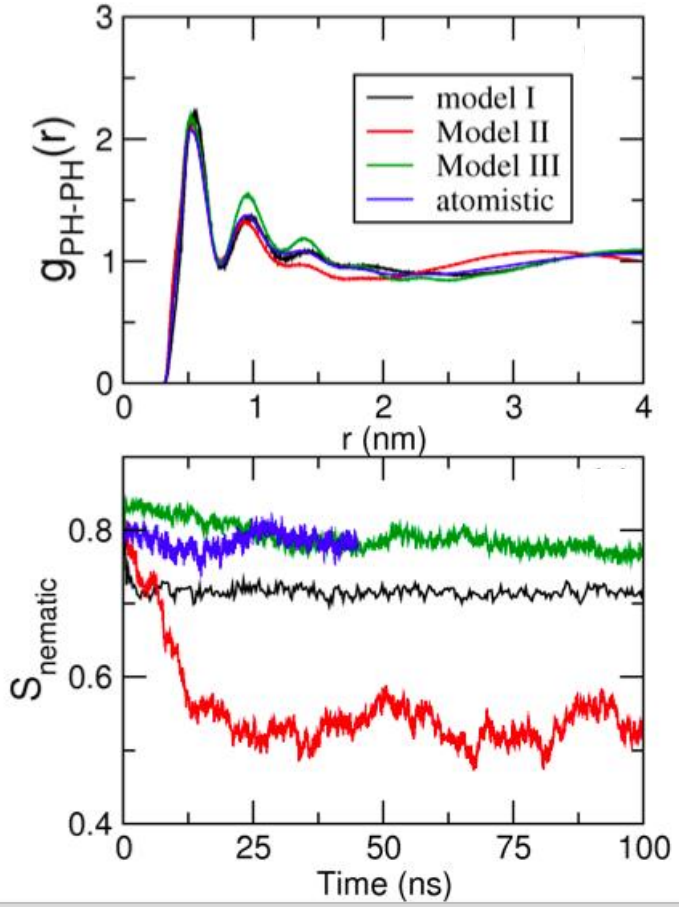
globally isotropic
super-cooled liquid
with local order

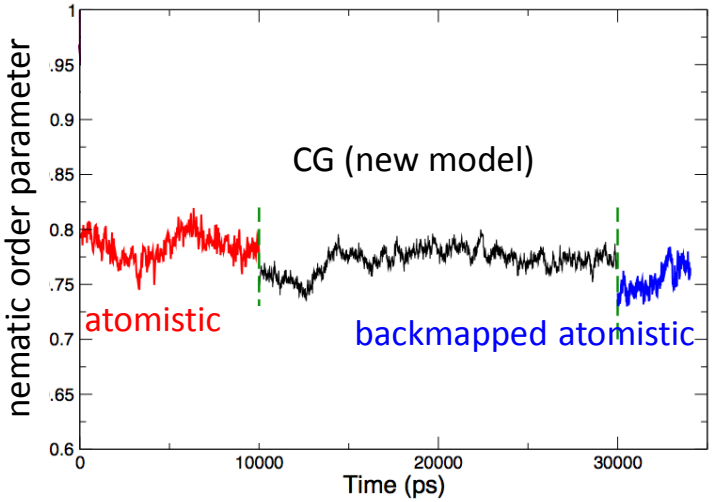
$$g_2(r) = \langle \frac{\sum_{i=1}^{(N-1)} \sum_{j=i+1}^{N} \delta(r - |\mathbf{r_i} - \mathbf{r_j}|) \mathbf{P_2}(\mathbf{u_i}(\mathbf{r_i}) \cdot \mathbf{u_j}(\mathbf{r_j}))}{\sum_{i=1}^{(N-1)} \sum_{j=i+1}^{N} \delta(r - |\mathbf{r_i} - \mathbf{r_j}|)} \rangle$$

