Coarse-graining using the relative entropy method in VOTCA

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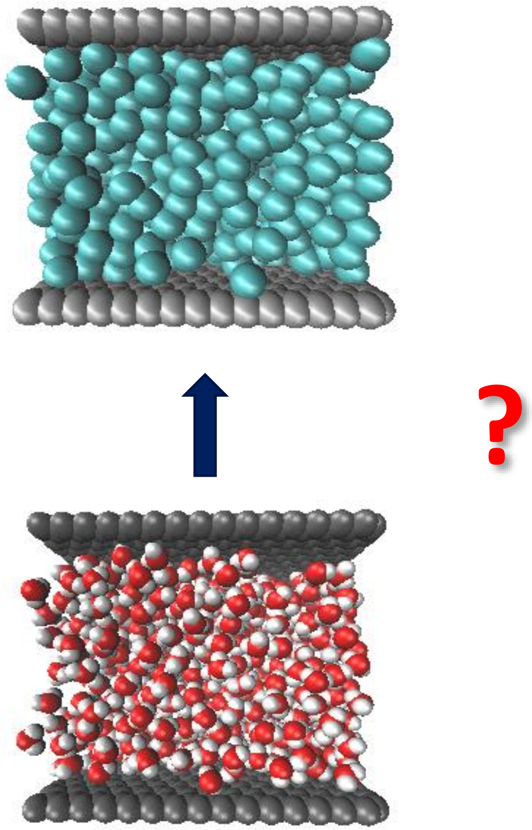
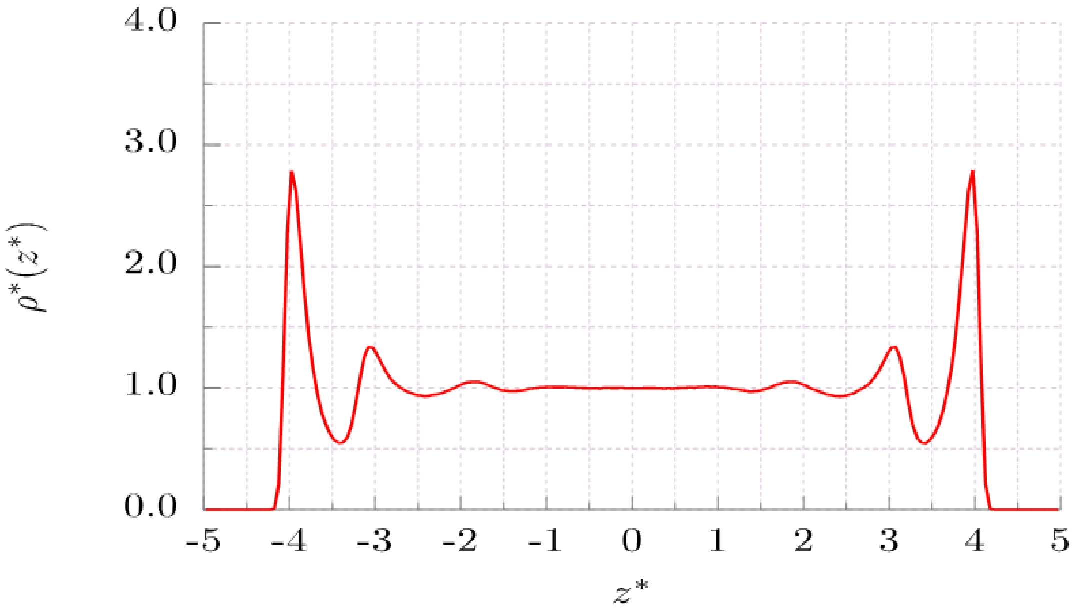
Coarse-grained model to predict the structure of confined water





Relative entropy is a generic systematic CG method. It can be used effectively to optimize structure-based CG potentials.

What is the goal of the systematic coarse-graining?

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What is relative entropy? And how it is useful for systematic coarse-graining?

