Information-theoretic approach to coarse-graining and multiscale simulations

April 17, 2012, KITP Multiscale Modeling

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ACS Petroleum Research Fund
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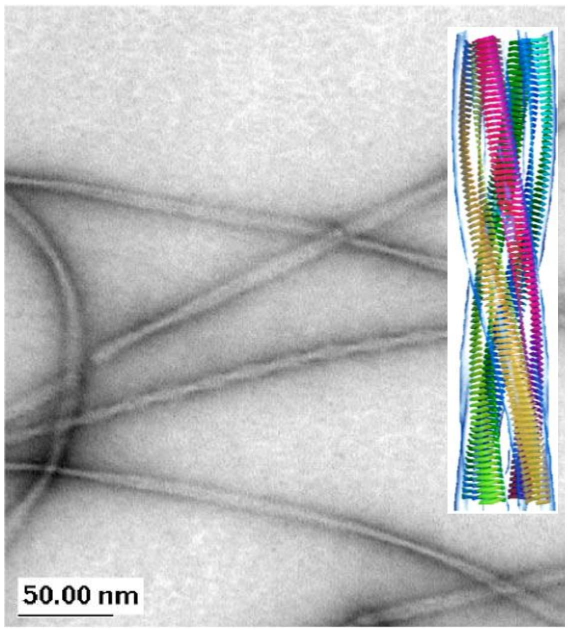
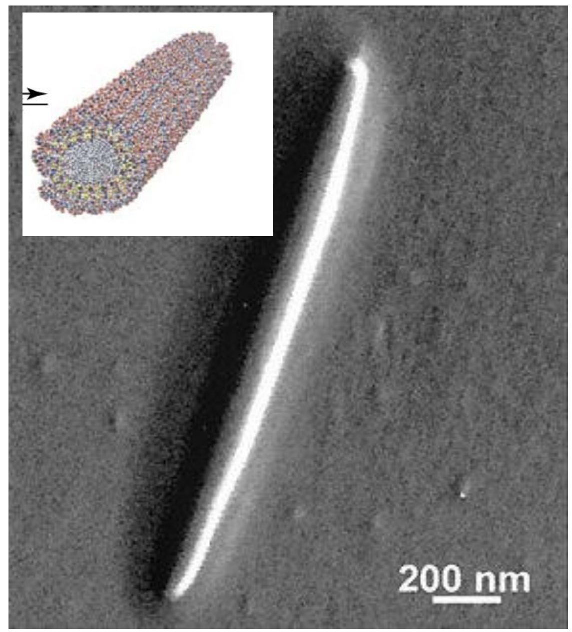
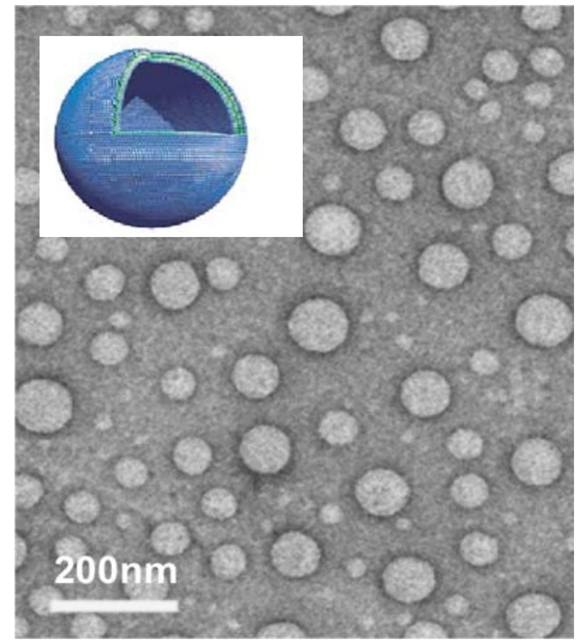
KLVFFAE
amyloid fibril



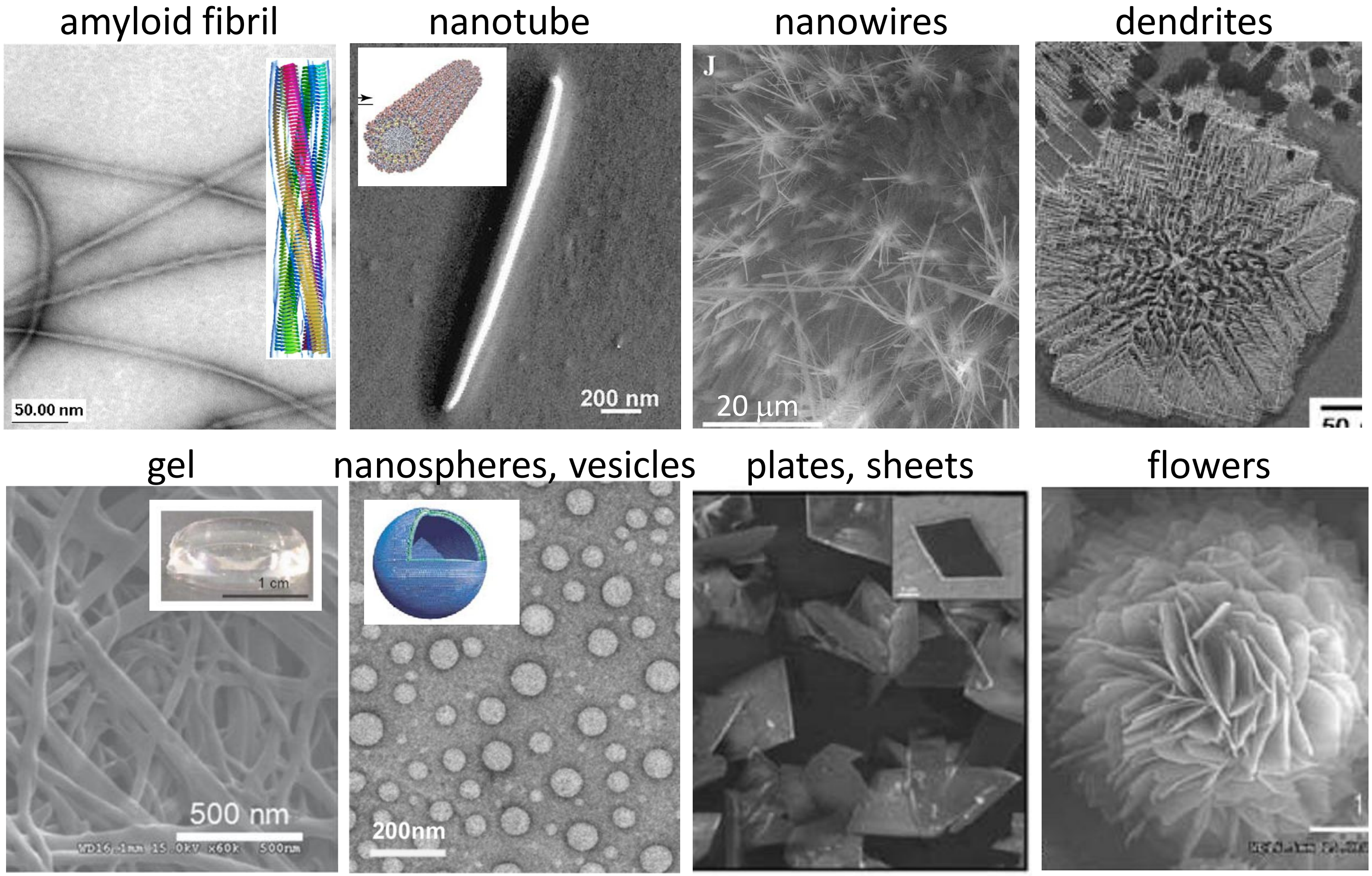
FF
nanotube



CFF
nanospheres, vesicles

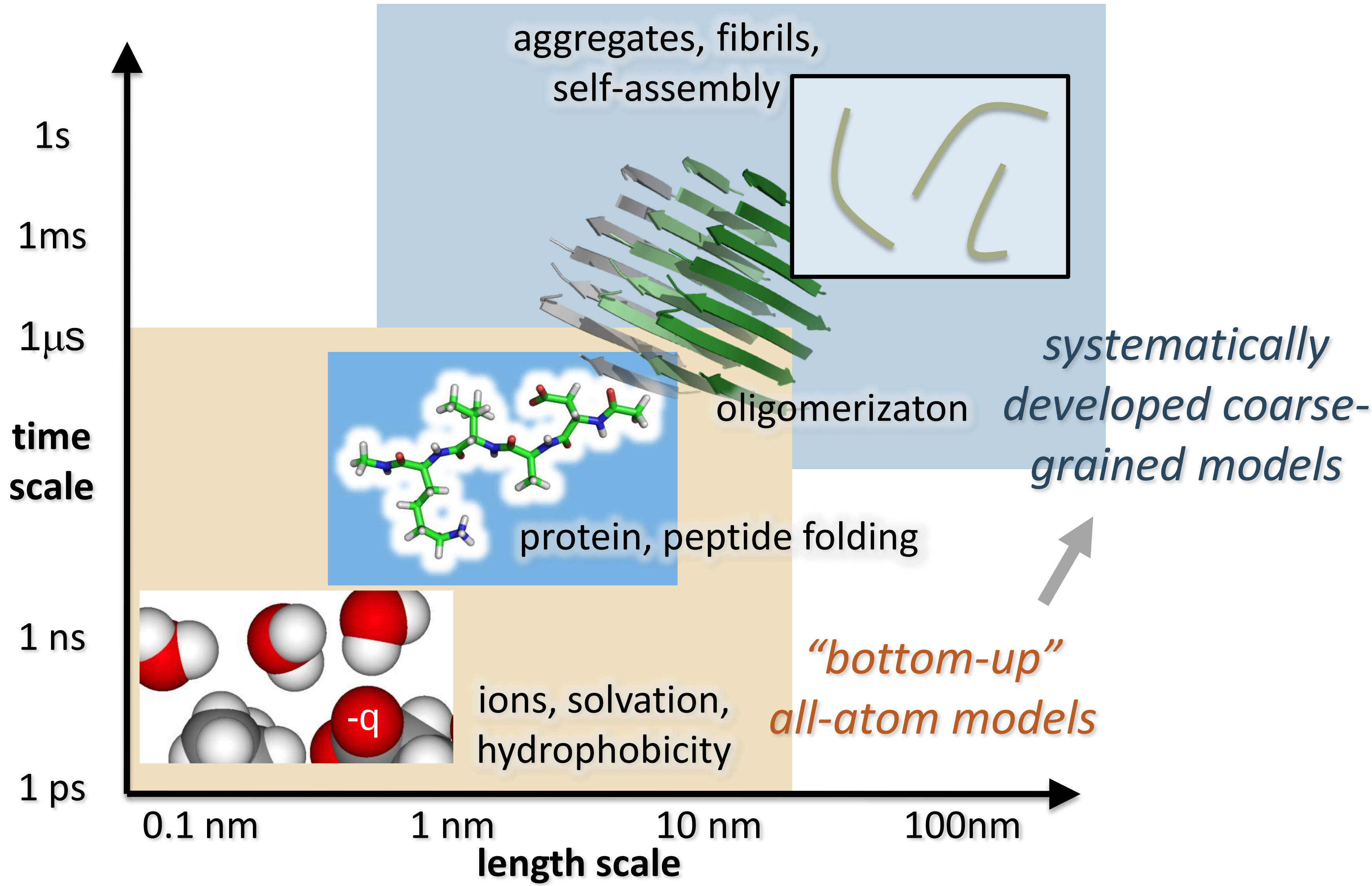


1. Tycko et al., Ann. Rev. of Phys. Chem. (2001)
2. Reches, et al. Science (2003)
4. Yan et al., Angewandte Chem. Int. Ed. (2007)



sequence, temperature, concentration, pH, salt additives → **mechanisms driving forces structures *predictions***

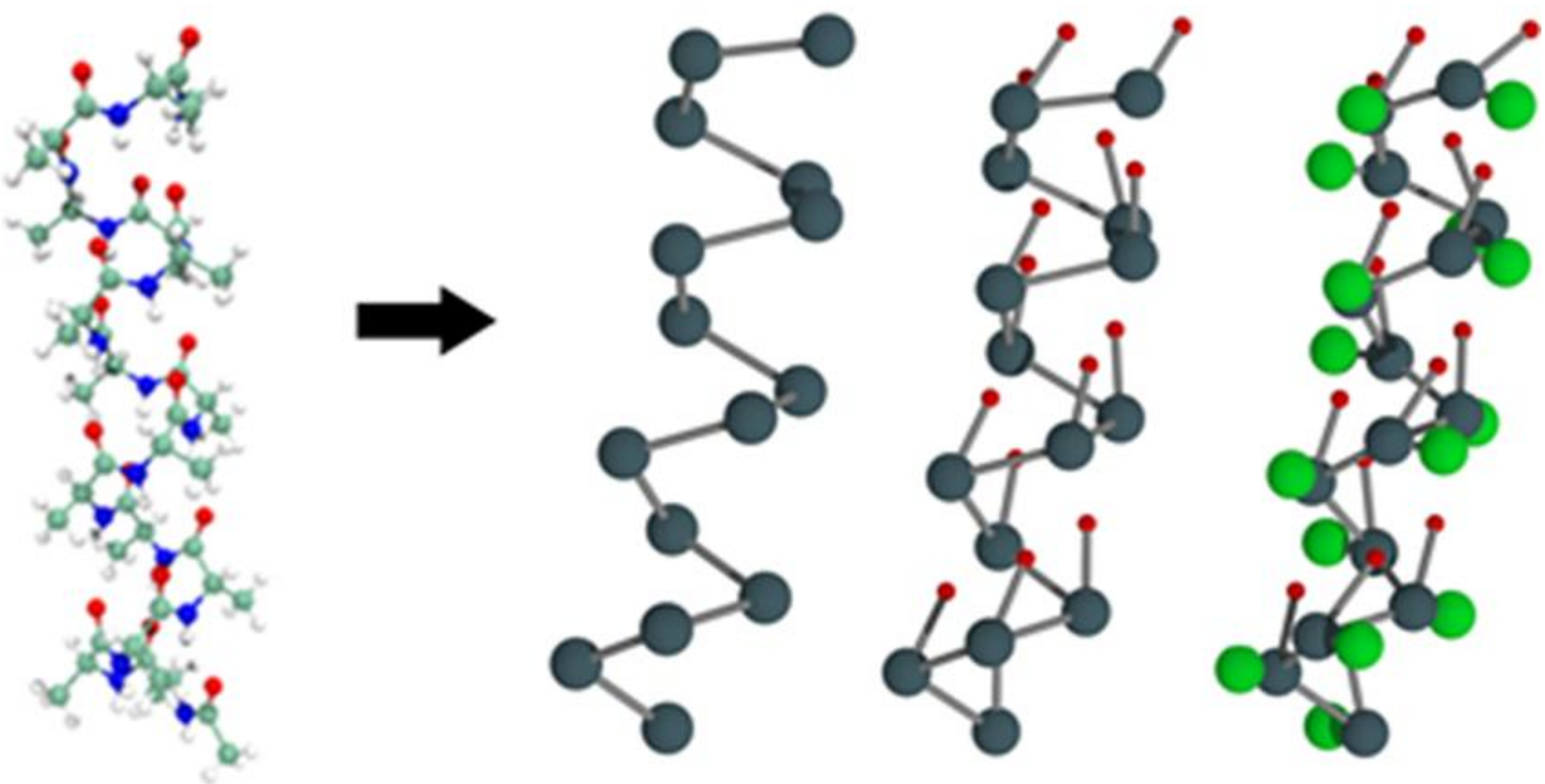
1. Tycko et al., Ann. Rev. of Phys. Chem. (2001)
2. Reches, et al. Science (2003)
3. Amdursky et al, Biomacromolecules (2011)
4. Han et al, Colloids and Biosurfaces B (2011)
5. Yan et al., Chem. Soc. Rev. (2010)
6. Yan et al., Angewandte Chem. Int. Ed. (2007)
7. Govindaraju et al, Supramolec. Chem. (2011)
8. Su et al, J. Mater. Chem. (2010)