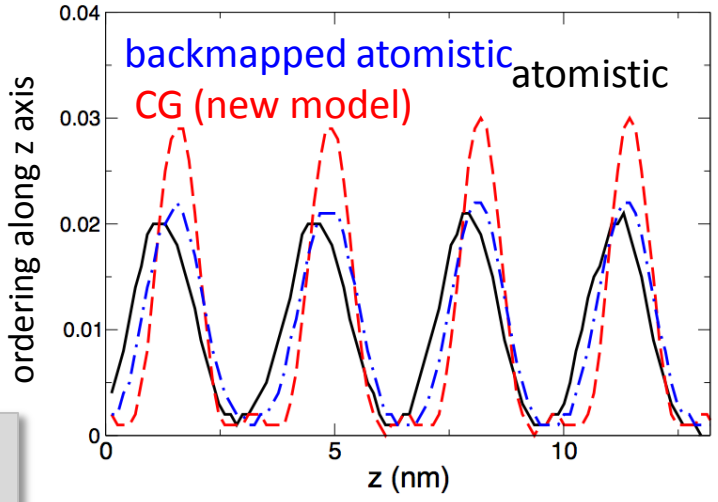


Example 2: LC phase transitions







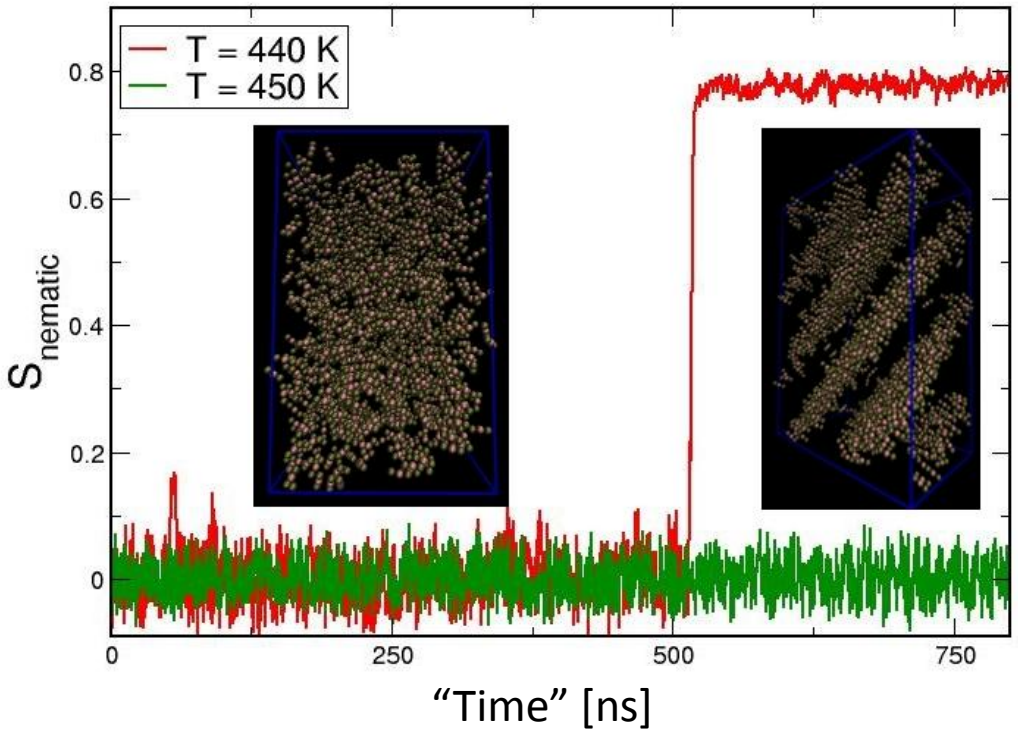


➪ CG model reproduces LC structure …

Mukherjee, Delle Site, Kremer, CP *JPC B* **2012**

Example 2: LC phase transitions

… and phase transition



- Smectic A phase develops spontaneously while cooling from the isotropic phase to T = 440 K (NpT).
- Smectic A melts to the isotropic phase on heating to T = 500 K.