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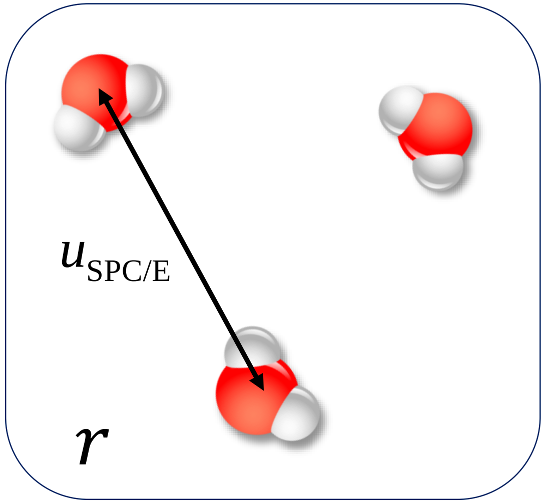
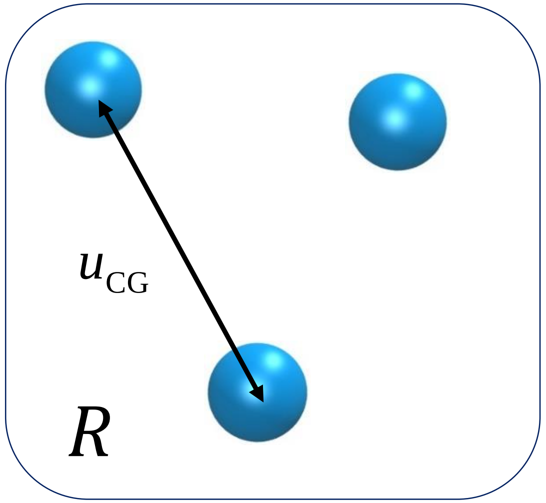
Examples of coarse-graining by relative entropy in VOTCA.

Main objective of systematic coarse-graining is to mimic finer-level system.