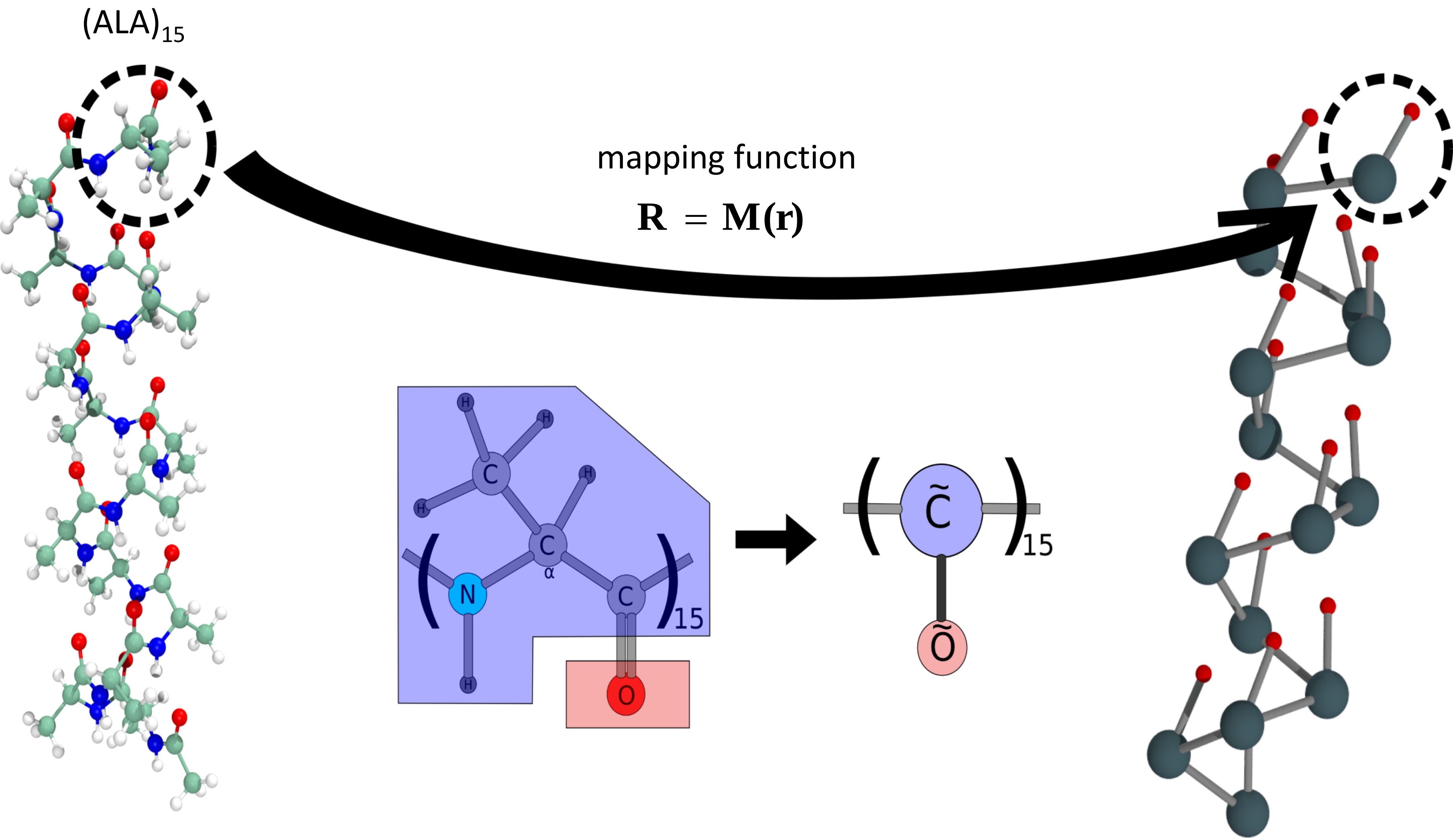


aggregates, fibrils,
self-assembly
1s
1ms
1μs
time
scale
1 ns
1 ps
systematically
developed coarse-
grained models
oligomerizaton
protein, peptide folding
-q
ions, solvation,
hydrophobicity
"bottom-up"
all-atom models
0.1 nm
1 nm
10 nm
100nm
length scale

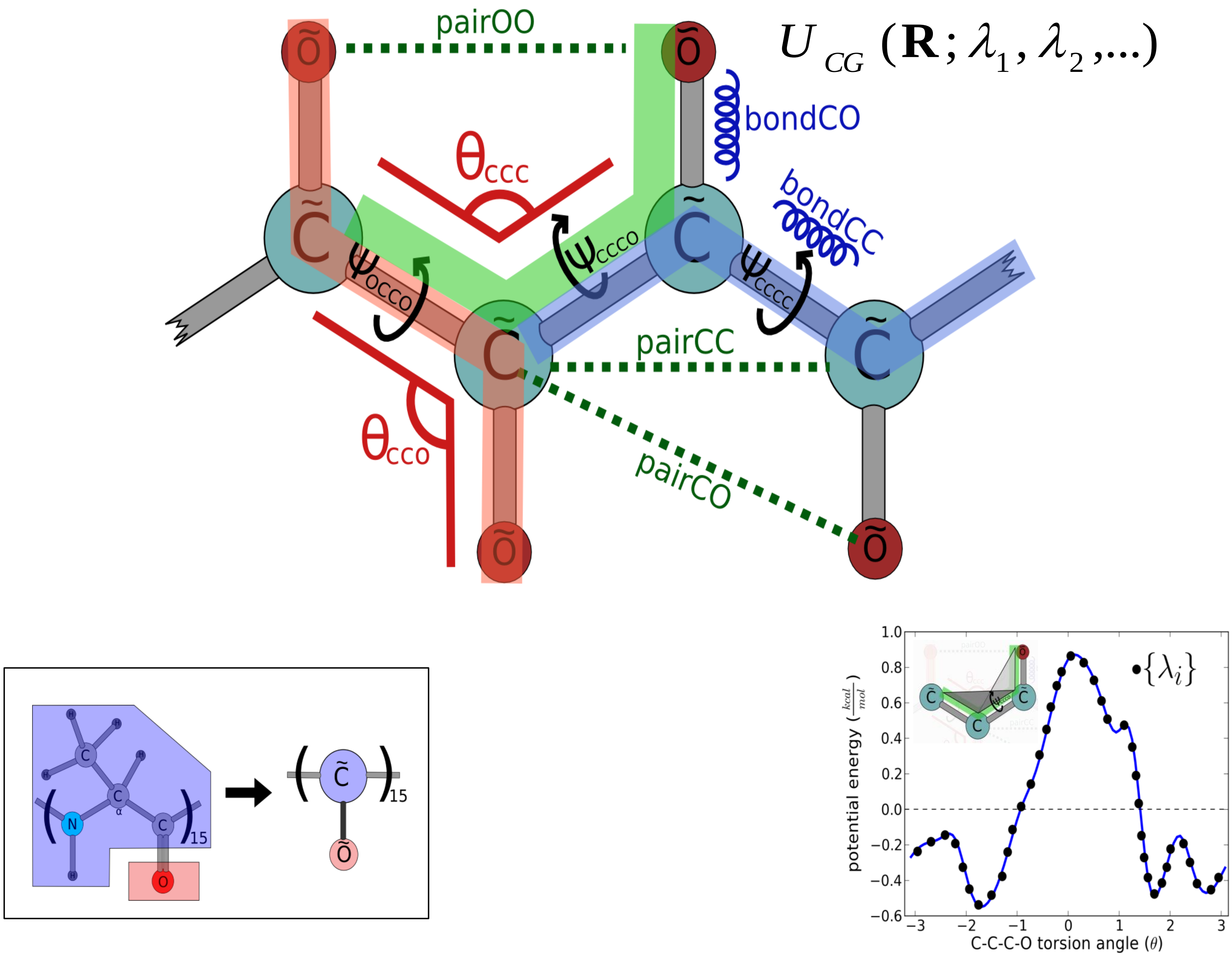
all-atom peptide model

coarse-grained models of varying detail





(ALA)15
mapping function
R = M(r)
H
H
C
H
H
C
α
N
C
H
O
15
C̃
Õ
15



pairOO
$U_{CG}(\mathbf{R}; \lambda_1, \lambda_2, \ldots)$
Õ
bondCO
θccc
C̃
ψccco
bondCC
ψocco
ψcccc
pairCC
θcco
pairCO
C
H
N
O
α
15
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
−3
−2
−1
0
1
2
3
potential energy ($\frac{kcal}{mol}$)
C-C-C-O torsion angle (θ)
$\bullet \{\lambda_i\}$

What to match?

structure

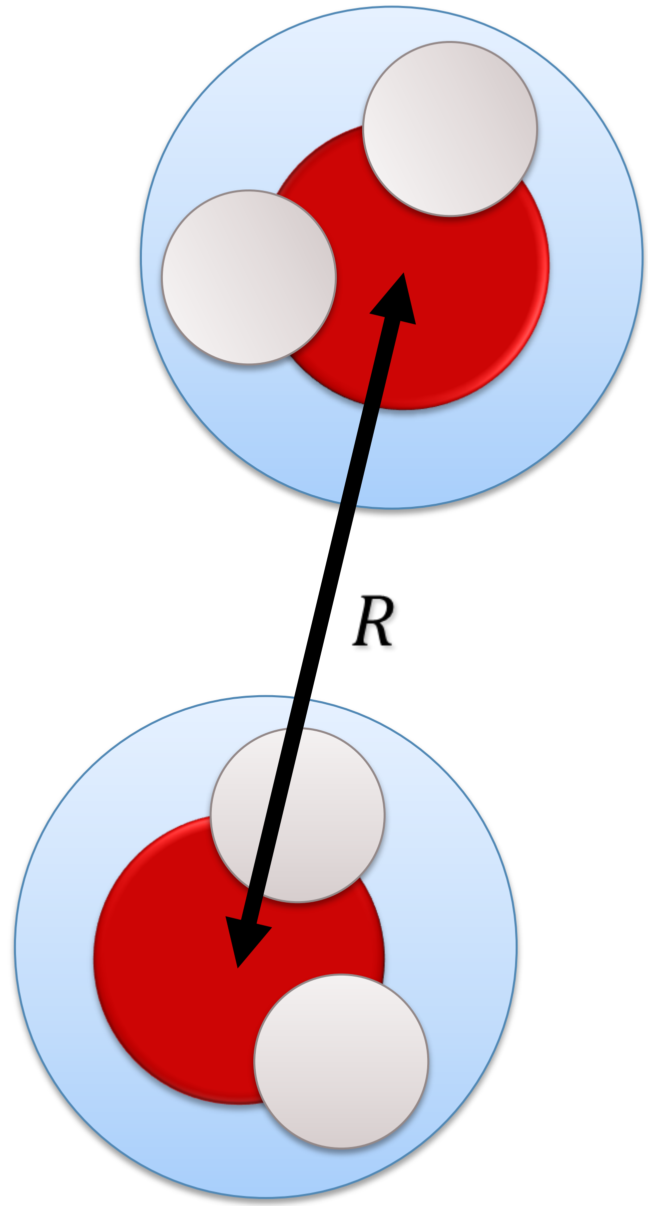
$g_{AA}(R) = g_{CG}(R)$

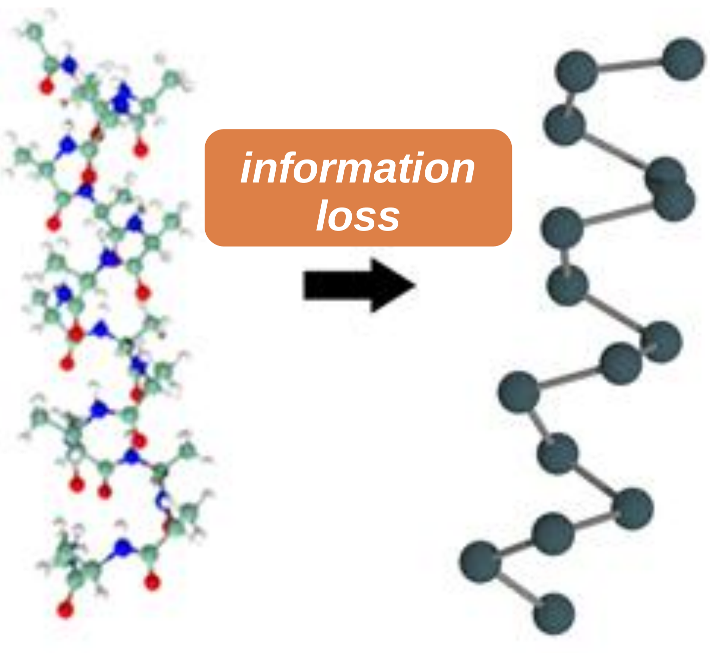
energies

$\langle U_{AA}(R) \rangle = U_{CG}(R)$

forces

$\langle f(R) \rangle_{AA} = f_{CG}(R)$





$$S_{\text{rel}} = \sum_{\text{configs. } i} p_A(i) \ln \frac{p_A(i)}{p_{CG}(i)}$$

$p_A(i)$ ***atomistic*** ensemble probability for configuration i, determined by $U_{AA}(\mathbf{r})$

$p_{CG}(i)$ ***coarse-grained*** ensemble probability for configuration i, determined by $U_{CG}(\mathbf{R})$