➪ Characterize phase behavior

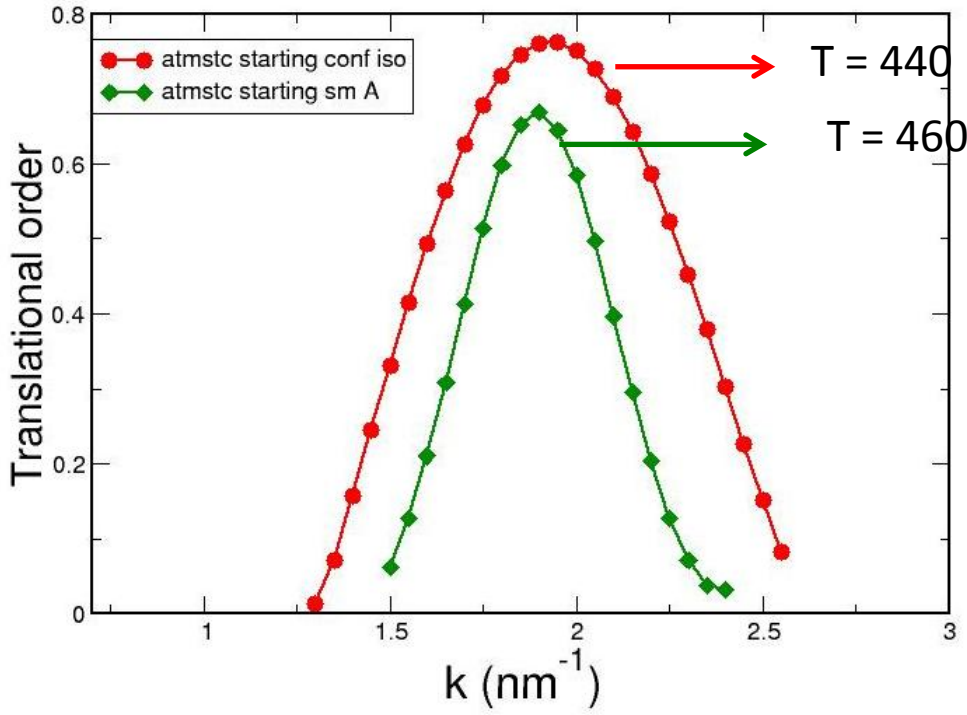
➪ Dynamics in the CG model

➪ Growth of LC domains

➪ Photoinduced transition

Example 2: LC phase transitions

structure of the “spontaneous” phase:
layer spacing perpendicular to director ~ reference



