Hamiltonian Adaptive Resolution Simulations

Pep Español

UNED

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Work in collaboration

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April 2012 Kavli ITP at Santa Barbara

Coarse-Graining

Using fewer degrees of freedom to describe a system, but still retaining realism

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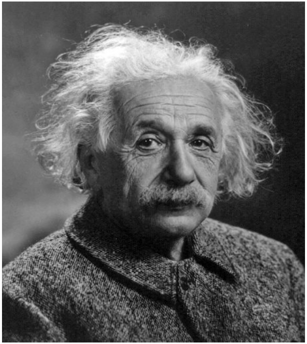

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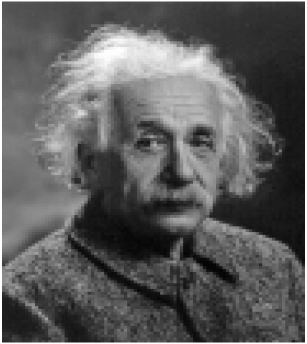

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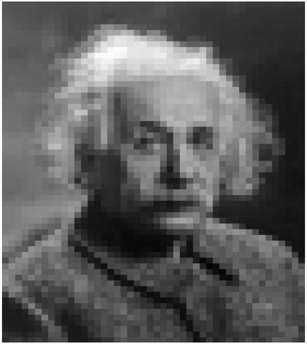

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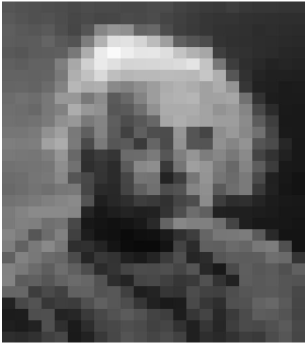

Two strategies for Coarse-Graining

- "Vertical" or "Bottom-up" CG: Construct CG models and obtain the parameters of the CG model through MD.

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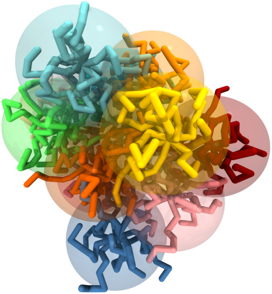
- "Vertical" or "Bottom-up" CG: Construct CG models and obtain the parameters of the CG model through MD.
- "Horizontal" or "parallel" CG: Hybrid schemes that couple CG models and MD. (Requires the former!)

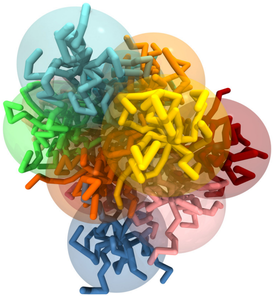
Bottom up Coarse-Graining



Example: Star polymer melt

Hijón, vanden Eijden, Delgado-Buscalioni, Español, Faraday Discuss **144**, 302 (2010)

Bottom up Coarse-Graining



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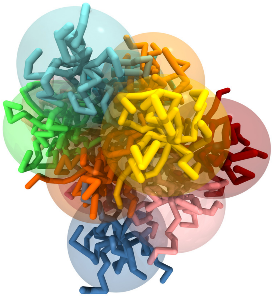

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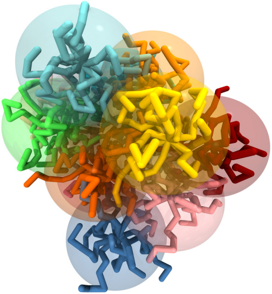

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Blob dynamics in star polymers

Dissipative Particle Dynamics but with microscopically defined parameters.

$$\begin{aligned} \partial_t \mathbf{R}_\mu &= \mathbf{V}_\mu \\ \partial_t \mathbf{P}_\mu &= -\frac{\partial V^{\text{eff}}}{\partial \mathbf{R}_\mu}(R) - \sum_\nu \gamma_{\mu\nu}(R)\mathbf{V}_{\mu\nu} + \tilde{\mathbf{F}}_\mu \end{aligned}$$

with

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\end{aligned}
$$

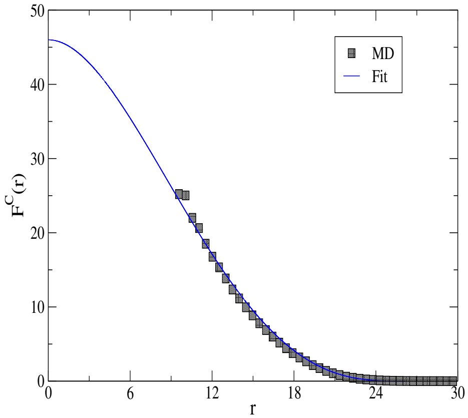
with

$$
V^{\text{eff}}(R) = -k_B T \ln \int dz \rho^{\text{eq}}(z)\delta(R(z) - R)
$$

$$
\gamma_{\mu\nu}(R) = \frac{1}{k_B T}\int_0^\infty dt \langle \delta \mathbf{F}_\mu \delta \mathbf{F}_\mu(t)\rangle^R
$$