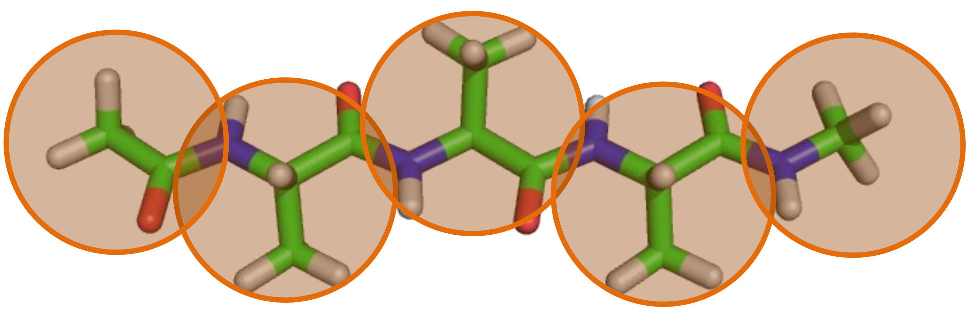
$$S_{\text{rel}} \geq 0$$

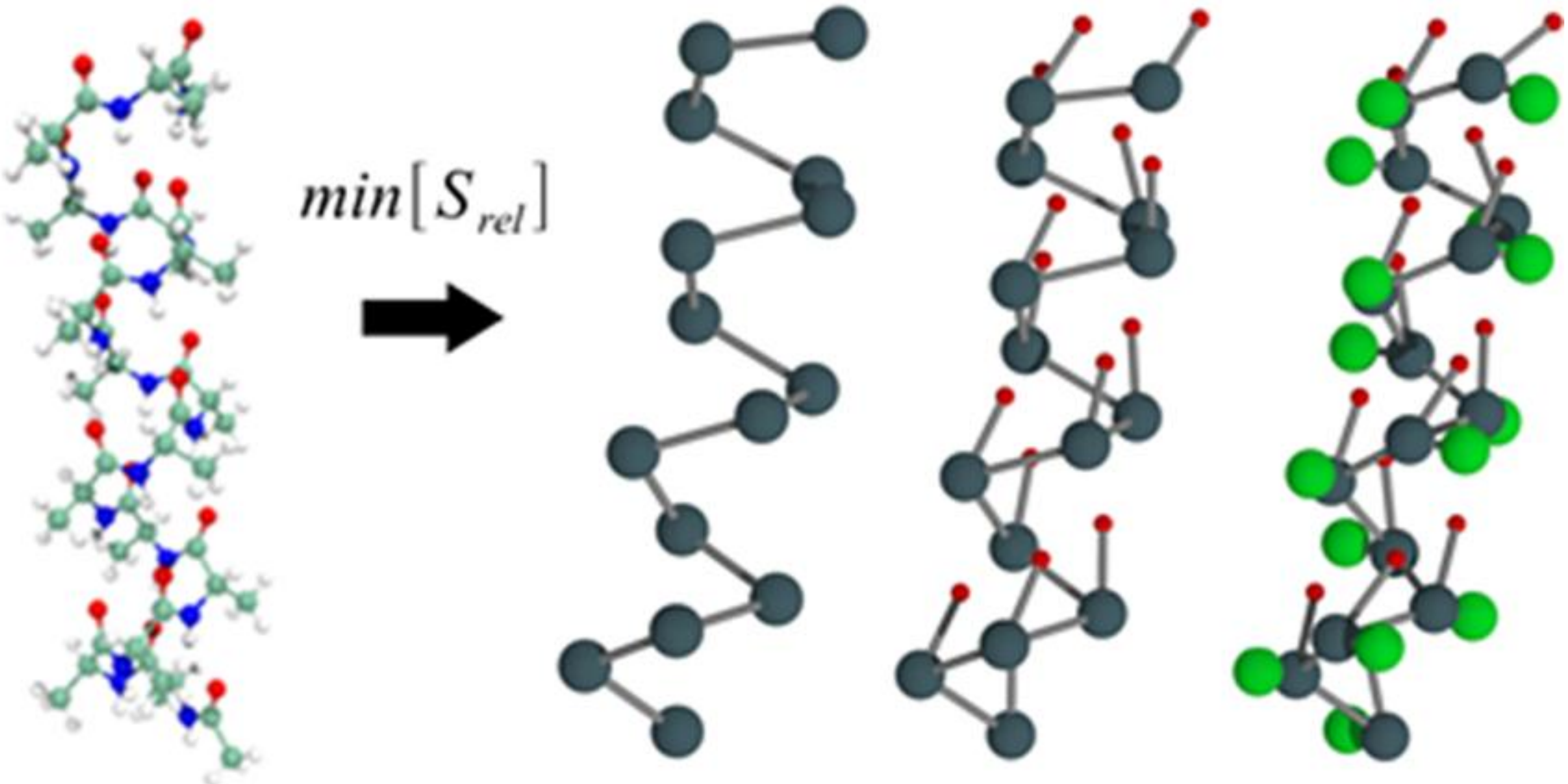
Shell, JCP (2008); Chaimovich and Shell, PRE (2010); Chaimovich and Shell, JCP (2011)

$$S_{\text{rel}} = \sum_{\text{configs. } i} p_A(i) \ln \frac{p_A(i)}{p_{CG}\left(M(i)\right)} + S_{\text{map}}$$

M = mapping function for turning atomistic configurations into CG ones

entropy due to loss of degrees of freedom





$$S_{rel} = \beta \left\langle U_{CG} - U_{A} \right\rangle_{A} - \beta \left(A_{CG} - A_{A} \right) + S_{map}$$

$$= \ln \left\langle e^{\Delta - \langle \Delta \rangle_{A}} \right\rangle_{A} \qquad \Delta \equiv \beta \left(U_{A} - U_{CG} \right)$$

What to match?

structure

$$\frac{\delta S_{\text{rel}}}{\delta\left[u_{CG,pair}(R)\right]} = 0 \quad \rightarrow \quad g_{AA}(R) = g_{CG}(R)$$

energies

$$S_{\text{rel}} = \ln\left\langle e^{\Delta - \langle\Delta\rangle_{AA}}\right\rangle_{AA} \approx \text{var}_{AA}(\beta U_{AA} - \beta U_{CG})$$

forces

$$\frac{\delta S_{\text{rel}}}{\delta U_{CG}} = 0 \quad \rightarrow \quad U_{CG} = PMF_{AA} \quad \rightarrow \quad \langle f\rangle_{AA} = f_{CG}$$

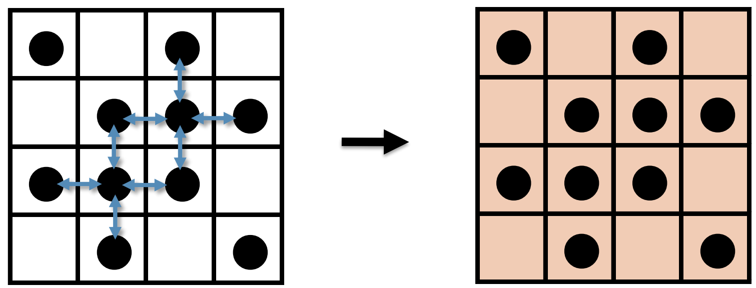
Constraints

Lagrange multiplier

$$S_{\mathrm{rel}} - \lambda(\langle X \rangle_{AA} - \langle X \rangle_{CG})$$

atomistic
2D lattice gas, pairwise

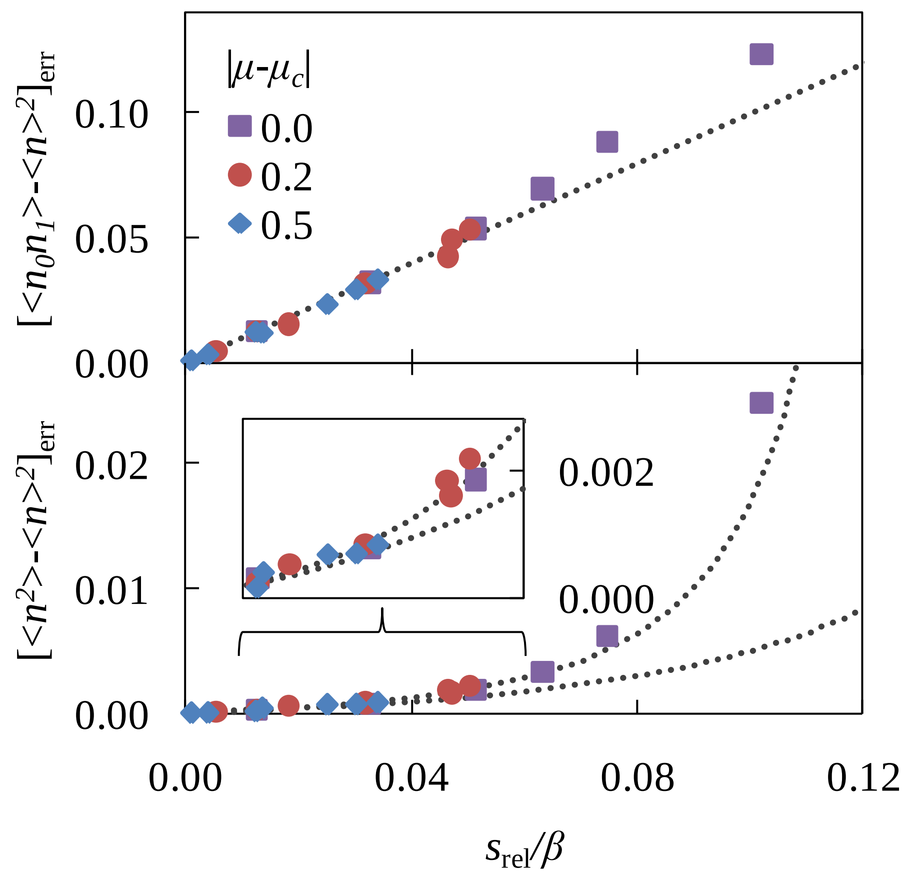
coarse-grained
2D lattice gas, mean-field



errors in particle fluctuations

nearest-neighbor

bulk



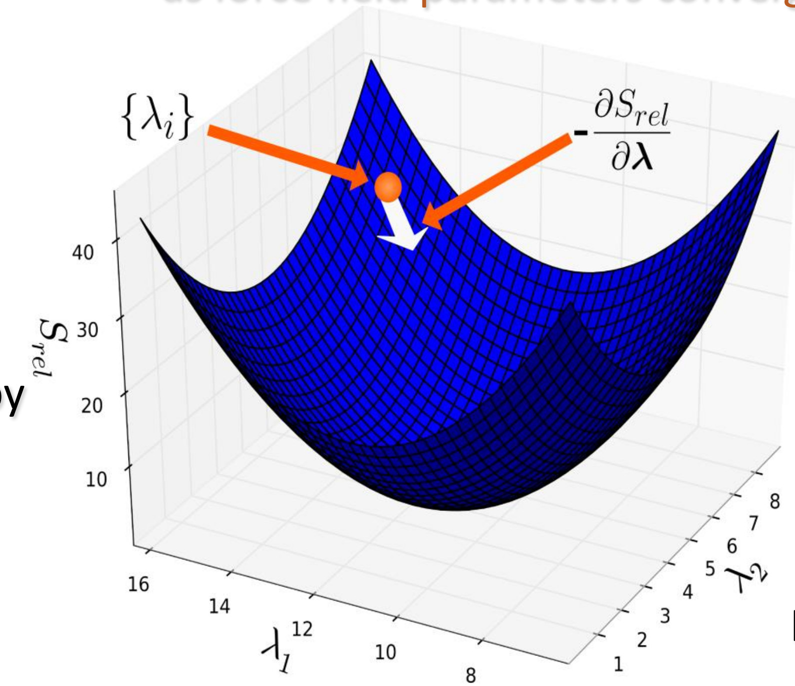
Chaimovich and Shell, J. Chem. Phys.(2011)

$$\lambda^{(k+1)} = \lambda^{(k)} - \left(\partial S_{\text{rel}} / \partial \lambda\right) / \left(\partial^2 S_{\text{rel}} / \partial \lambda^2\right)$$

$$= \lambda^{(k)} - \frac{\left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{CG} - \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{A}}{\left\langle \frac{\partial^2 U}{\partial \lambda^2} \right\rangle_{CG} + \beta \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{CG}^2 - \beta \left\langle \left(\frac{\partial U}{\partial \lambda} \right)^2 \right\rangle_{CG} - \left\langle \frac{\partial^2 U}{\partial \lambda^2} \right\rangle_{A}}$$

from single reference atomistic simulation

from iterative CG simulations as force field parameters converge



relative entropy

parameter space (potentials)

$$\boldsymbol{\lambda} = \{\lambda_1, \lambda_2, \dots\}$$

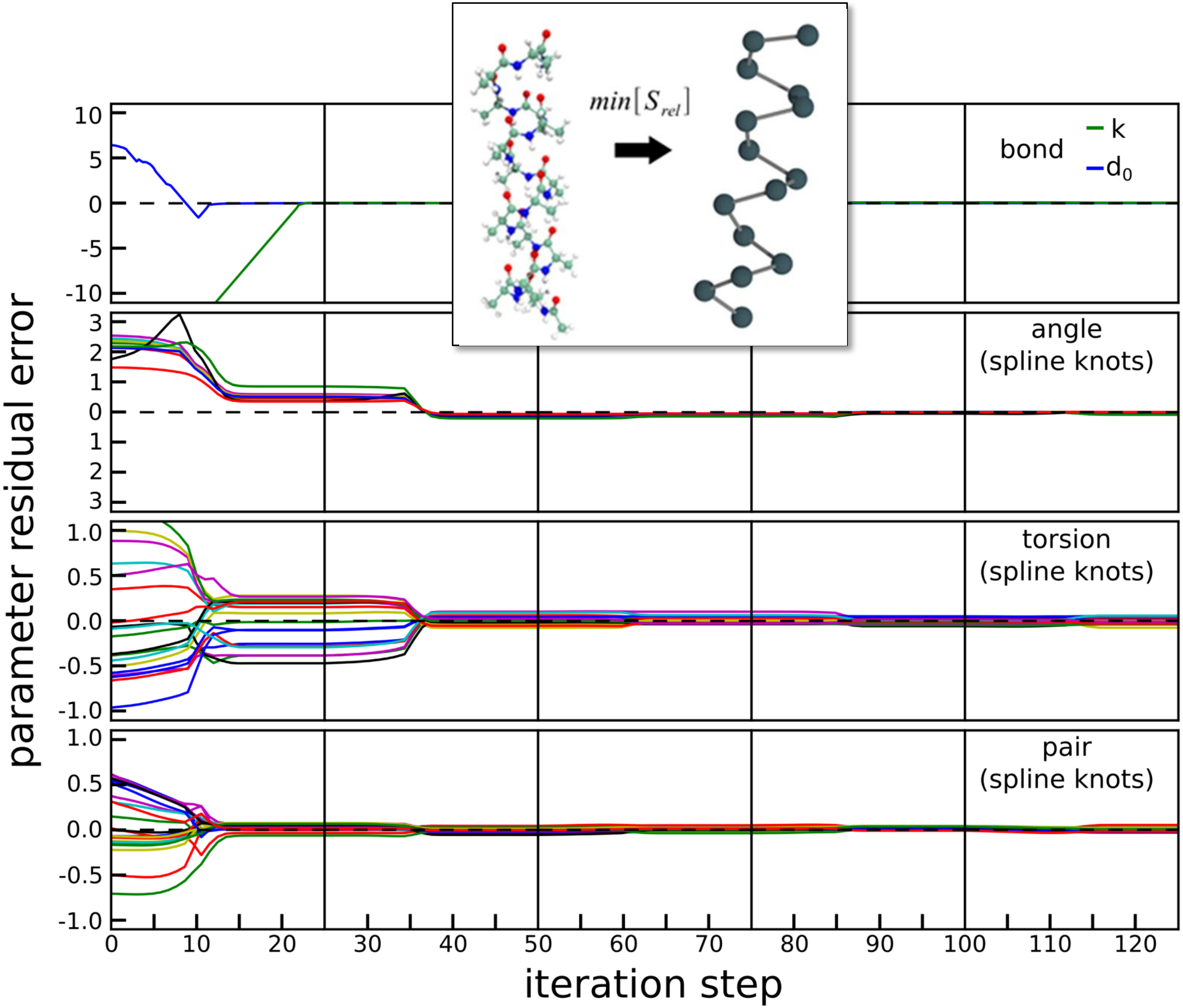
$$\frac{\partial^2 S_{\text{rel}}}{\partial \boldsymbol{\lambda}^2} \qquad \frac{\partial S_{\text{rel}}}{\partial \boldsymbol{\lambda}}$$

$$\boldsymbol{\lambda}^{k+1} = \boldsymbol{\lambda}^k - \chi_{NR} \mathbf{H}^{-1} \left[\beta \left\langle \frac{\partial U_{CG}}{\partial \boldsymbol{\lambda}} \right\rangle_A - \left\langle \frac{\partial U_{CG}}{\partial \boldsymbol{\lambda}} \right\rangle_{CG} \right]$$