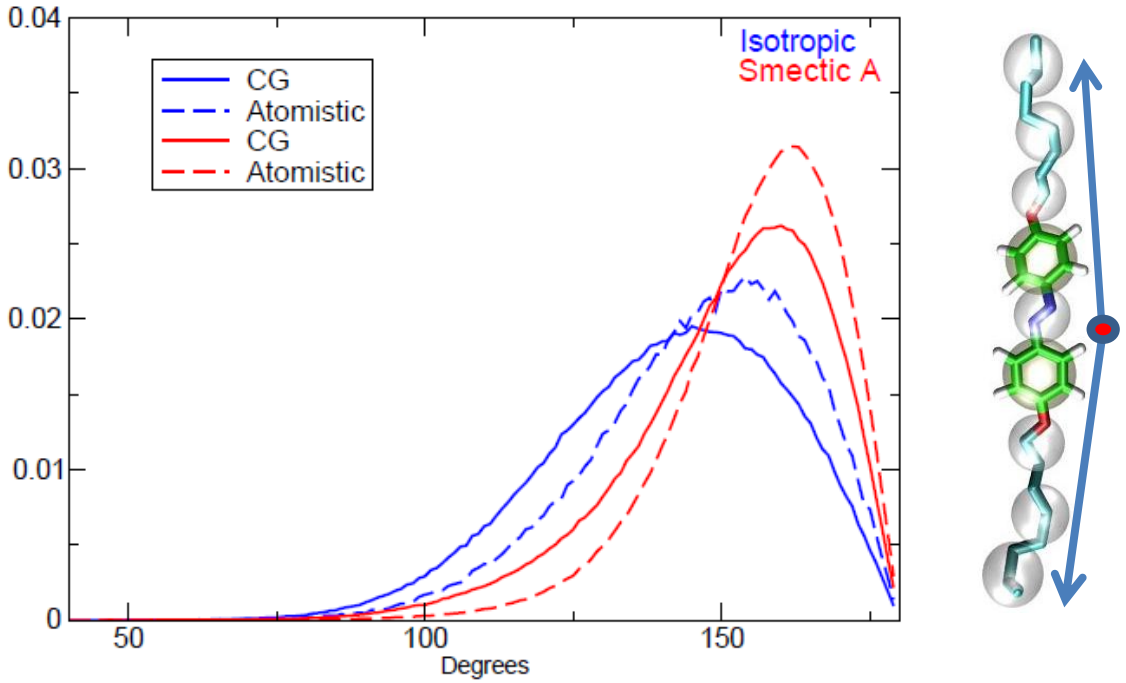
T = 440 K, NPT, spontaneous phase

T = 460 K, NVT, reference

Example 2: LC phase transitions

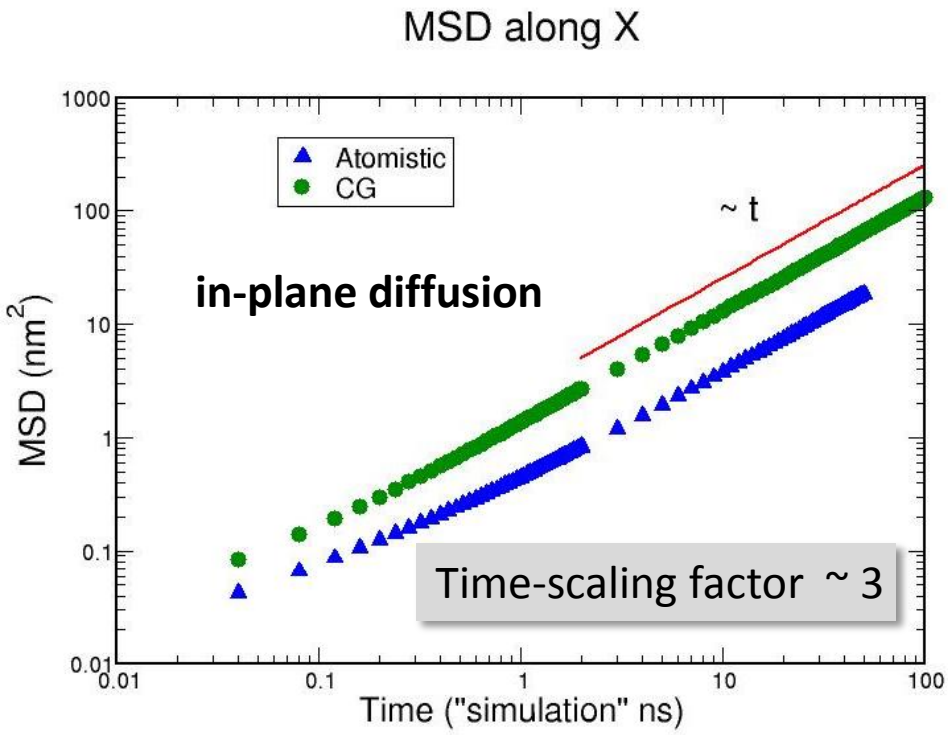
density & molecule shape at the phase transition