COM Mapping

$$R = M(r)$$

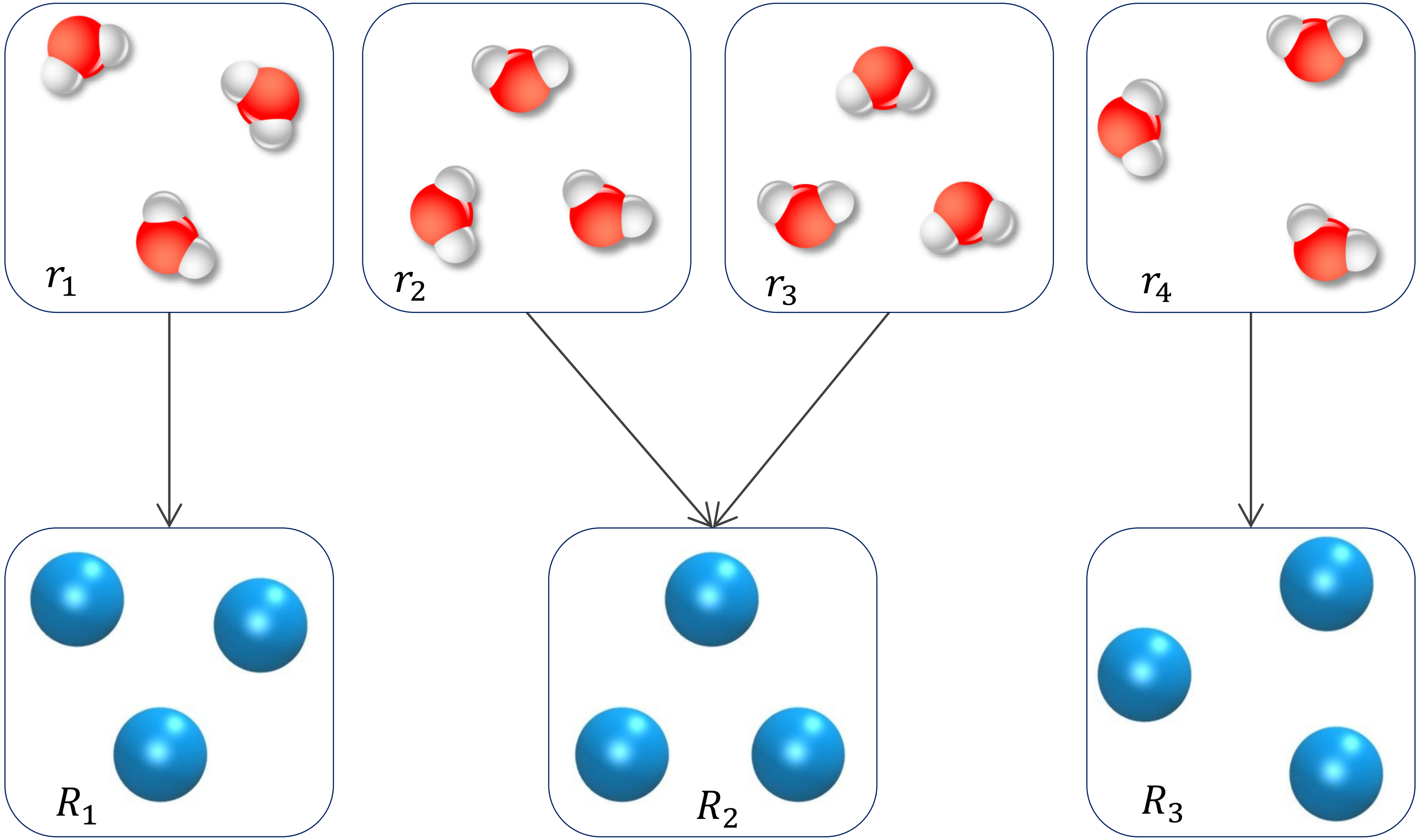


AA

CG

CG should mimic AA

$$P_{\mathrm{AA}}\left(M(r)\right) = P_{\mathrm{CG}}\left(R\right)$$



$$P_{\mathrm{AA}}\left(M\left(r\right)\right)=P_{\mathrm{CG}}\left(R\right)$$

$$\left\langle \alpha\left(M\left(r\right)\right)\right\rangle_{\mathrm{AA}}=\left\langle \alpha\left(R\right)\right\rangle_{\mathrm{CG}}$$

Relative entropy is a metric of an error between AA and CG configurational probabilities.

$$S_{\mathrm{rel}} = \sum_i p_{\mathrm{AA}}(r_i) \ln\left(\frac{p_{\mathrm{AA}}(r_i)}{p_{\mathrm{CG}}\left(M(r_i)\right)} \right) + S_{\mathrm{map}}$$

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

In canonical ensemble

$$S_{\mathrm{rel}} = \beta \langle U_{\mathrm{CG}} - U_{\mathrm{AA}} \rangle_{\mathrm{AA}} - \beta (A_{\mathrm{CG}} - A_{\mathrm{AA}}) + S_{\mathrm{map}}$$

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

Minimize relative entropy to optimize CG potentials.

CG interaction function: $$u_{\text{CG}}\left(\lambda_1,\lambda_2,\ldots,\lambda_n\right)$$

Minimize S_{rel}: $$\frac{\partial S_{\text{rel}}}{\partial \boldsymbol{\lambda}}=0$$

Newton-Raphson update: $$\boldsymbol{\lambda}^{k+1}=\boldsymbol{\lambda}^{k}-\chi\mathbf{H}^{-1}\cdot\nabla_{\lambda}S_{\text{rel}}$$