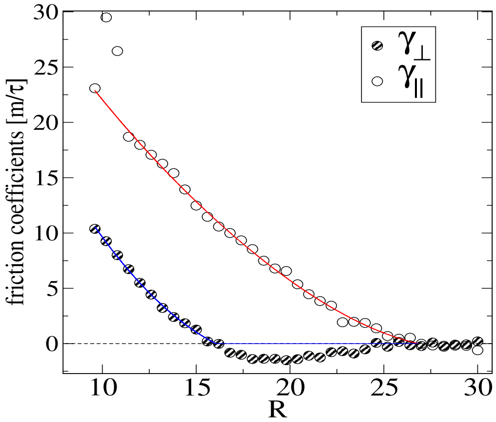
Blob dynamics in star polymers

The average force $\langle \mathbf{F}_{\mu\nu} \rangle^{R_{\mu\nu}}$



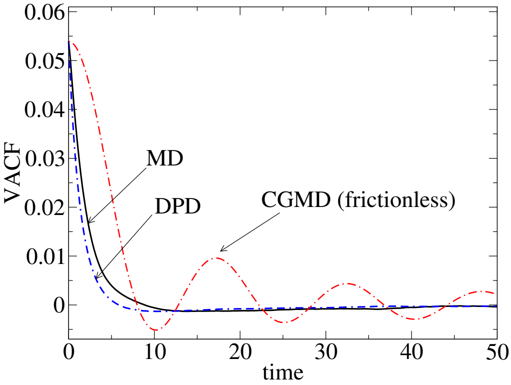
Blob dynamics in star polymers

The friction coefficient $\gamma(R_{\mu\nu}) = A(R_{\mu\nu})\mathbf{1} + B(R_{\mu\nu})\mathbf{e}_{\mu\nu}\mathbf{e}_{\mu\nu}$



Blob dynamics in star polymers

The velocity autocorrelation function of the CoM



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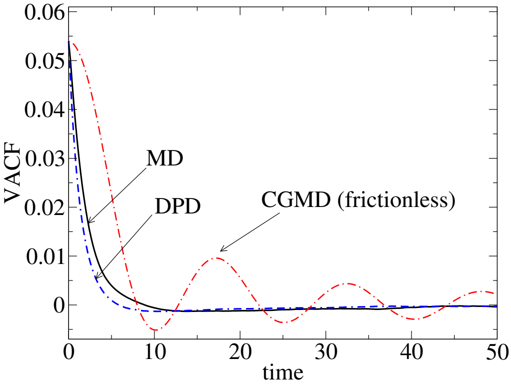
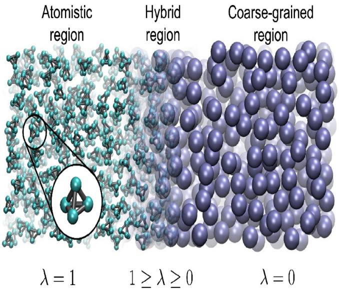


Friction is crucial for dynamic properties!

Adaptive Resolution



AdResS: resolution depends on the region

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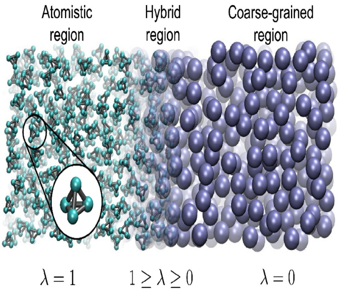

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Atomic detail where it is needed

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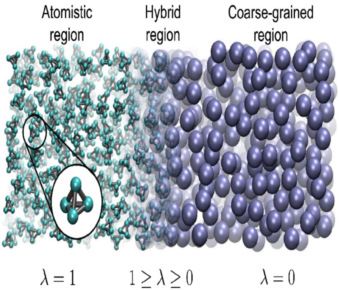