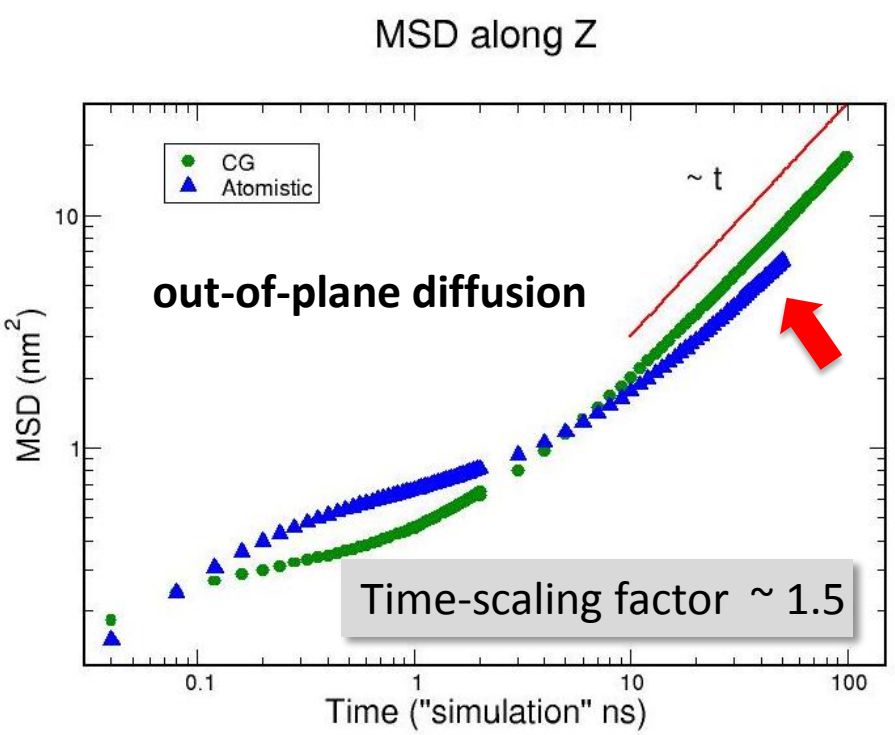
- Density change ~ 0.85 % (comparable to typical low molecular weight LC compounds; hard rod models typically ~ 10 %)