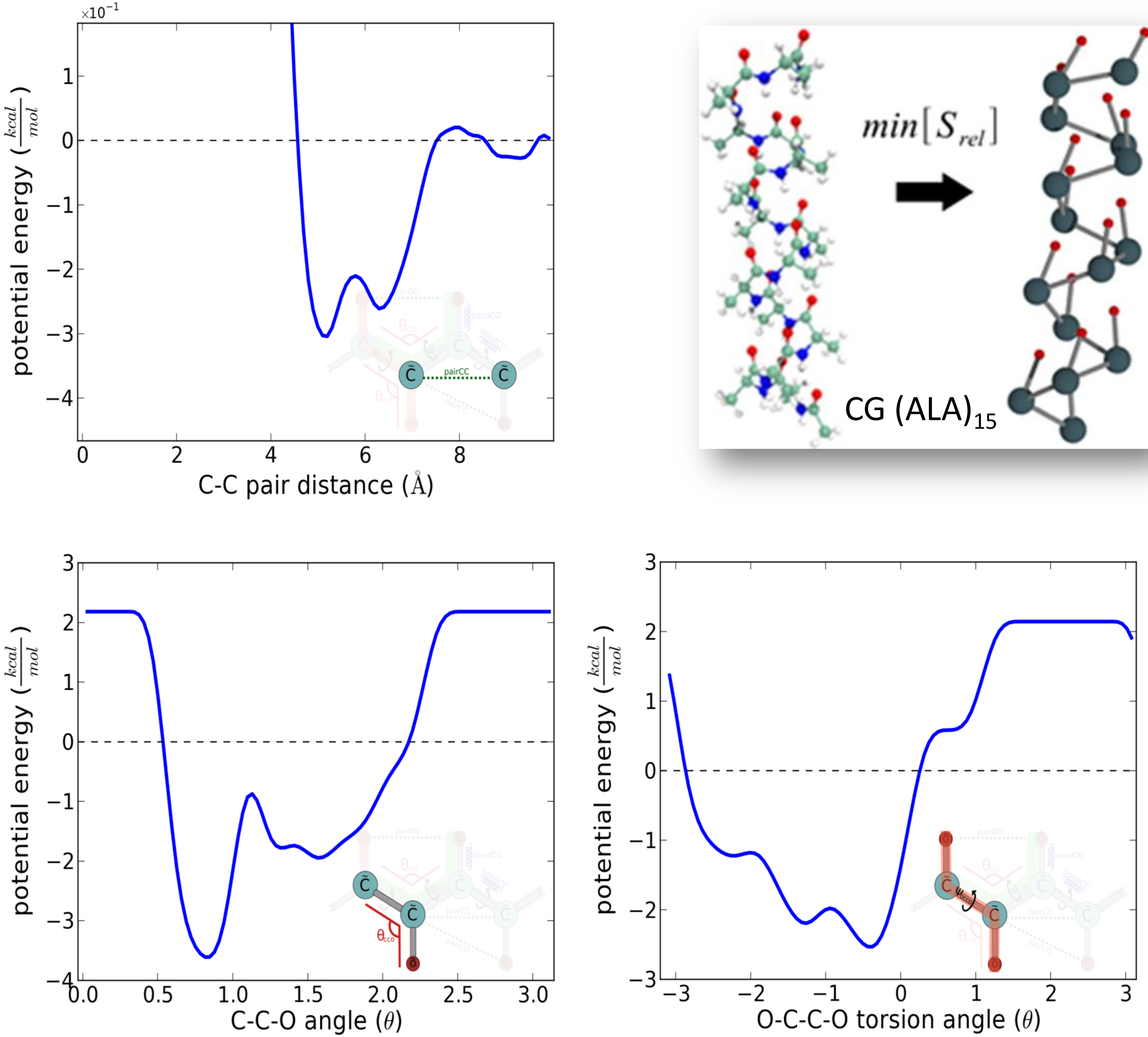
reference all-atom simulation

trial coarse grained simulation(s)

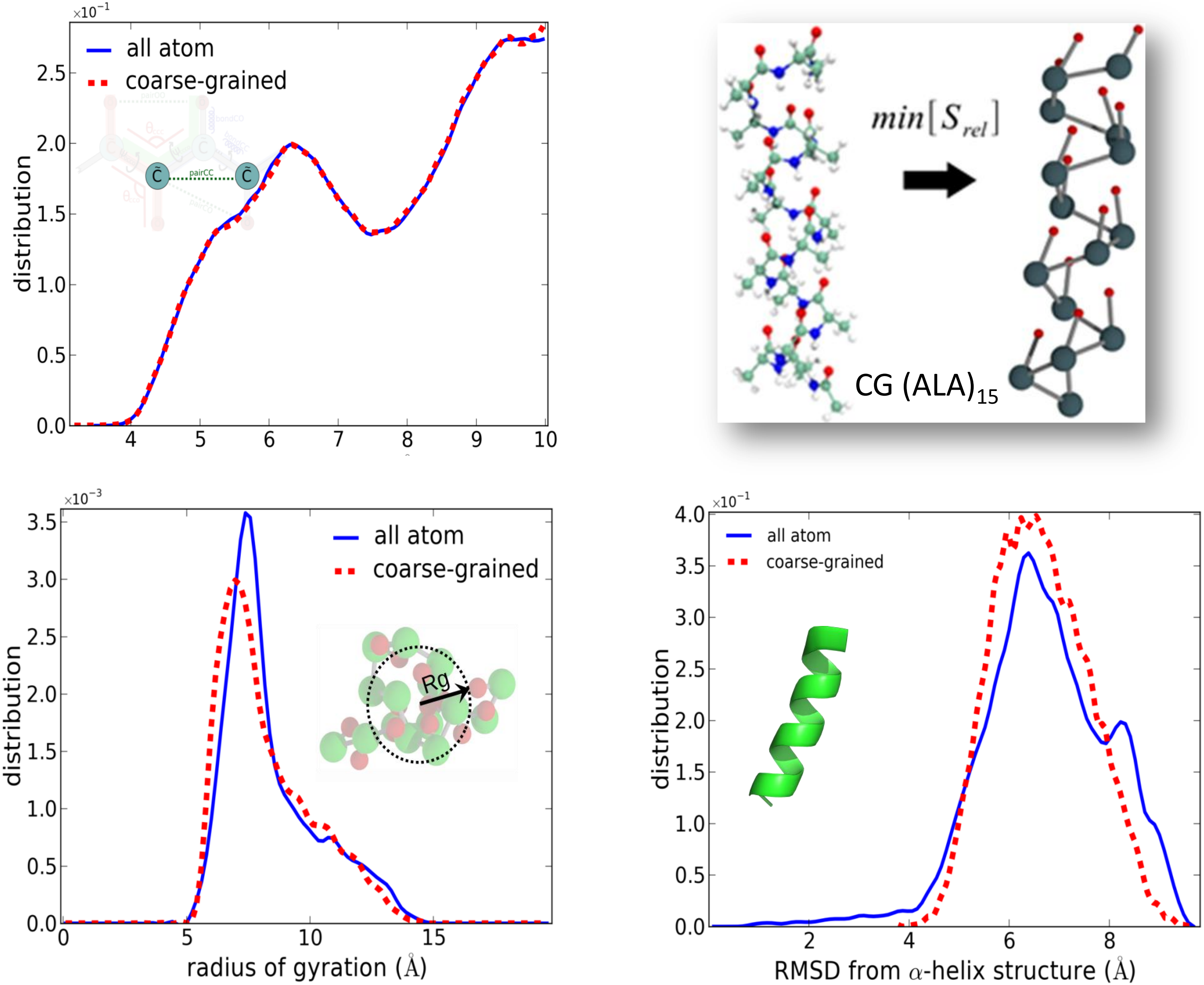
$$w \equiv e^{\beta(U_{CG,\lambda_0} - U_{CG,\lambda})} \qquad \frac{\left\langle \frac{\partial U_{CG}}{\partial \boldsymbol{\lambda}} w \right\rangle_{CG,\boldsymbol{\lambda}_0}}{\langle w \rangle_{CG,\boldsymbol{\lambda}_0}}$$



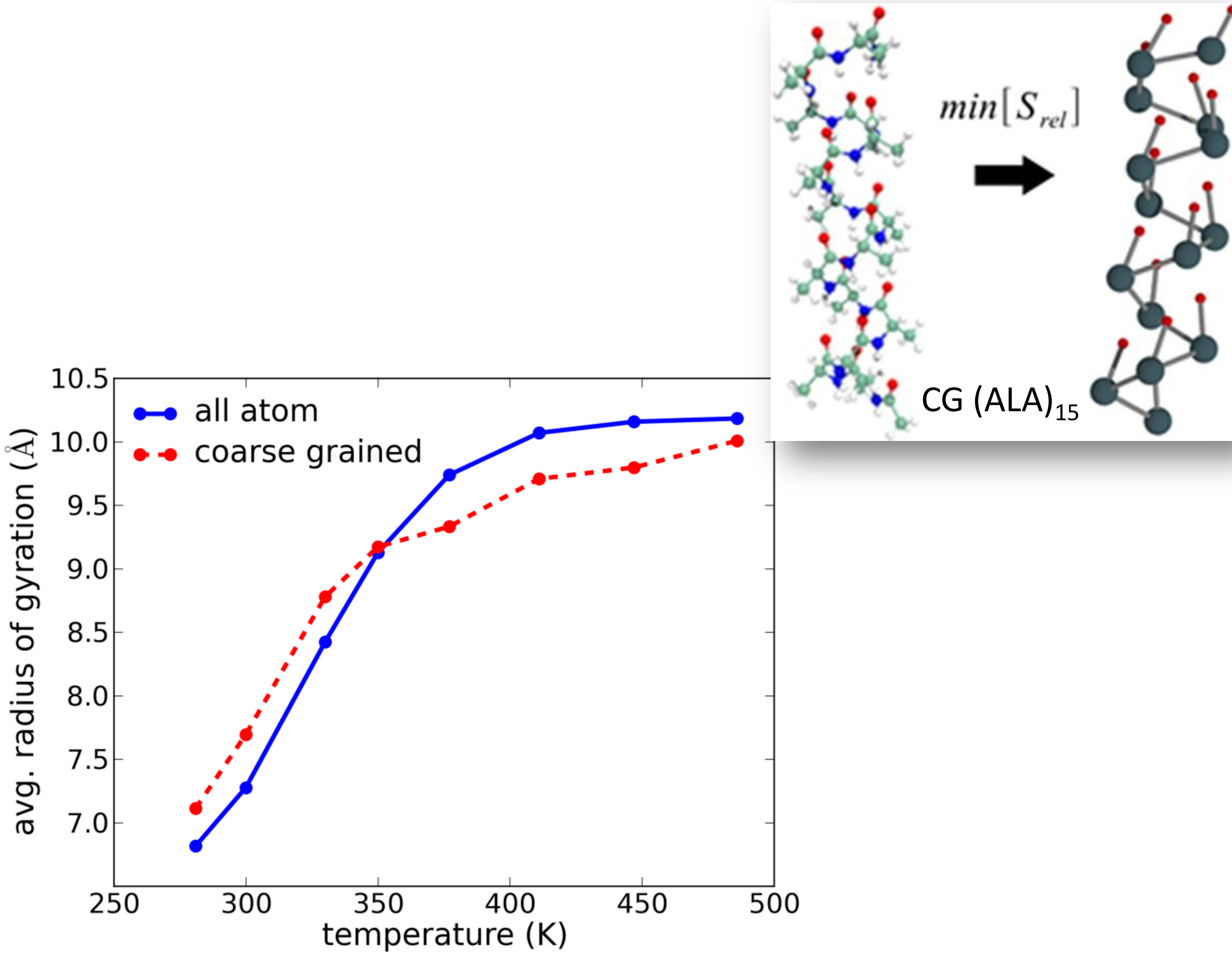
Carmichael and Shell, JCP (2012)



×10^-1
potential energy (kcal/mol)
C-C pair distance (Å)
pairCC
min[S_rel]
CG (ALA)15
potential energy (kcal/mol)
C-C-O angle (θ)
θcco
potential energy (kcal/mol)
O-C-C-O torsion angle (θ)