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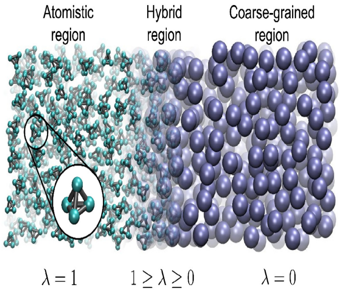

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M. Praprotnik, L. Delle Site, K. Kremer J.Chem.Phys. **123**, 224106 (2005), Ann.Rev.Phys.Chem. **59**, 545 (2008)

The microscopic model

The microscopic Hamiltonian

$$H^1(r,p) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \sum_\mu^M \left(V_\mu^{\mathrm{intra}}(r) + V_\mu^{\mathrm{inter}}(r) \right)$$

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$$V_\mu^{\text{intra}}(r) = \frac{1}{2} \sum_{i_\mu j_\mu}^{N} \phi^{\text{intra}}(r_{i_\mu j_\mu})$$

$$V_\mu^{\text{inter}}(r) = \frac{1}{2} \sum_{\nu \neq \mu}^{M} \sum_{i_\mu j_\nu}^{N} \phi^{\text{inter}}(r_{i_\mu j_\nu})$$

The CG model

CoM variables

$$\hat{\mathbf{R}}_\mu(r) = \sum_{i_\mu}^{N_\mu} \mathbf{r}_{i_\mu} \frac{m_{i_\mu}}{M_\mu} \qquad \hat{\mathbf{P}}_\mu(r) = \sum_{i_\mu}^{N_\mu} \mathbf{p}_{i_\mu} \qquad M_\mu = \sum_{i_\mu} m_{i_\mu}$$

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The potential of mean force

$$e^{-\beta V^{\mathrm{mf}}(R)} \equiv \int \frac{d^{3N}r}{\Lambda^{3N}} e^{-\beta\left[V^{\mathrm{intra}}(r)+V^{\mathrm{inter}}(r)\right]} \prod_\mu^M \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu)$$

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Many body potential!

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Many body potential!

Approximate $V^{\mathrm{mf}}(R) \approx \sum_\mu V^0_\mu(R) = \frac{1}{2}\sum_{\mu\nu}^M V^0(\hat{\mathbf{R}}_\mu - \hat{\mathbf{R}}_\nu)$

Matching the two models

In AA region

$$\dot{\mathbf{r}}_{i_\mu} = \frac{\mathbf{p}_{i_\mu}}{m_{i_\mu}}$$

$$\dot{\mathbf{p}}_{i_\mu} = -\frac{\partial V_\mu^{\mathrm{intra}}}{\partial \mathbf{r}_{i_\mu}} - \sum_\nu^M \frac{\partial V_\nu^1}{\partial \mathbf{r}_{i_\mu}}$$

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The CoM of the blobs move with a CG pair potential $V^0(R)$ that approximates $V^{\mathrm{mf}}(R)$.

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$$\dot{\mathbf{R}}_\mu = \frac{\mathbf{P}_\mu}{m_\mu}$$

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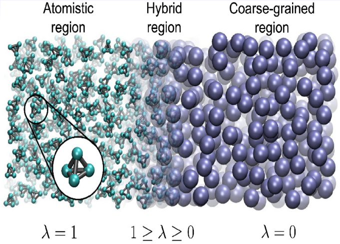
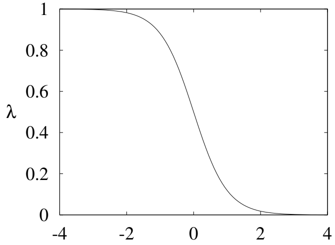
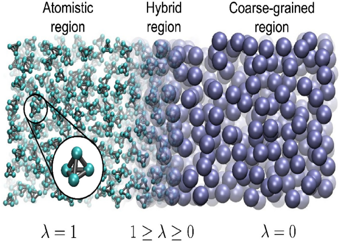
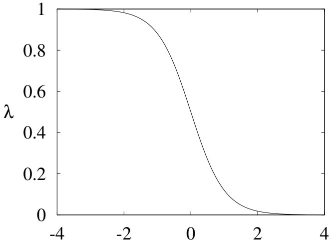
H-AdResS


Atomistic region
Hybrid region
Coarse-grained region
$\lambda = 1$
$1 \geq \lambda \geq 0$
$\lambda = 0$