Evaluation of $\boldsymbol{H}$ and ∇S_{rel} requires only the derivatives of U_{CG} w. r. t. $\boldsymbol{\lambda}$

$$\nabla_\lambda S_{\mathrm{rel}} = \beta \left\langle \frac{\partial U_{\mathrm{CG}}}{\partial \lambda} \right\rangle_{\mathrm{AA}} - \beta \left\langle \frac{\partial U_{\mathrm{CG}}}{\partial \lambda} \right\rangle_{\mathrm{CG}}$$

$$H_{ij} = \beta \left\langle \frac{\partial^2 U_{\mathrm{CG}}}{\partial \lambda_i \partial \lambda_j} \right\rangle_{\mathrm{AA}} - \beta \left\langle \frac{\partial^2 U_{\mathrm{CG}}}{\partial \lambda_i \partial \lambda_j} \right\rangle_{\mathrm{CG}} + \beta^2 \left\langle \frac{\partial U_{\mathrm{CG}}}{\partial \lambda_i} \frac{\partial U_{\mathrm{CG}}}{\partial \lambda_j} \right\rangle_{\mathrm{CG}} - \beta^2 \left\langle \frac{\partial U_{\mathrm{CG}}}{\partial \lambda_i} \right\rangle_{\mathrm{CG}} \left\langle \frac{\partial U_{\mathrm{CG}}}{\partial \lambda_j} \right\rangle_{\mathrm{CG}}$$

Equivalence of relative entropy minimization with other coarse-graining system:

Structure: IBI / IMC

$$\frac{\delta S_{\text{rel}}}{\delta u_{\text{CG, pair}}(R)} = 0$$

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

Forces: FM

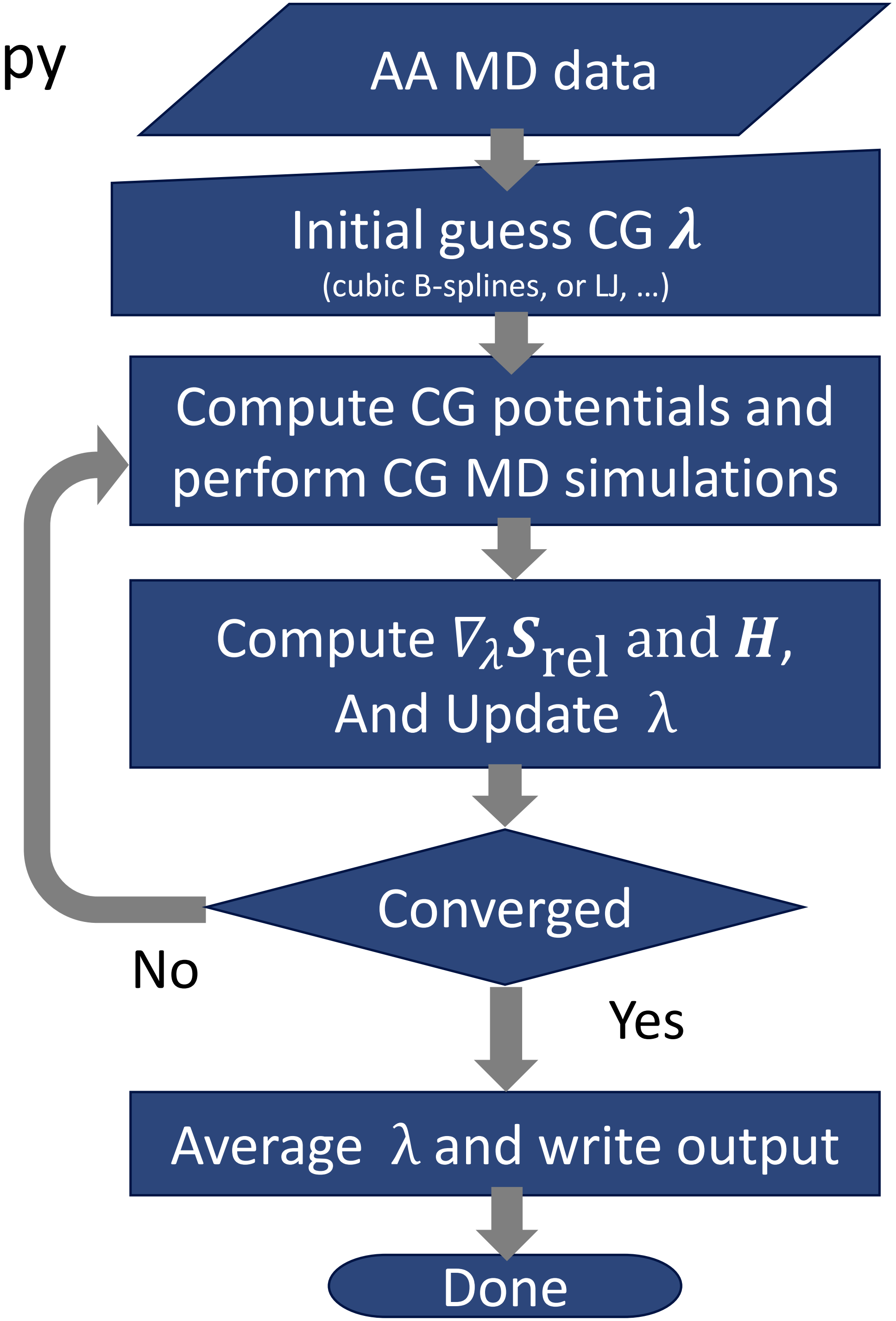
$$\frac{\delta S_{\text{rel}}}{\delta U_{\text{CG}}} = 0$$