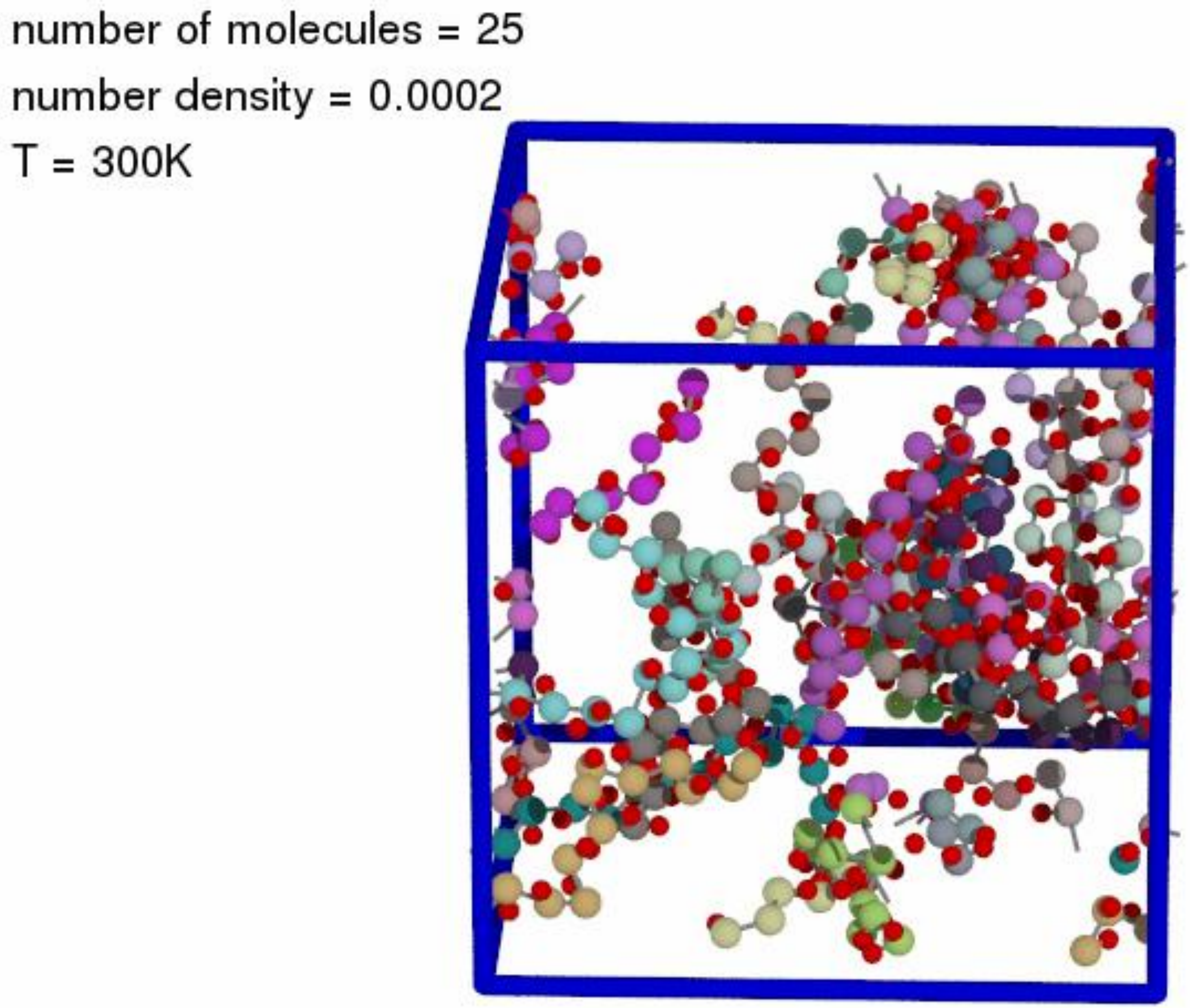


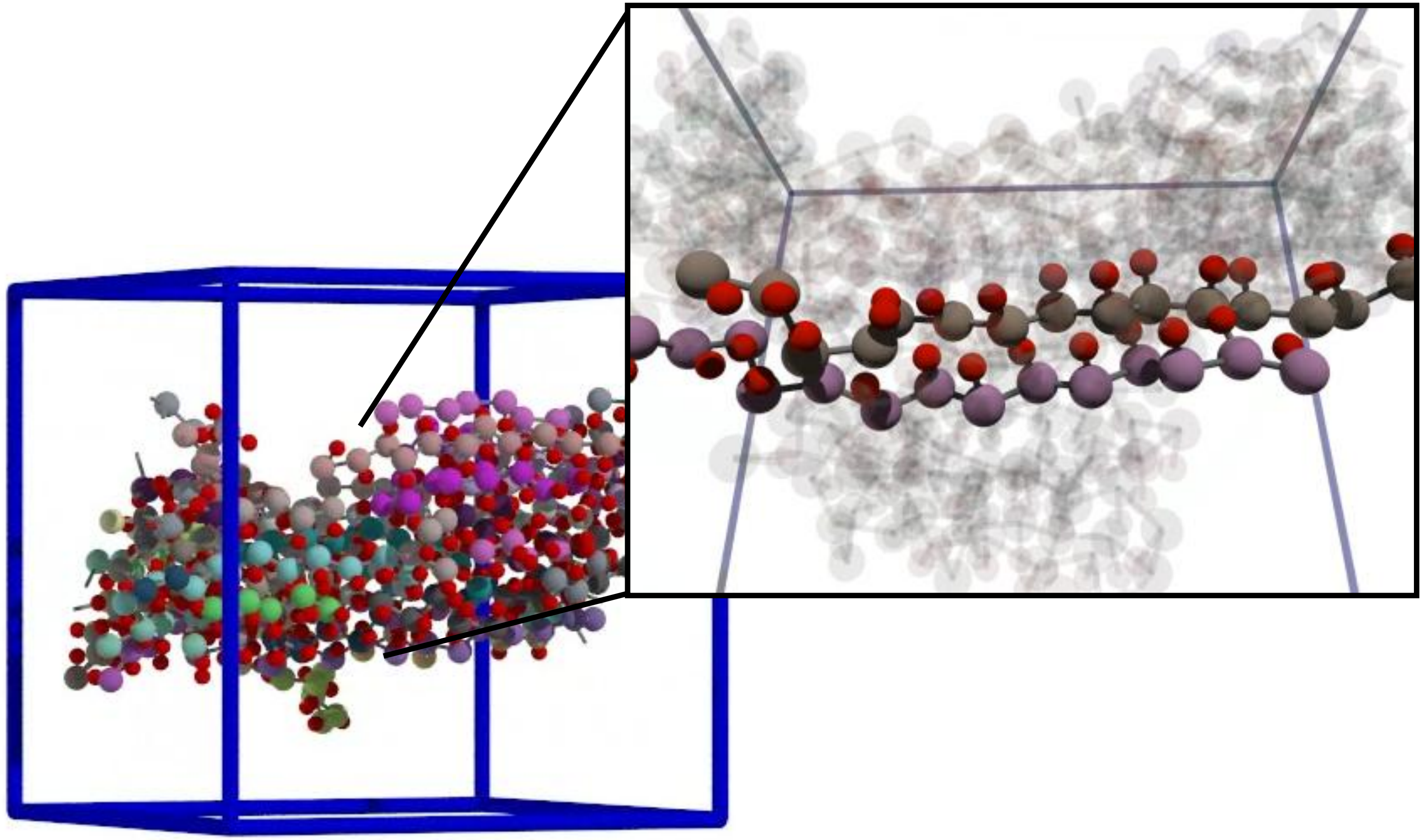
×10⁻¹
all atom
coarse-grained
pairCC
distribution
min[S_rel]
CG (ALA)15
×10⁻³
all atom
coarse-grained
Rg
distribution
radius of gyration (Å)
×10⁻¹
all atom
coarse-grained
distribution
RMSD from α-helix structure (Å)

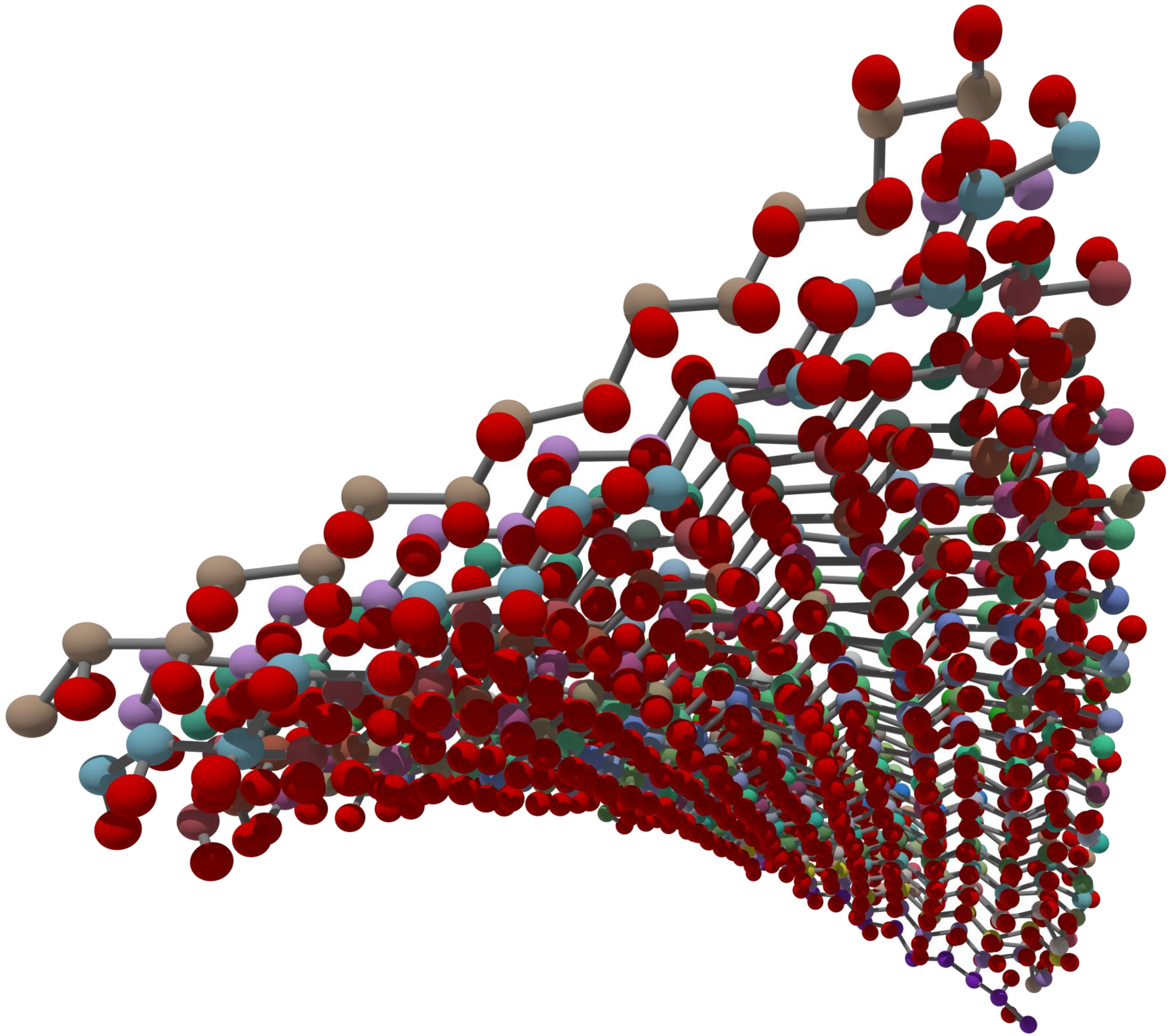


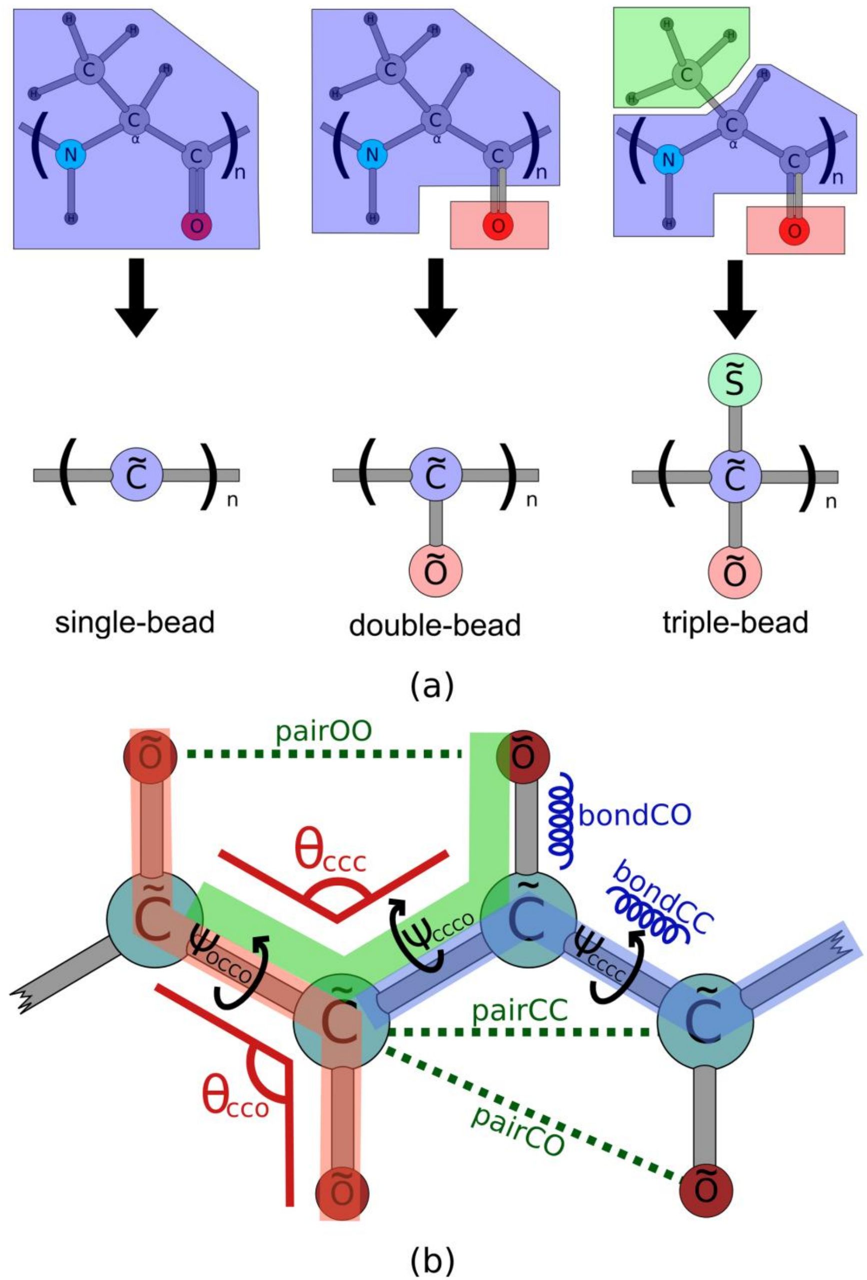
min[S_rel]
CG (ALA)15
all atom
coarse grained
avg. radius of gyration (Å)
temperature (K)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
250
300
350
400
450
500