λ
1
0.8
0.6
0.4
0.2
0
-4
-2
0
2
4

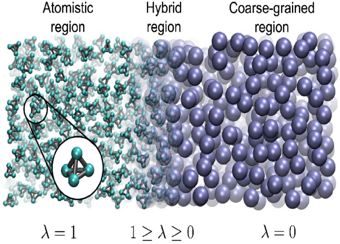
H-AdResS

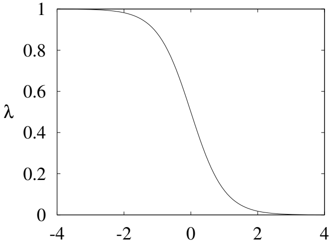




$$H_{[\lambda]}(r,p) = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} + \sum_\mu^M V_\mu^{\text{intra}}(r)$$

H-AdResS

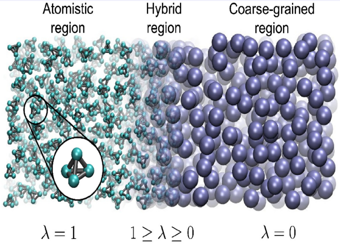


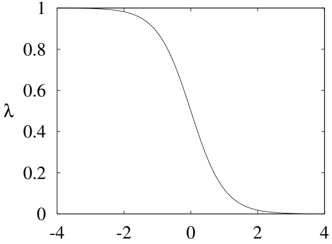


$$H_{[\lambda]}(r,p) = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} + \sum_\mu^M V_\mu^{\text{intra}}(r)$$

$$+ \sum_\mu^M \lambda(\hat{\mathbf{R}}_\mu) V_\mu^1(r) + \sum_\mu^M (1 - \lambda(\hat{\mathbf{R}}_\mu)) V_\mu^0(R)$$

H-AdResS





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The equations of motion

$$\dot{\mathbf{r}}_{i_\mu} = \frac{\mathbf{p}_{i_\mu}}{m_{i_\mu}}$$

$$\dot{\mathbf{p}}_{i_\mu} = -\frac{\partial V_\mu^{\mathrm{intra}}}{\partial \mathbf{r}_{i_\mu}} - \sum_\nu^M \lambda(\hat{\mathbf{R}}_\nu)\frac{\partial V_\nu^1}{\partial \mathbf{r}_{i_\mu}} - \sum_\nu^M (1-\lambda(\hat{\mathbf{R}}_\nu))\frac{\partial V_\nu^0}{\partial \mathbf{r}_{i_\mu}}$$

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$$- \nabla\lambda(\mathbf{R}_\mu)\frac{m_{i_\mu}}{m_\mu}\left(V_\mu^1 - V_\mu^0 + \Delta\mathcal{F}'(\lambda(\hat{\mathbf{R}}_\mu))\right)$$

Free energies

$$F_{[\lambda]} = -k_B T \ln \int \frac{d^{3N} r}{\Lambda^{3N}} \exp\left\{-\beta V_{[\lambda]}(r)\right\}$$

$$F_{[\lambda]} = -k_B T \ln \int \frac{d^{3M} R}{\Lambda_0^{3M}} \exp\left\{-\beta \left[\sum_{\mu}^{M} (1-\lambda(\mathbf{R}_\mu)) V_\mu^0(R) + V_{[\lambda]}^{\mathrm{mf}}(R) + \sum_{\mu}^{M} \Delta\mathcal{F}(\lambda(\mathbf{R}_\mu))\right]\right\}$$

$$V_{[\lambda]}^{\mathrm{mf}}(R) \equiv -k_B T \ln \int \frac{d^{3N} r}{\Lambda^{3N}} \exp\left\{-\beta \left[V^{\mathrm{intra}}(r) + \sum_{\mu}^{M} \lambda(\mathbf{R}_\mu) V_\mu^1(r)\right]\right\} \Lambda_0^{3M} \prod_{\mu}^{M} \delta(\mathbf{R}_\mu - \hat{\mathbf{R}}_\mu)$$

Free energies

At constant $\lambda(\mathbf{r}) = 0, 1$

$$F_{[1]} = -k_B T \ln \int \frac{d^{3M}R}{\Lambda_0^{3M}} \exp\left\{-\beta V_{[1]}^{\mathrm{mf}}(R)\right\}$$

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Thermodynamic consistency

$$F_{[0]} = F_{[1]}$$

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Thermodynamic consistency

$$F_{[0]} = F_{[1]}$$

$\Delta\mathcal{F}$ corrects errors of using $V^0(R)$ instead of $V_{[1]}^{\mathrm{mf}}(R)$.