$$U_{\text{CG}} = \text{PMF}_{\text{AA}}$$

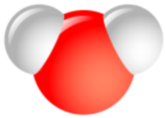
$$\langle f \rangle_{\text{AA}} = f_{\text{CG}}$$

Chaimovich and Shell, JCP (2011); Rudzinski and Noid, JCP (2011)

Algorithm: Relative entropy minimization in VOTCA



Coarse-graining SPC/E bulk water:



All Atom
SPC/E

Coarse-grained
Cubic B-Splines

$$T = 300\ \mathrm{K}$$

$$\rho = 1.0\ \mathrm{g/cm^3}$$

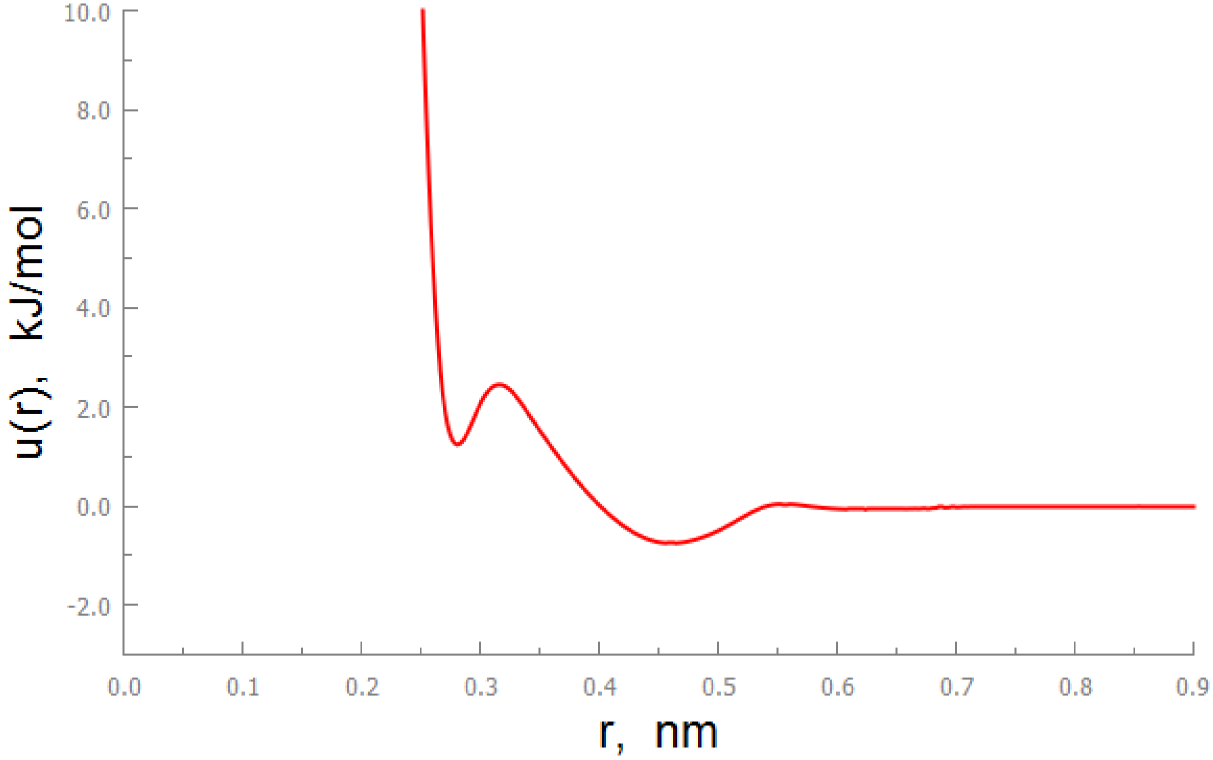
$$r_{\mathrm{cut}} = 0.9\ \mathrm{nm}$$

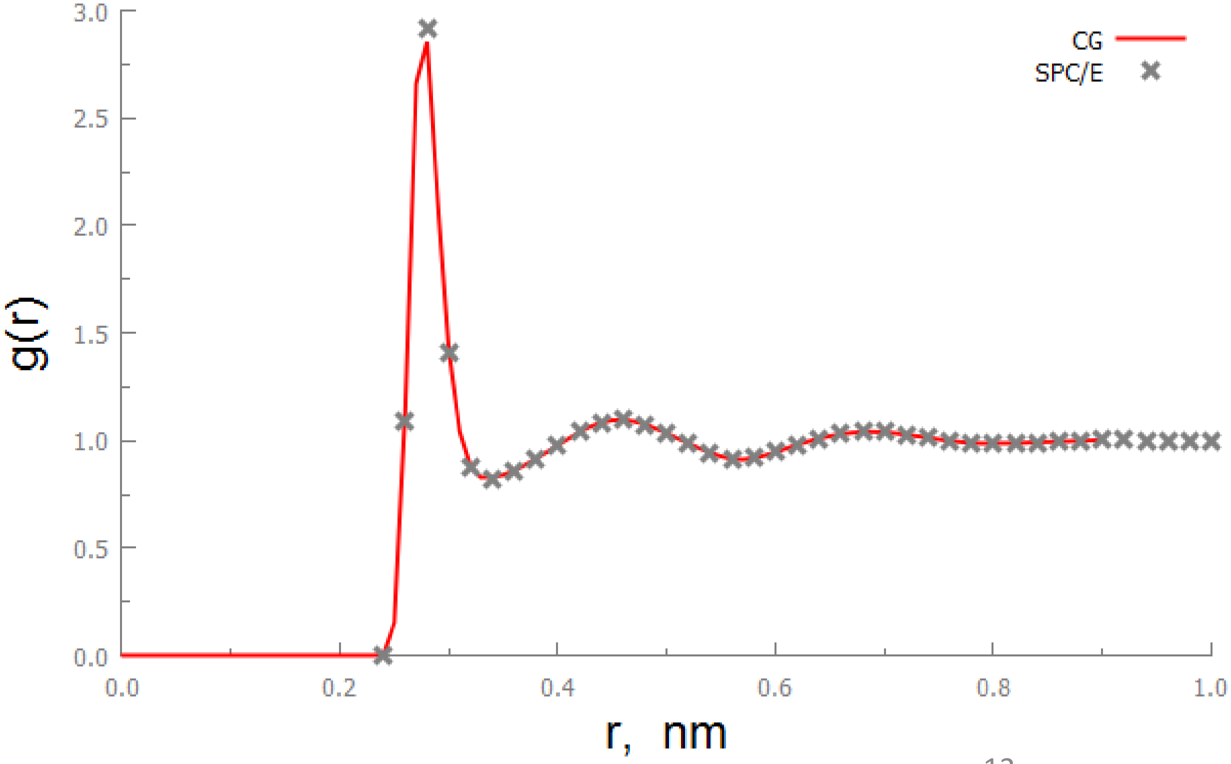
$$\Delta r = 0.02\ \mathrm{nm}$$

Coarse-graining SPC/E bulk water:

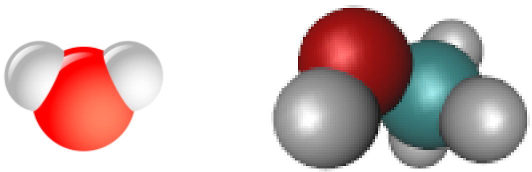
All Atom
SPC/E

Coarse-grained