25 chains of $(ALA)_{15}$

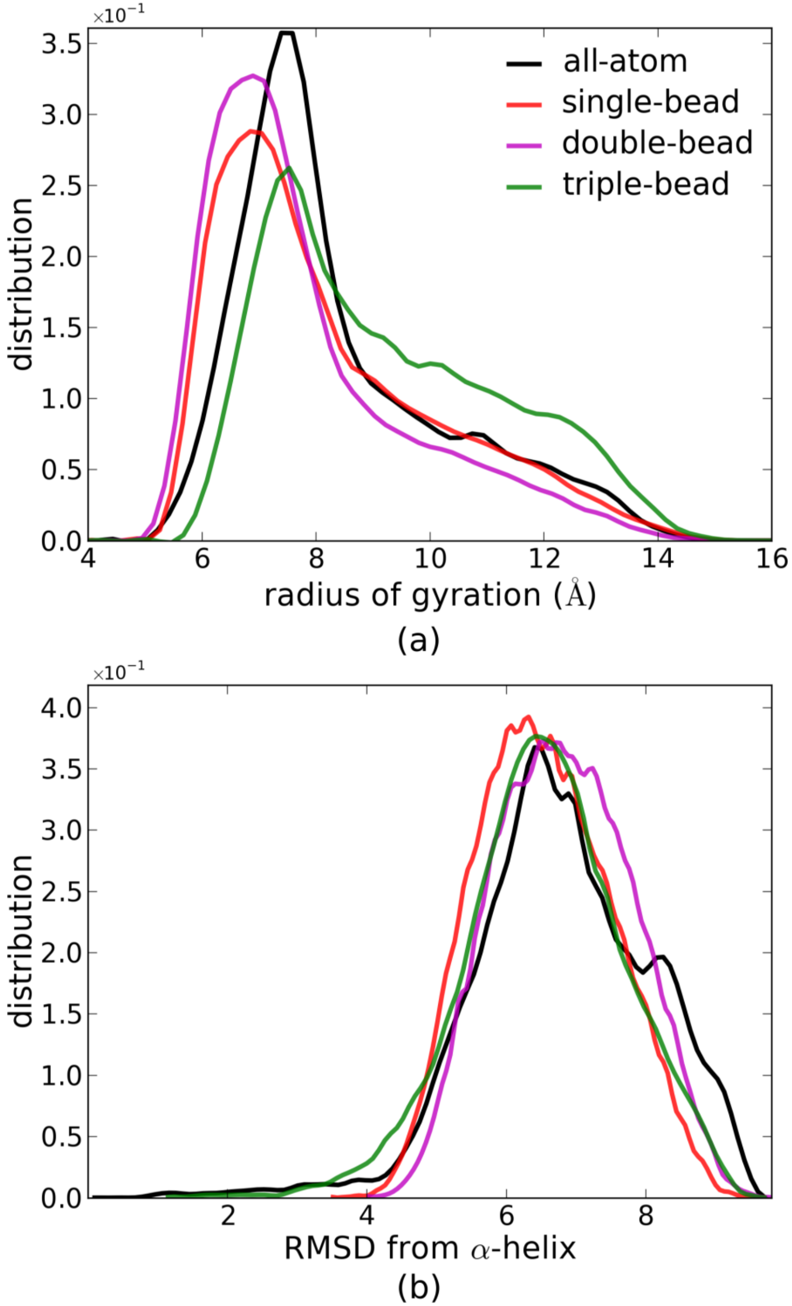


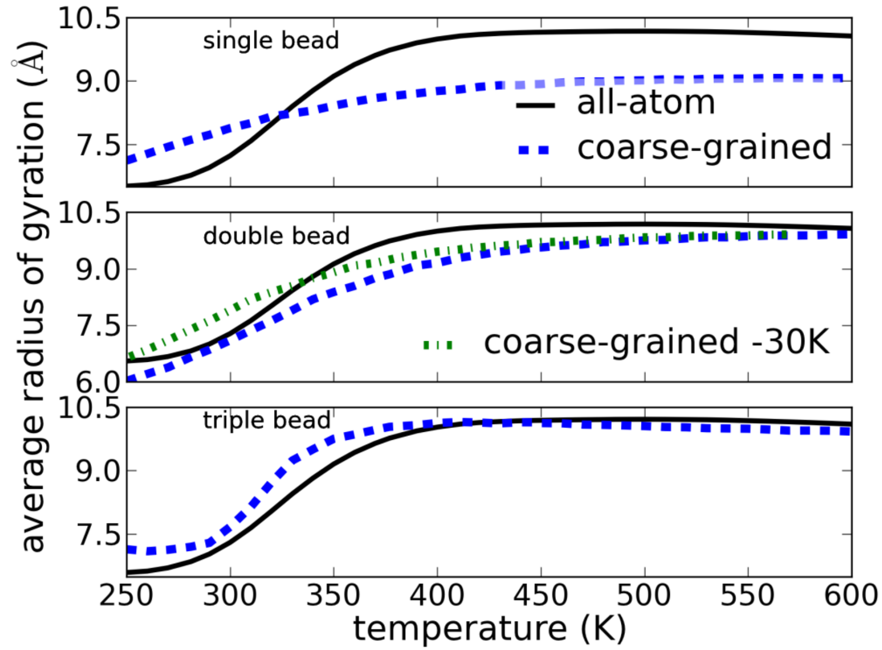






82–444 parameters





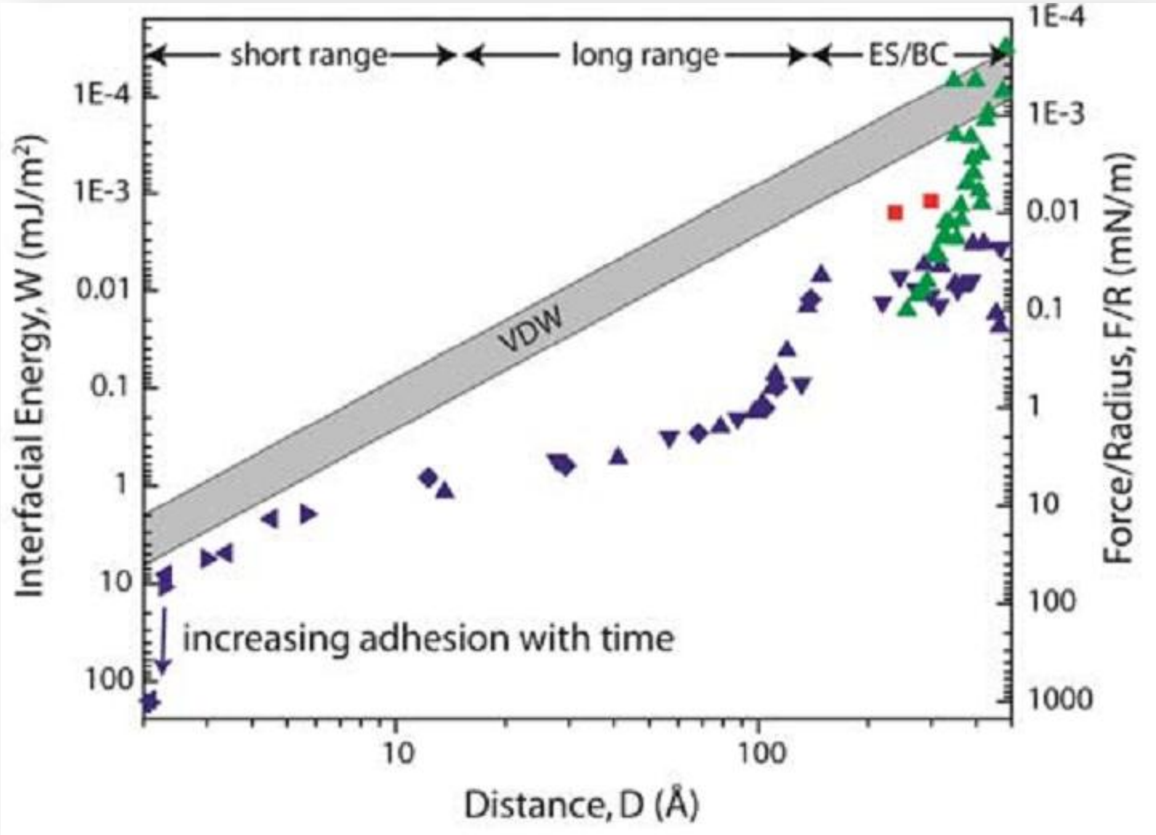
Carmichael and Shell, JCP (2012)

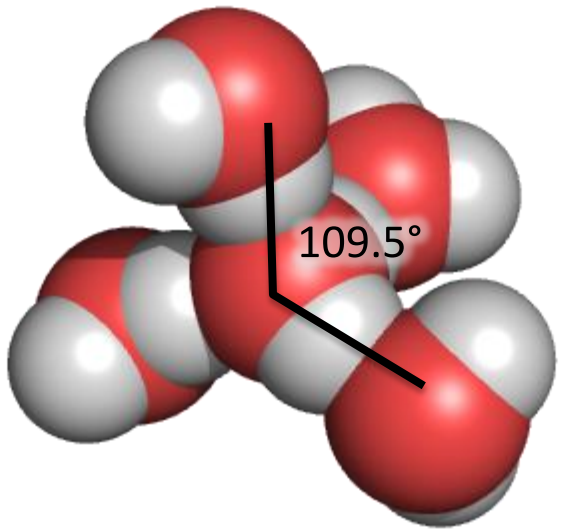
The search for the hydrophobic force law

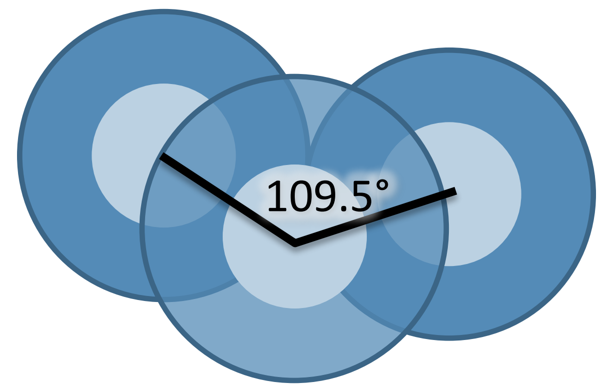
Malte U. Hammer, Travers H. Anderson, Aviel Chaimovich, M. Scott Shell and Jacob Israelachvili*

Faraday Discuss. 146, 299 (2010)

surface force apparatus
OTE chemisorbed on mica





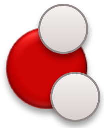


detailed, all-atom picture

accessibility of hydrogen bonding interactions

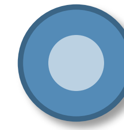
two length scale picture

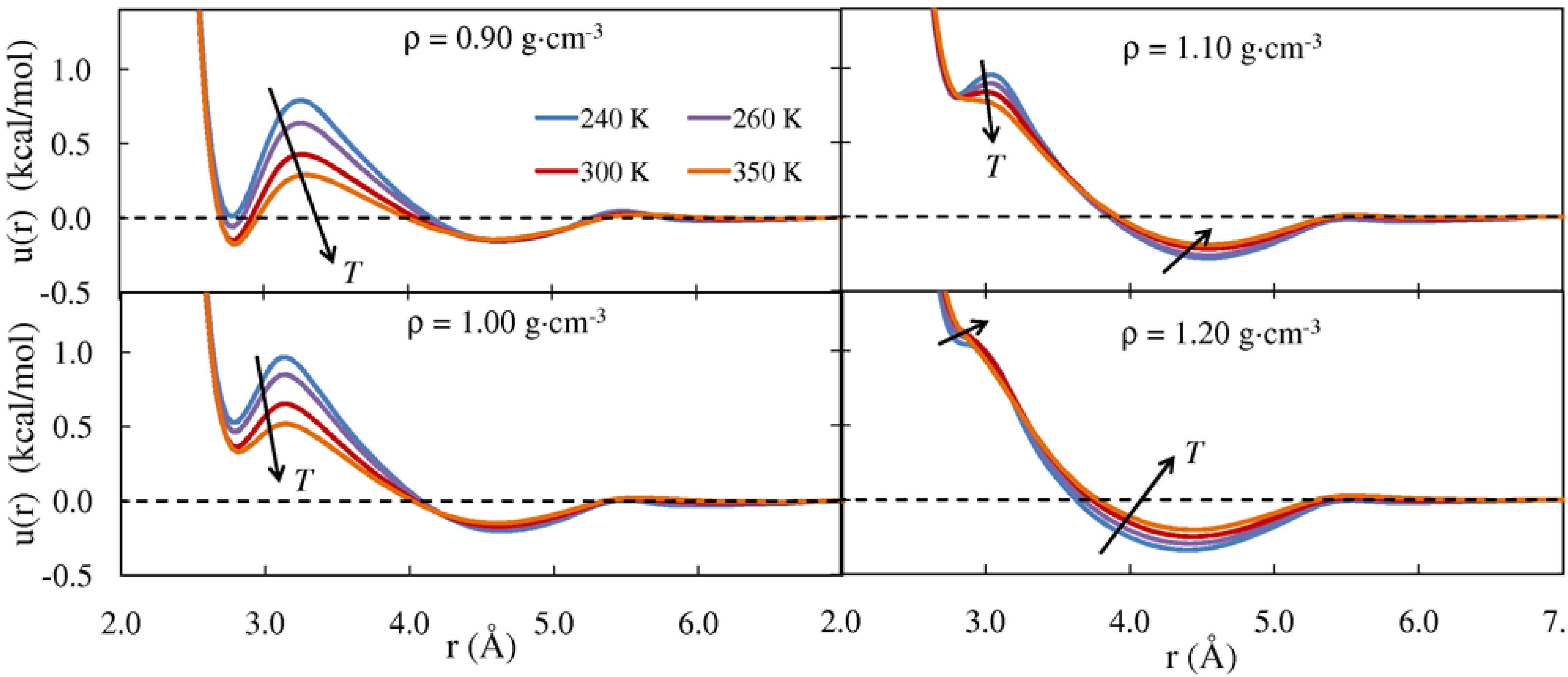
open, tetrahedral structure in competition with close-packing