Equations of state: The temperature

The kinetic energy density field is

$$k_{\mathbf{r}} \equiv \sum_{\mu}^{M} \frac{m_\mu}{2} \mathbf{V}_\mu^2 \delta(\mathbf{r} - \mathbf{R}_\mu)$$

with average

$$\langle k_{\mathbf{r}} \rangle^{[\lambda]} = \frac{3k_B T}{2} \langle n_{\mathbf{r}} \rangle^{[\lambda]}$$

The temperature field

$$k_B T(\mathbf{r}) \equiv \frac{2}{3} \frac{\langle k_{\mathbf{r}} \rangle^{[\lambda]}}{\langle n_{\mathbf{r}} \rangle^{[\lambda]}} = k_B T$$

Equations of state: The pressure

Consider the momentum density field

$$\hat{\mathbf{g}}_{\mathbf{r}}(z) \equiv \sum_{\mu}^{M} \hat{\mathbf{P}}_{\mu} \delta(\hat{\mathbf{R}}_{\mu} - \mathbf{r}) \qquad iL\hat{\mathbf{g}}_{\mathbf{r}} = -\nabla \hat{\boldsymbol{\Sigma}}_{\mathbf{r}} - \frac{\delta H^{[\lambda]}}{\delta \lambda(\mathbf{r})} \nabla \lambda(\mathbf{r})$$

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Irwing-Kirkwood stress tensor

$$\hat{\mathbf{\Sigma}}_{\mathbf{r}} = \sum_{\mu}^{M} \hat{\mathbf{P}}_{\mu}\hat{\mathbf{V}}_{\mu}\delta(\hat{\mathbf{R}}_{\mu} - \mathbf{r}) + \frac{1}{2}\sum_{\mu\nu}\hat{\mathbf{G}}_{\mu\nu}\mathbf{R}_{\mu\nu}\int_0^1 d\epsilon\delta(\mathbf{R}_{\nu} + \epsilon\mathbf{R}_{\mu\nu} - \mathbf{r})$$

$$\hat{\mathbf{G}}_{\mu\nu} \equiv \left[\frac{\lambda(\hat{\mathbf{R}}_{\mu}) + \lambda(\hat{\mathbf{R}}_{\nu})}{2}\right]\mathbf{F}^{1}_{\mu\nu}(R_{\mu\nu}) + \left[1 - \frac{\lambda(\hat{\mathbf{R}}_{\mu}) + \lambda(\hat{\mathbf{R}}_{\nu})}{2}\right]\mathbf{F}^{0}_{\mu\nu}(R_{\mu\nu})$$

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$$\frac{\delta H_{[\lambda]}}{\delta\lambda(\mathbf{r})} = u^1_{\mathbf{r}} - u^0_{\mathbf{r}} + \Delta\mathcal{F}'(\lambda(\mathbf{r}))n_{\mathbf{r}}$$

where

$$u^1_{\mathbf{r}} \equiv \sum_{\mu}^{M} V^1_{\mu}\delta(\hat{\mathbf{R}}_{\mu} - \mathbf{r})$$

$$u^0_{\mathbf{r}} \equiv \sum_{\mu}^{M} V^0_{\mu}\delta(\hat{\mathbf{R}}_{\mu} - \mathbf{r})$$

$$n_{\mathbf{r}} \equiv \sum_{\mu}^{M} \delta(\hat{\mathbf{R}}_{\mu} - \mathbf{r})$$

Equations of state: The pressure

The average gives the condition of mechanical equilibrium

$$\langle iL\hat{\mathbf{g}}_{\mathbf{r}}\rangle^{[\lambda]} = -\nabla \left\langle \hat{\mathbf{\Sigma}}_{\mathbf{r}} \right\rangle^{[\lambda]} - \left\langle \frac{\delta H^{[\lambda]}}{\delta \lambda(\mathbf{r})} \right\rangle^{[\lambda]} \nabla \lambda(\mathbf{r})$$

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Crucial relation that allows to specify the free energy compensation term $\Delta\mathcal{F}(\lambda)$.