- Response of molecular conformations to phase change correct

And finally a bit of dynamics





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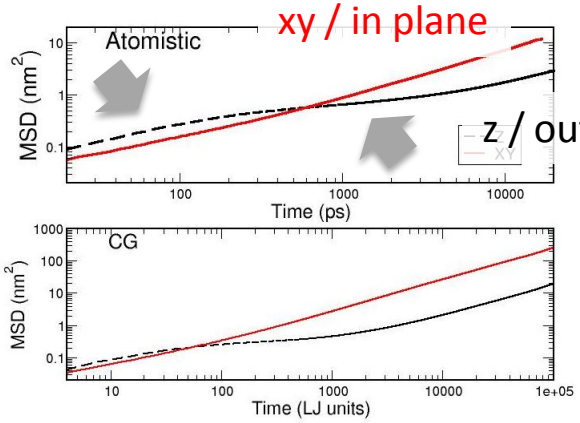
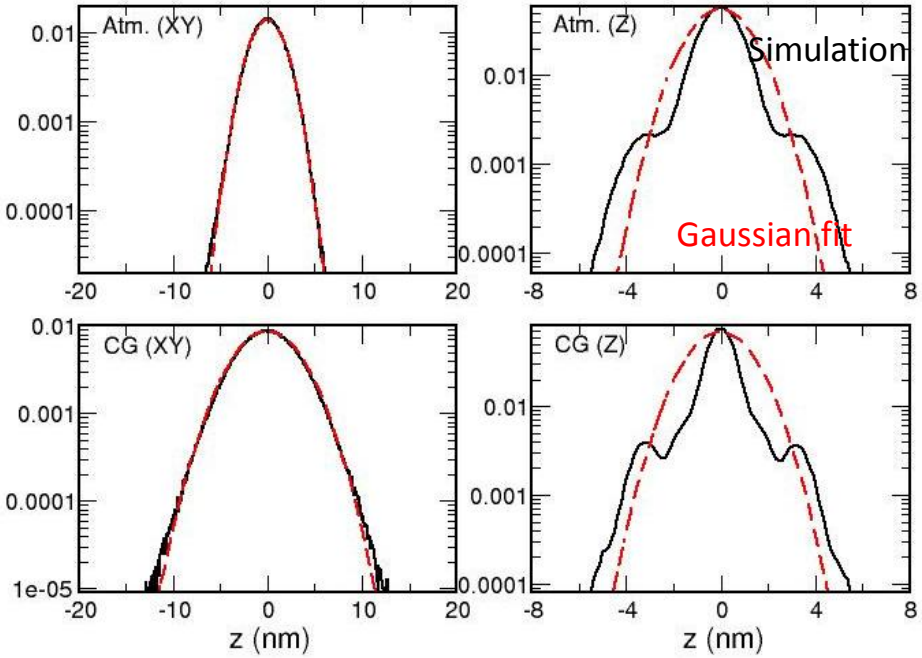
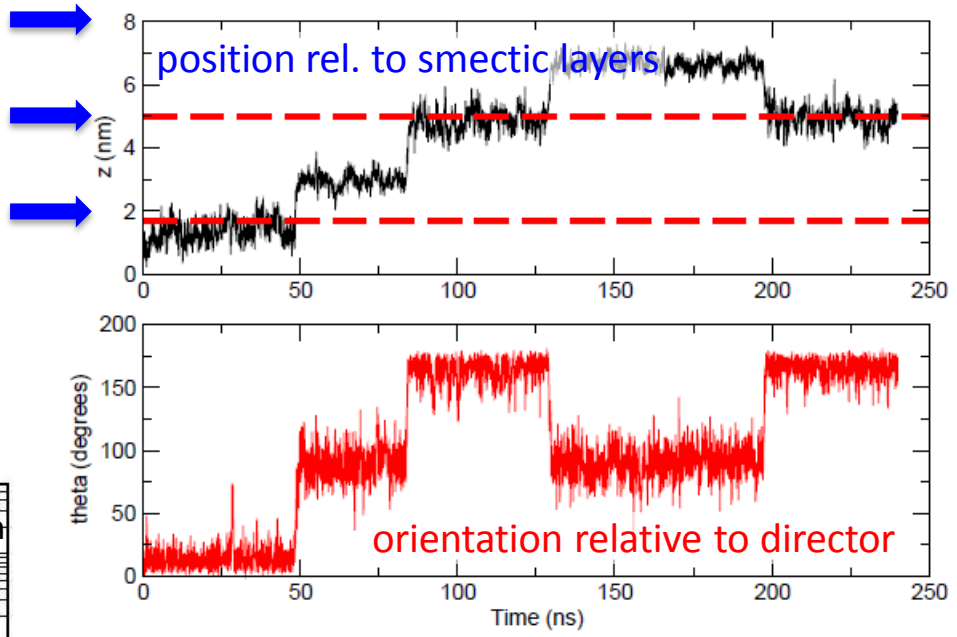
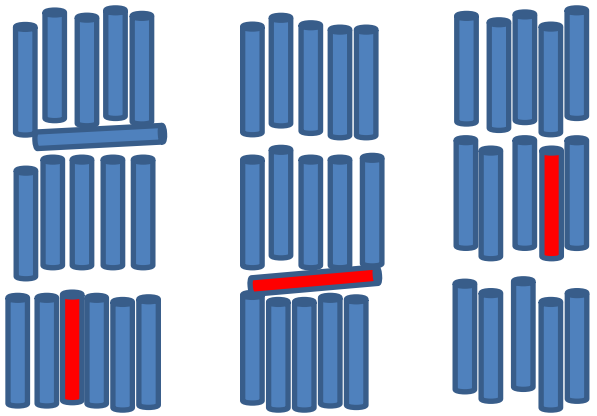