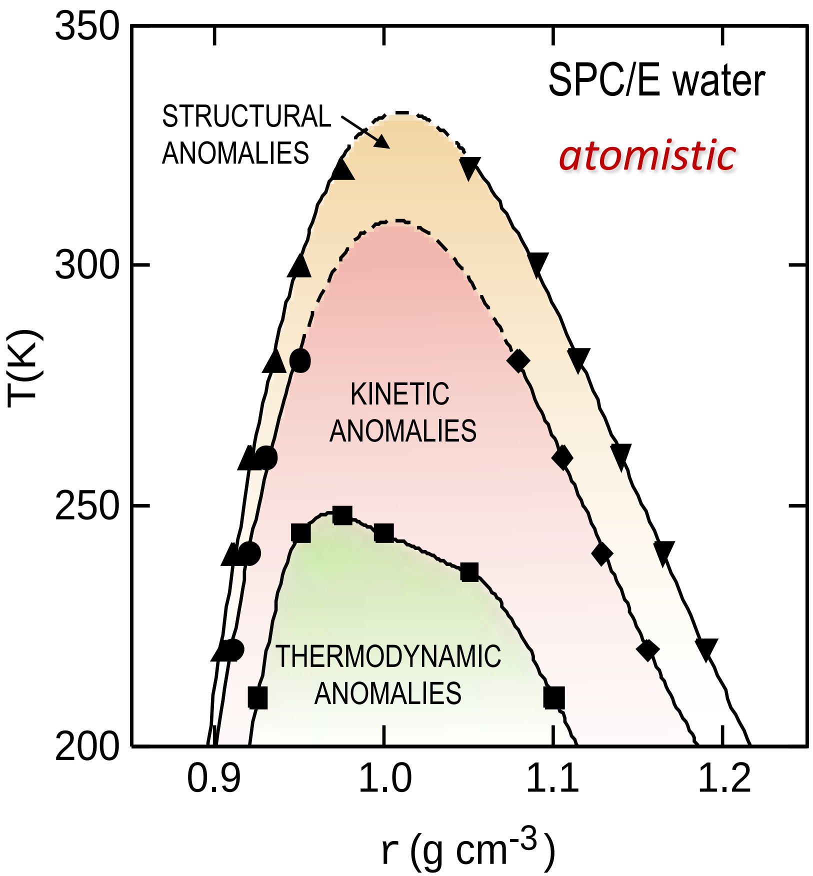
atomistic
SPC/E water

coarse-grained
spline potential

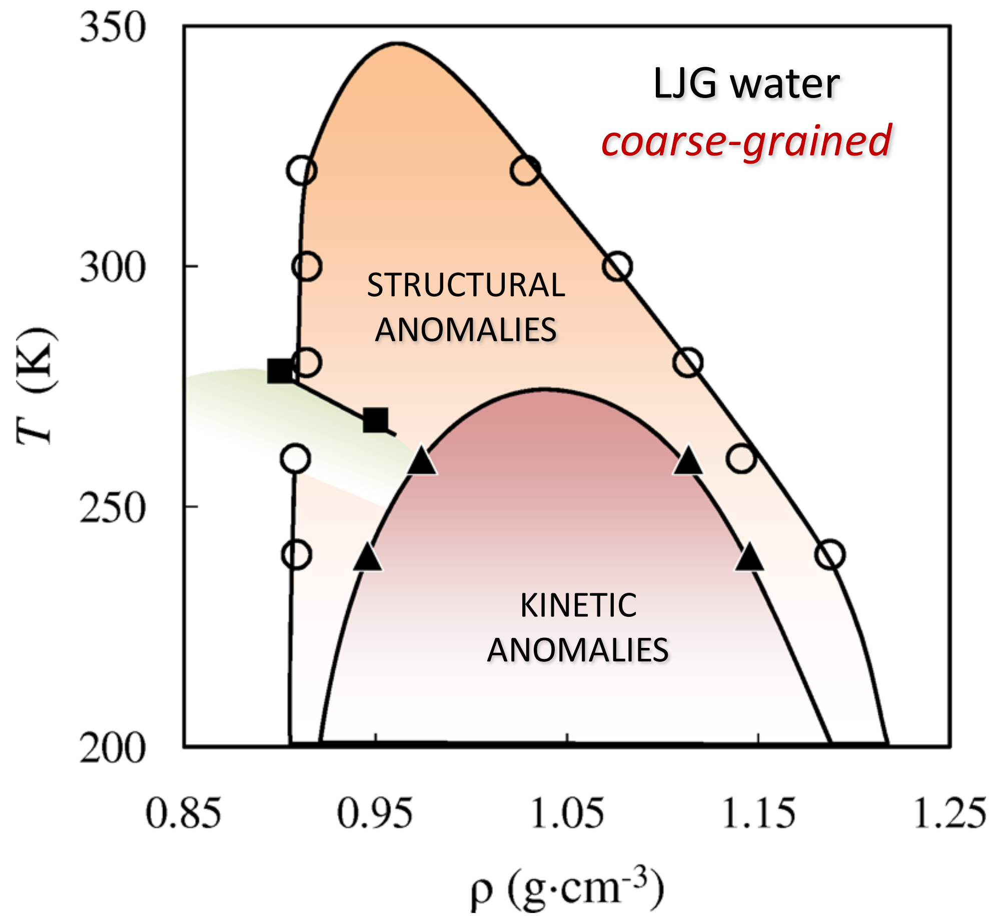




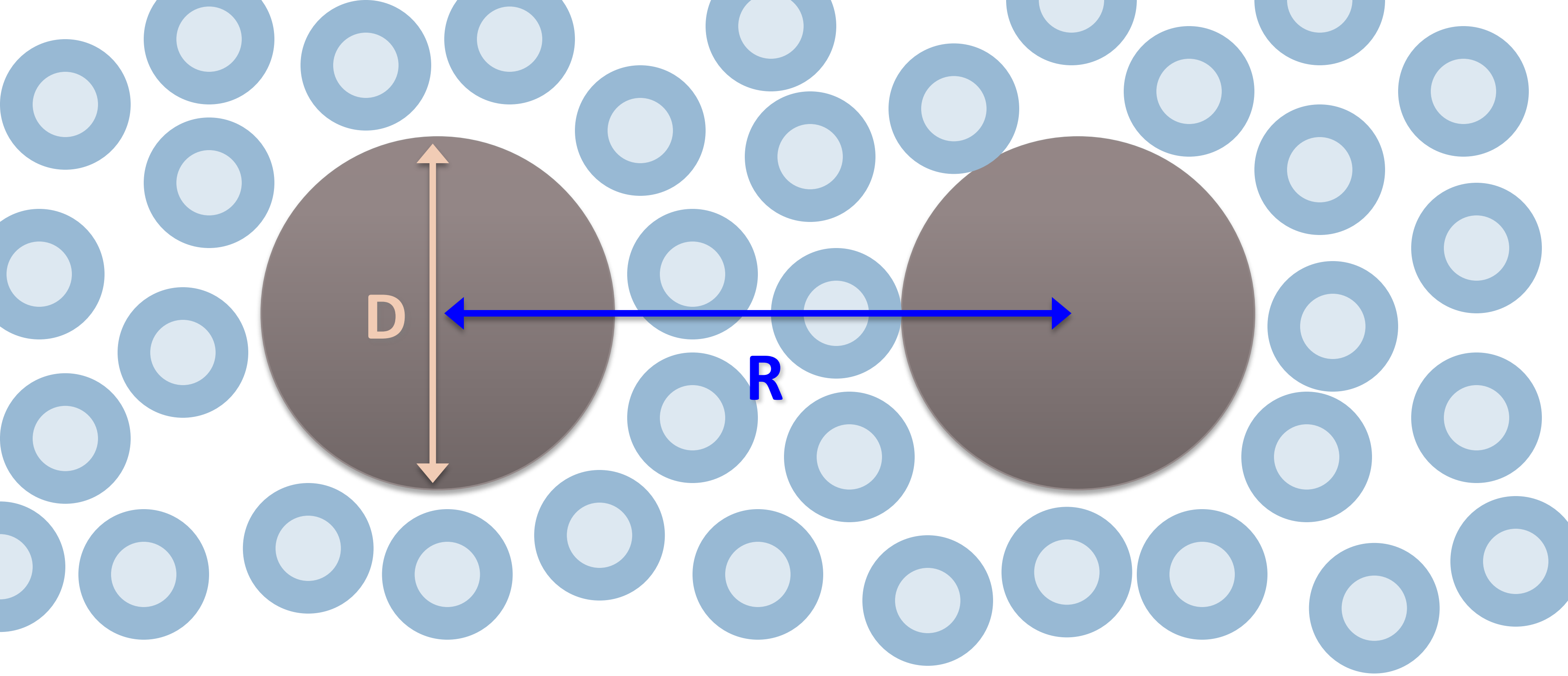
Chaimovich and Shell, PCCP (2009)



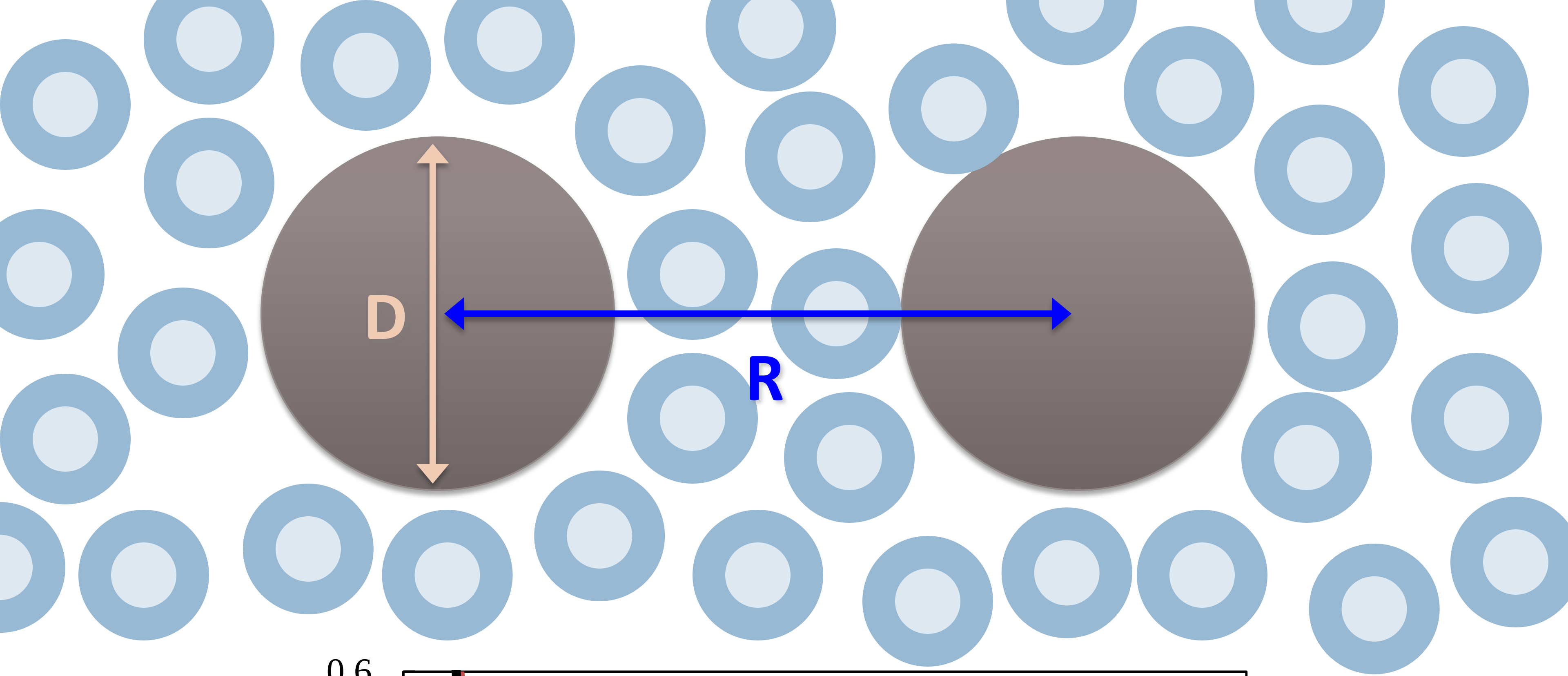
Errington & Debenedetti,
Nature 409, 318 (2001).

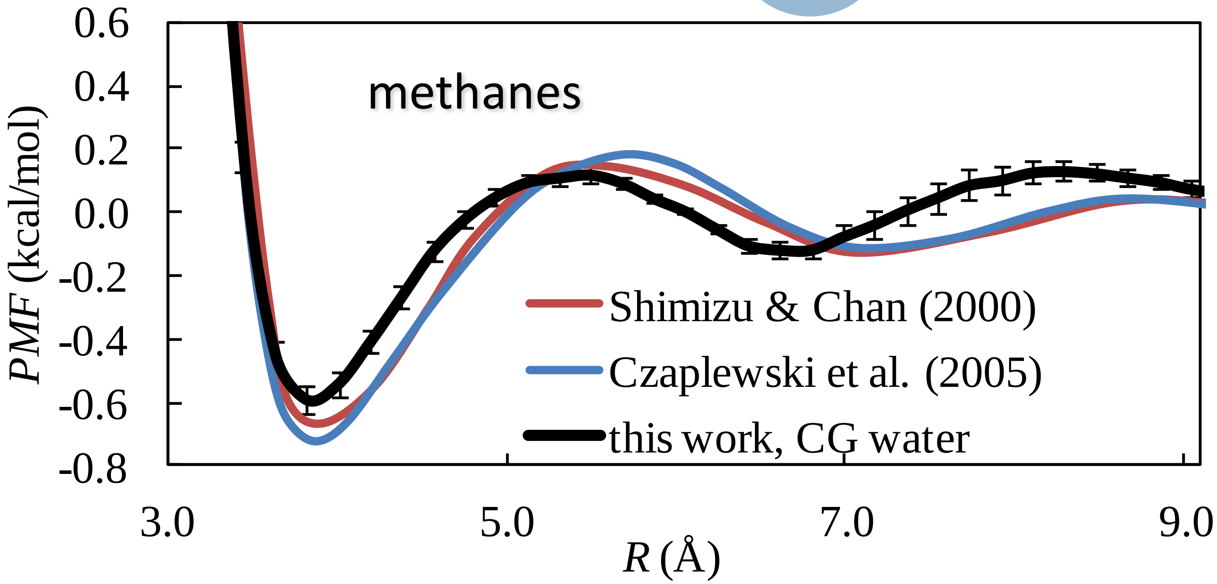


Chaimovich and Shell, PCCP (2009)