UNED

The compensating term

$$\nabla \mathbf{\Sigma}(\mathbf{r}) = k_B T \nabla n(\mathbf{r}) + \nabla \mathbf{\Pi}(\mathbf{r}) = -\left\langle u^1_{\mathbf{r}} - u^0_{\mathbf{r}} \right\rangle^{[\lambda]} - \Delta \mathcal{F}'(\lambda(\mathbf{r})) \left\langle n_{\mathbf{r}} \right\rangle^{[\lambda]}$$

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Constant stress

$$\Delta \mathcal{F}'(\lambda(\mathbf{r})) = -\frac{\left\langle u_{\mathbf{r}}^1 - u_{\mathbf{r}}^0 \right\rangle^{[\lambda]}}{\left\langle n_{\mathbf{r}} \right\rangle^{[\lambda]}}$$

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Constant stress

$$\Delta \mathcal{F}'_{n+1}(\lambda(\mathbf{r})) = -\frac{\left\langle u^1_{\mathbf{r}} - u^0_{\mathbf{r}} \right\rangle^{[\lambda, \Delta \mathcal{F}_n]}}{\left\langle n_{\mathbf{r}} \right\rangle^{[\lambda, \Delta \mathcal{F}_n]}}$$

The compensating term

$$\nabla \boldsymbol{\Sigma}(\mathbf{r}) = k_B T \nabla n(\mathbf{r}) + \nabla \boldsymbol{\Pi}(\mathbf{r}) = - \left\langle u^1_{\mathbf{r}} - u^0_{\mathbf{r}} \right\rangle^{[\lambda]} - \Delta \mathcal{F}'(\lambda(\mathbf{r})) \left\langle n_{\mathbf{r}} \right\rangle^{[\lambda]}$$

Constant density

$$\Delta \mathcal{F}'(\lambda(\mathbf{r})) = - \frac{\nabla \boldsymbol{\Pi}(\mathbf{r}) + \left\langle u^1_{\mathbf{r}} - u^0_{\mathbf{r}} \right\rangle^{[\lambda]}}{\left\langle n_{\mathbf{r}} \right\rangle^{[\lambda]}}$$

The compensating term **without** iterations

$$\nabla \mathbf{\Sigma}(\mathbf{r}) = k_B T \nabla n(\mathbf{r}) + \nabla \mathbf{\Pi}(\mathbf{r}) = -\left\langle u^1_{\mathbf{r}} - u^0_{\mathbf{r}} \right\rangle^{[\lambda]} - \Delta \mathcal{F}'(\lambda(\mathbf{r})) \left\langle n_{\mathbf{r}} \right\rangle^{[\lambda]}$$

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Assume local equilibrium: Constant stress

$$\left\langle n_{\mathbf{r}} \right\rangle^{[\lambda]} \Delta \mathcal{F}'(\lambda(\mathbf{r})) = -\left\langle u_{\mathbf{r}}^1 - u_{\mathbf{r}}^0 \right\rangle^{\lambda=\lambda(\mathbf{r})}$$

The compensating term **without** iterations

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Assume local equilibrium: Constant stress

$$M \Delta \mathcal{F}'(\lambda) = -\left\langle U^1 - U^0 \right\rangle^{\lambda}$$

The compensating term **without** iterations

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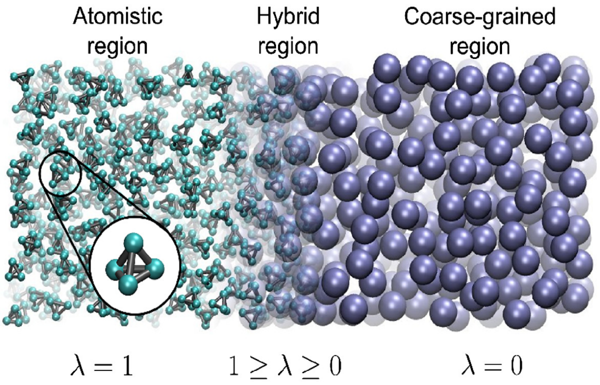
Kirkwood Thermodynamic Integration

$$\Delta\mathcal{F}(\lambda) = -\frac{1}{M}\int_0^{\lambda} d\lambda' \left\langle \frac{\partial U}{\partial \lambda'} \right\rangle^{\lambda'}$$

$$U \equiv \lambda U^1 + (1-\lambda)U^0$$

Results

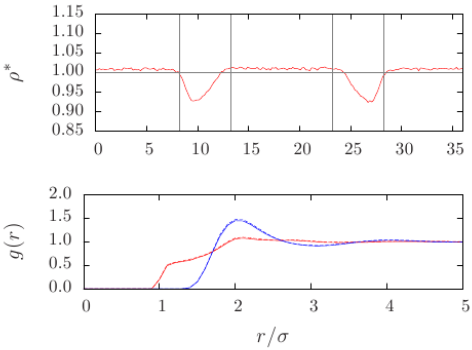
Potestio *et al.* Phys.Rev.Lett. **110**, 108301 (2013)