$G_s(z,t) = (1/N)\ \Sigma_i\ \delta[z - (z_i(t_0 + t) - z_i(t))]$







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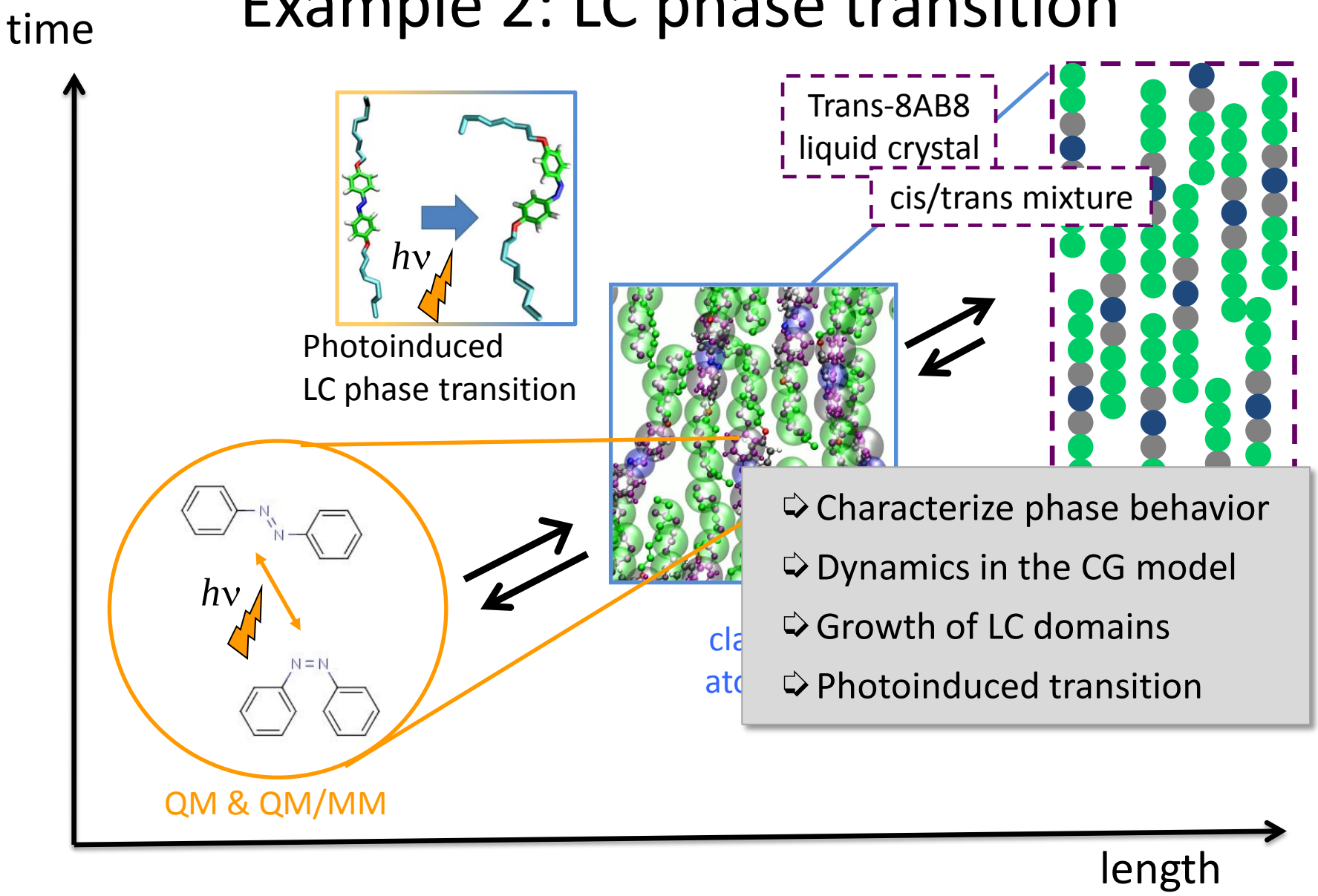
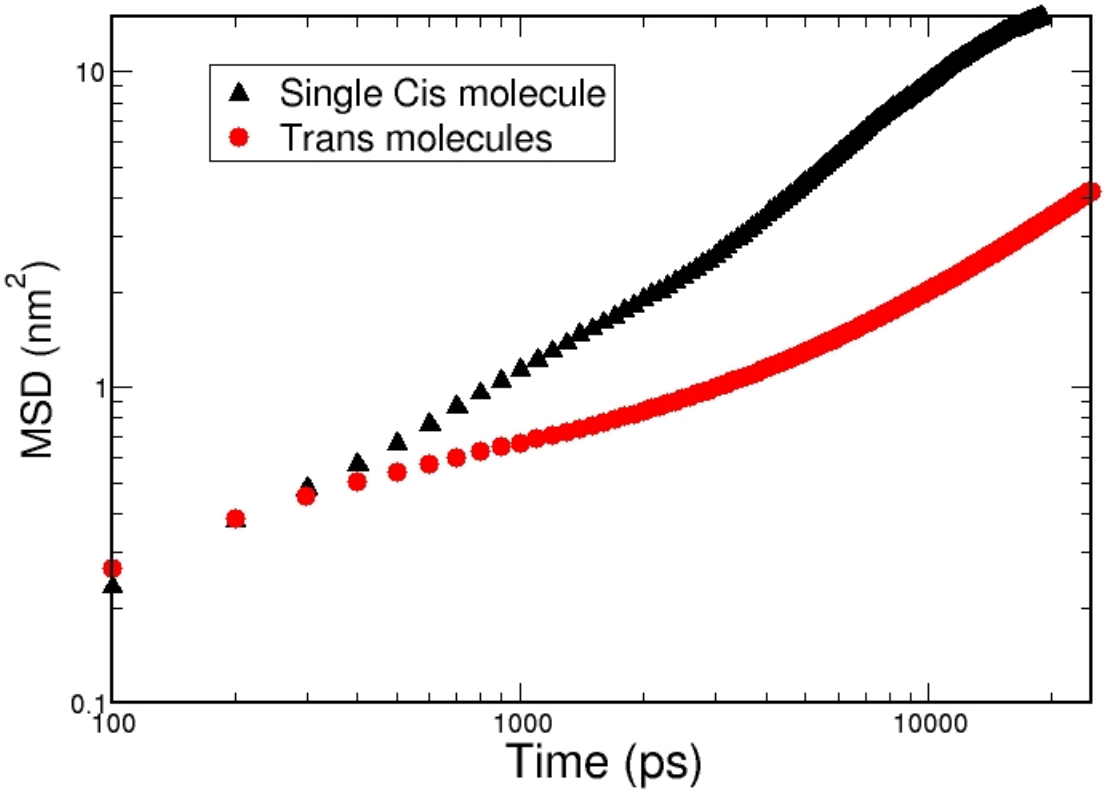


M. Böckmann, D. Marx, CP, L. Delle Site, K. Kremer, N. Doltsinis, *PCCP*, **2011**

The cis molecules are “fast”

Atomistic: MSD along Z (perpendicular to the smectic layers)



Let's "conclude" with questions

CG: How do I deal with the danger that the different "speed ups" distort my kinetics, pathways, and (out-of-equilibrium) the selection of resulting structures/motifs?

Atomistic/CG: How do the switched molecules behave? Form clusters?

Atomistic/QM: Find a criterion to relate environment/local order parameter to switching time?

QM: Does presence of cis molecules/cis domains facilitate photoswitching (e.g. via local disorder)?

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