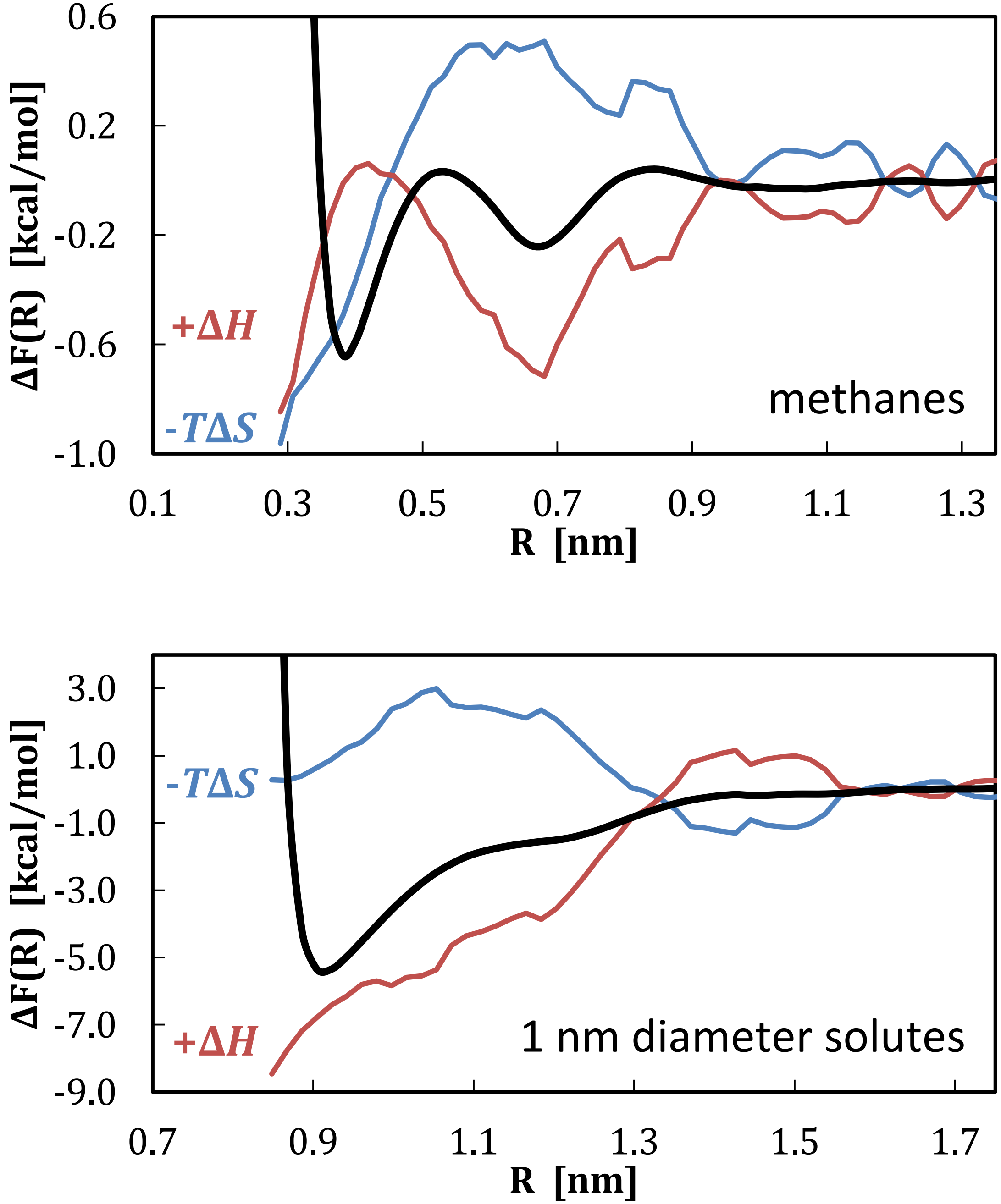


$$\Delta F(R; D, T)$$

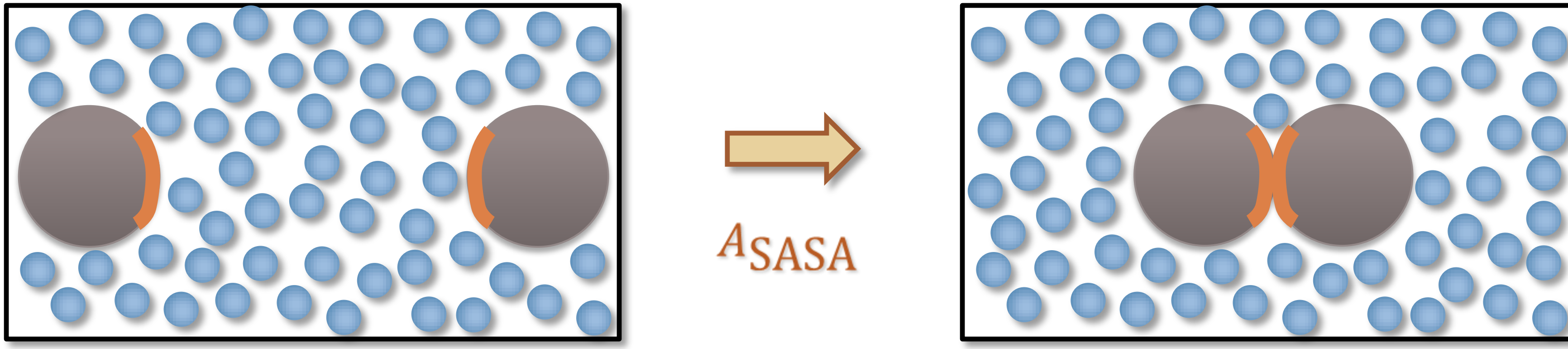




Hammer, Anderson, Chamovich, Shell, Israelachvili, Faraday Disc.(2010)

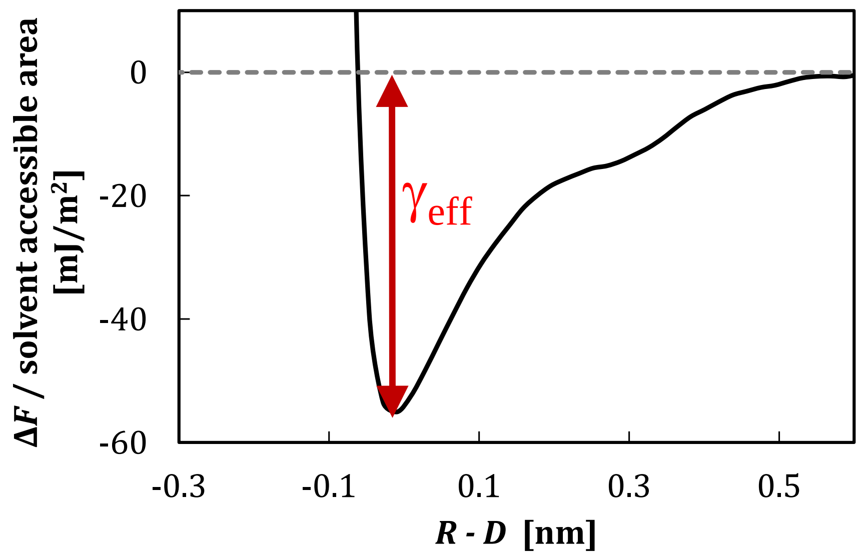


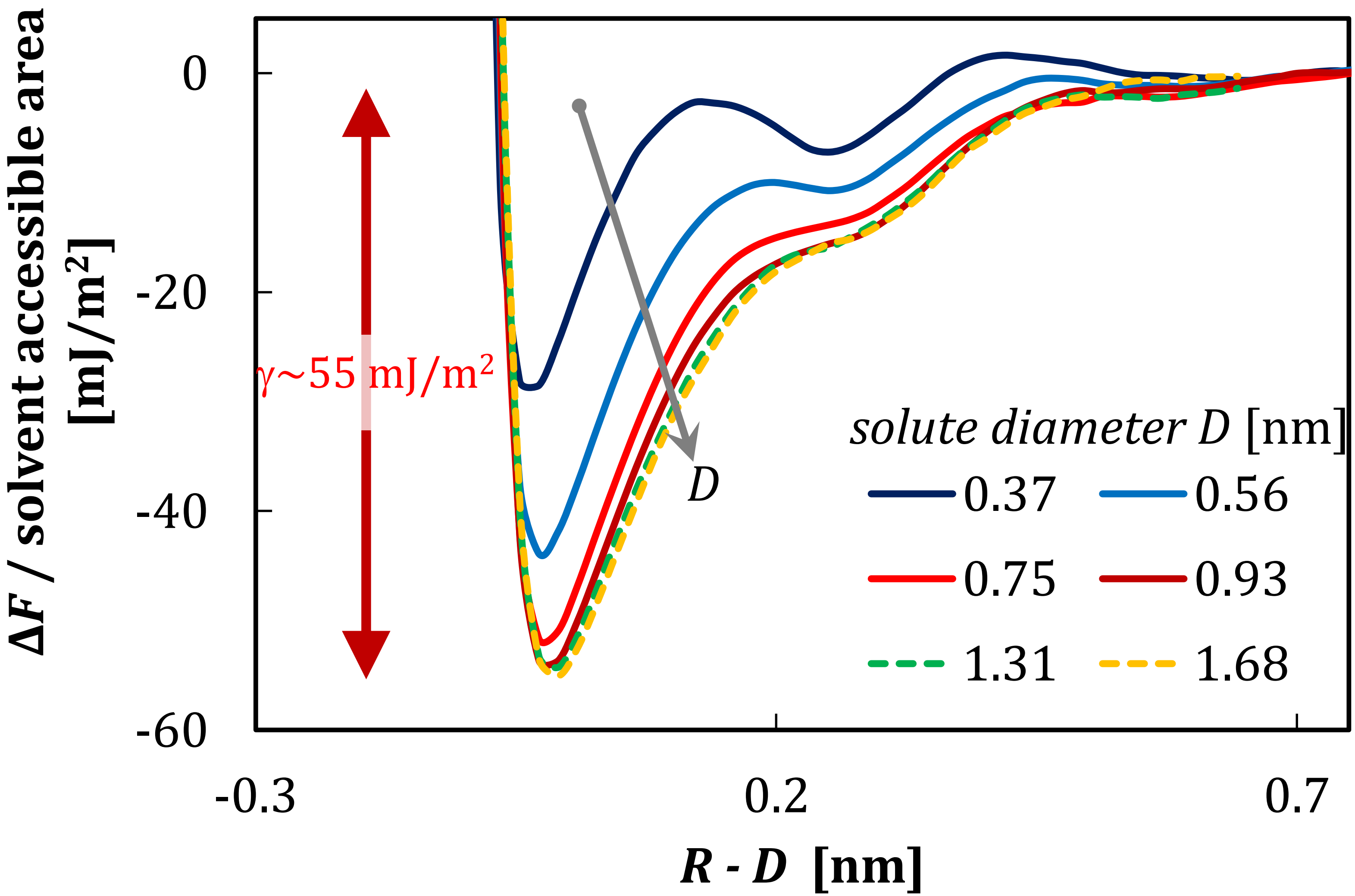
0.6
0.2
-0.2
-0.6
-1.0
ΔF(R) [kcal/mol]
+ΔH
-TΔS
methanes
0.1
0.3
0.5
0.7
0.9
1.1
1.3
R [nm]
3.0
1.0
-1.0
-3.0
-5.0
-7.0
-9.0
ΔF(R) [kcal/mol]
-TΔS
+ΔH
1 nm diameter solutes
0.7
0.9
1.1
1.3
1.5
1.7
R [nm]



large scale limit:

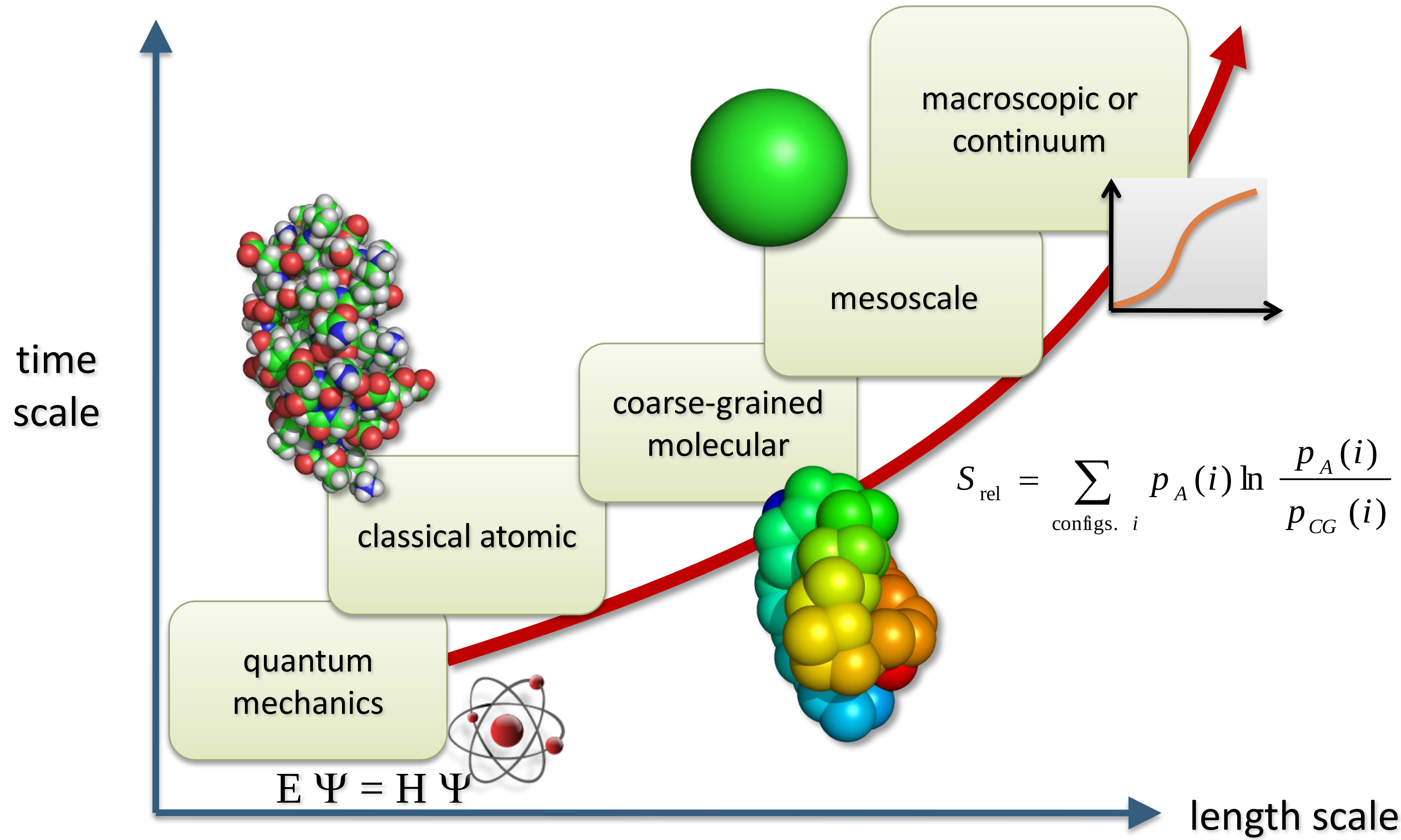
$$\gamma_{\mathrm{eff}} \sim \Delta F_{\mathrm{min}} / A_{\mathrm{SASA}}$$





experimental surface tensions for water-hydrocarbons ≈ 50 mJ/m²

Conclusions



The relative entropy provides a systematic strategy for moving to coarse-grained models and large-scale behavior.

Canonical ensemble

$$p(i) = \frac{e^{-\beta U(i)}}{Z}$$

$$S_{\text{rel}} = \sum_{\text{configs. } i} p_A(i) \ln \frac{p_A(i)}{p_{CG}(i)}$$

$$S_{rel} = \ln \left\langle e^{\Delta - \langle \Delta \rangle_A} \right\rangle_A \qquad \Delta \equiv \beta \left(U_A - U_{CG} \right)$$

$$S_{rel} = \beta \left\langle U_{CG} - U_A \right\rangle_A - \beta \left(A_{CG} - A_A \right)$$

optimize $U_{CG}(\mathbf{R}; \lambda_1, \lambda_2, \ldots)$

$$\frac{\partial S_{rel}}{\partial \lambda} = 0$$

$$\left\langle \frac{\partial U_{CG}}{\partial \lambda} \right\rangle_{CG} = \left\langle \frac{\partial U_{CG}}{\partial \lambda} \right\rangle_A$$

Variational mean field theory from S_{rel}

Canonical ensemble:

$$S_{rel} = \beta \langle U_{CG} - U_A \rangle_A - \beta (A_{CG} - A_A)$$

Positivity property:

$$S_{rel} \geq 0$$

Therefore:

$$A_{CG} \leq= A_A + \langle U_{CG} - U_A \rangle_A$$

Unconstrained S_{rel} minimization gives true PMFs

Canonical ensemble:

$$S_{rel} = \beta\left\langle U_{CG} - U_A \right\rangle_A - \beta\left(A_{CG} - A_A\right)$$

Minimization with unconstrained U_{CG}:

$$\frac{\delta S_{rel}}{\delta U_{CG}} = 0$$

Result:

$$e^{-\beta U_{CG}(\mathbf{R})} = \int e^{-\beta U_A(\mathbf{r})} \delta[\mathbf{R} - \mathbf{M}(\mathbf{r})] d\mathbf{r}$$
$$= e^{-\beta\, PMF_A(\mathbf{R})}$$

Connections of S_{rel} to other CG methods

Iterative Boltzmann inversion:

$$\frac{\delta S_{rel}}{\delta[u_{CG}(R_{ij})]} \Rightarrow g_{CG}(R) = g_A(R)$$

Force matching:

$$\frac{d}{dr}U_{CG}(r) = \frac{d}{dr}PMF_A(r) \Rightarrow f_{CG}(r) = \left\langle f_A(r) \right\rangle_A$$

Energy matching:

$$S_{rel} = \ln\left\langle e^{\Delta - \langle \Delta \rangle_A} \right\rangle_A = \left\langle \Delta^2 \right\rangle_A - \left\langle \Delta \right\rangle_A^2 + \text{higher order terms}$$

$$\Delta \equiv \beta\left(U_A - U_{CG}\right)$$