Results

Potestio *et al.* Phys.Rev.Lett. **110**, 108301 (2013)

If we use Boltzman inversion to get the CG potential



Results

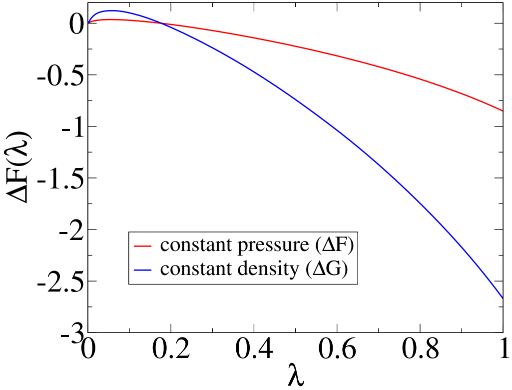
Density inhomogeneities are due to correlations in the hybrid zone

$$\langle n_{\mathbf{r}} \rangle^{[T_{\mathbf{a}}\lambda]} = \langle n_{\mathbf{r}+\mathbf{a}} \rangle^{[\lambda]}$$

$$\nabla \langle n_{\mathbf{r}} \rangle^{[\lambda]} = -\beta \int d\mathbf{r}' \left\langle \delta n_{\mathbf{r}} (u^1_{\mathbf{r}'} - u^0_{\mathbf{r}'} + \mathcal{F}'(\lambda(\mathbf{r}')) n_{\mathbf{r}'}) \right\rangle^{[\lambda]} \nabla' \lambda(\mathbf{r}')$$

Results

If we use a bad CG potential



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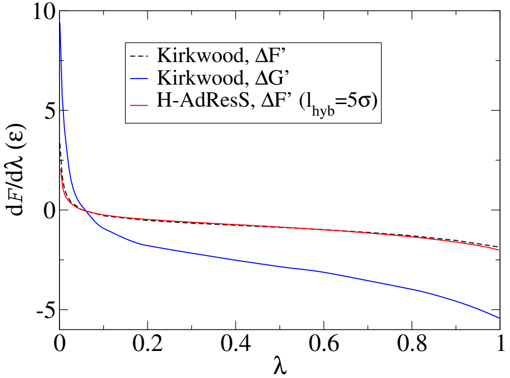

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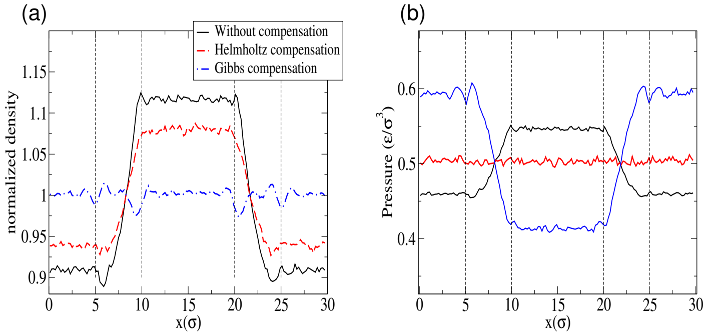
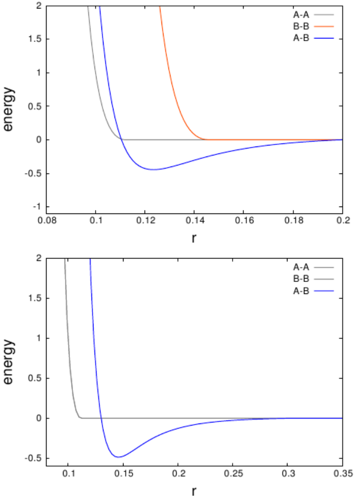


Results: Mixtures

Potestio *et al.* Phys.Rev.Lett. **111**, 060601 (2013)



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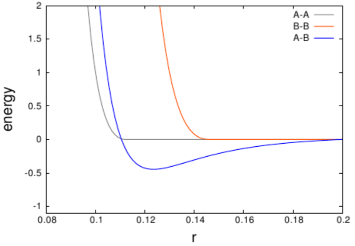
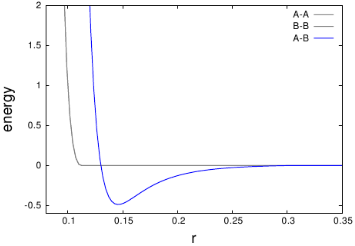
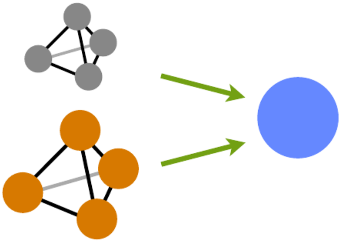
Potestio *et al.* Phys.Rev.Lett. **111**, 060601 (2013)







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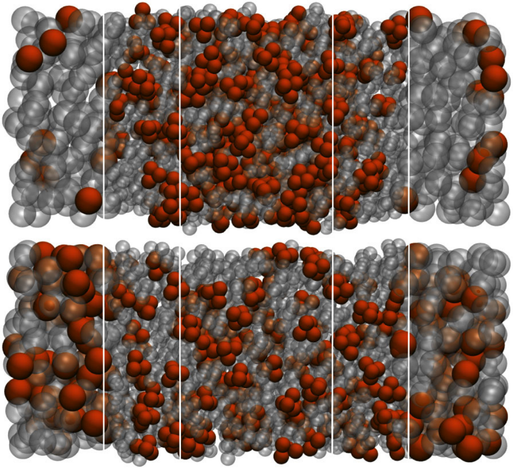

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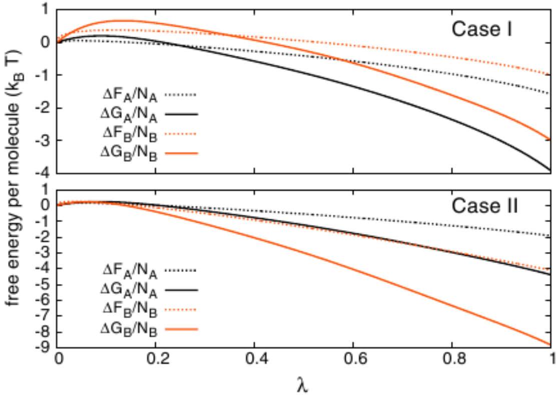
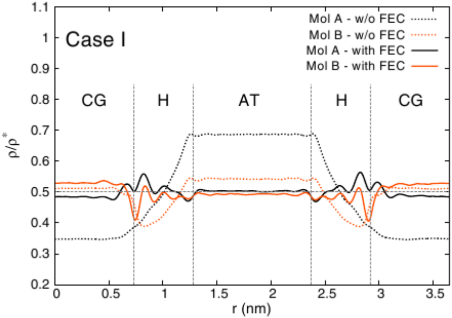


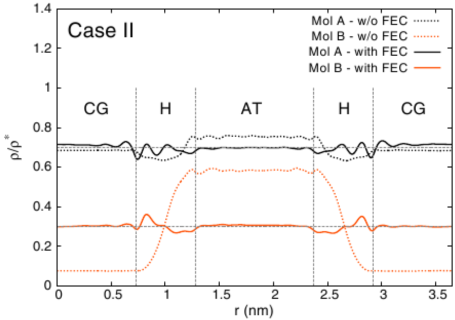
Results: Mixtures

Case I: Different size molecules, equal concentrations

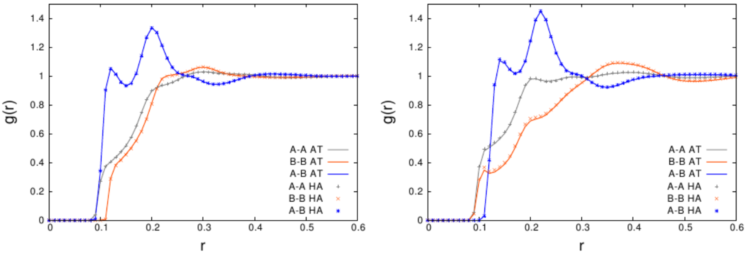


Results: Mixtures

Case II: Equal size molecules, 70 %-30 %

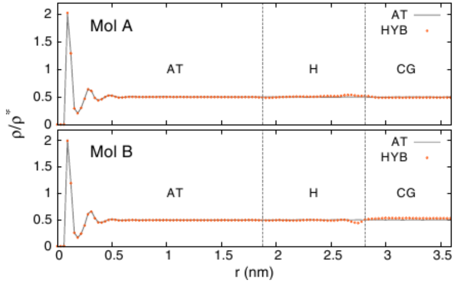


Results: Mixtures



Results: Mixtures

Density structure near a wall



Conclusion

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