Cubic B-Splines





Coarse-graining water-methanol mixture:



SPC/E water + OPLS methanol

CG water + CG methanol

	I	II	III
number of H_2O	3752	2000	248
number of MeOH	248	2000	3752
X_m	0.062	0.5	0.938
ρ g/cm^3	0.97	0.885	0.80

ME-ME:

$r_{cut} = 1.32$, $\Delta r = 0.02$ nm

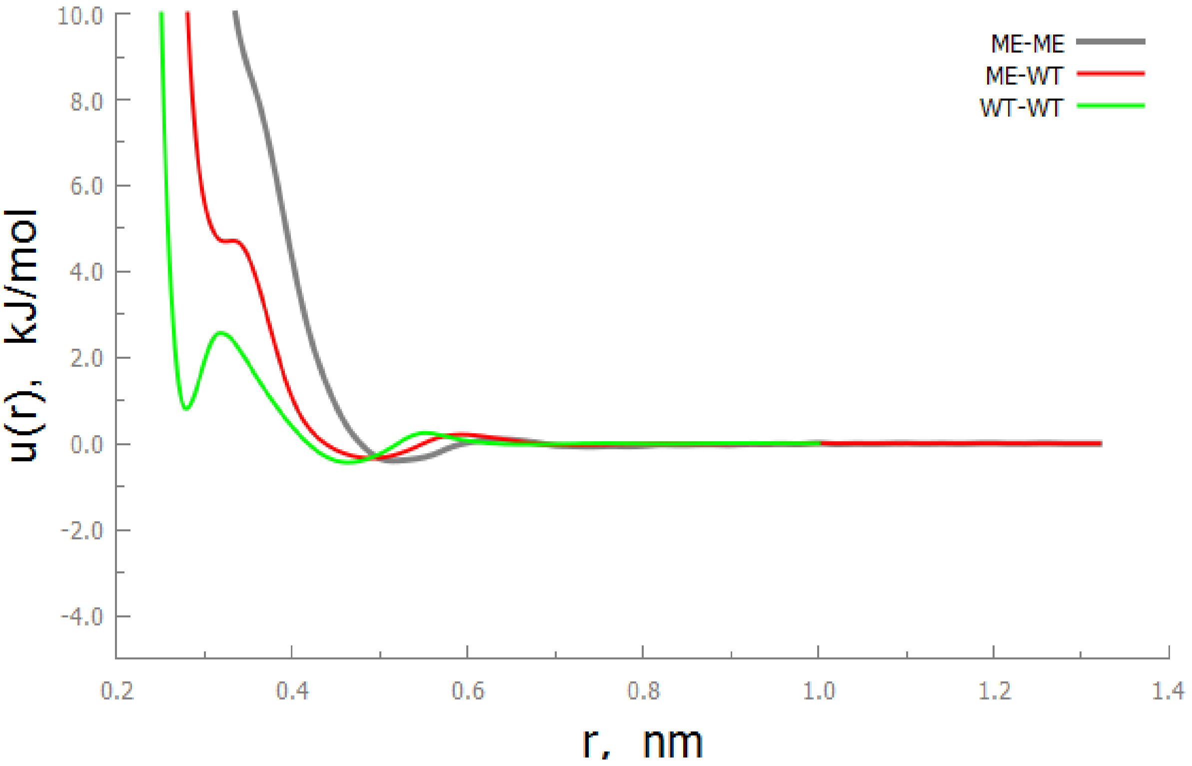
ME-WT:

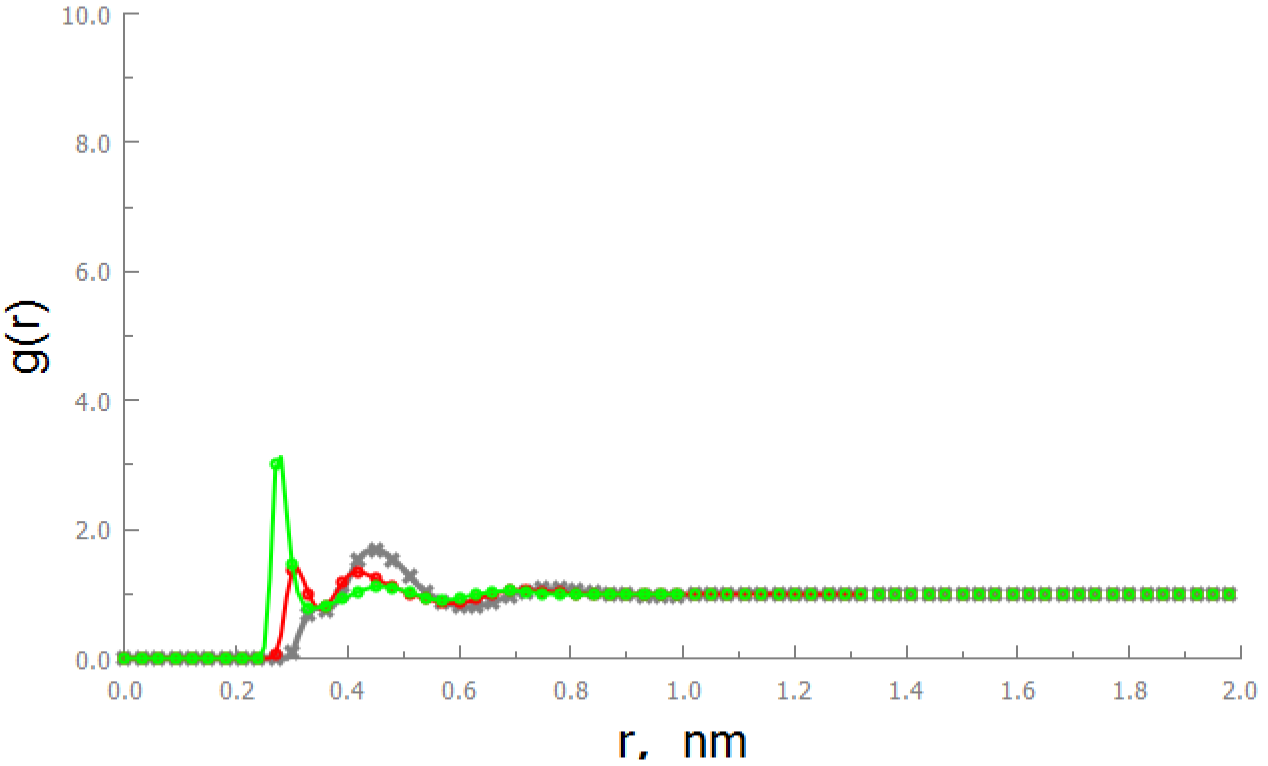
$r_{cut} = 1.32$, $\Delta r = 0.02$ nm

WT-WT:

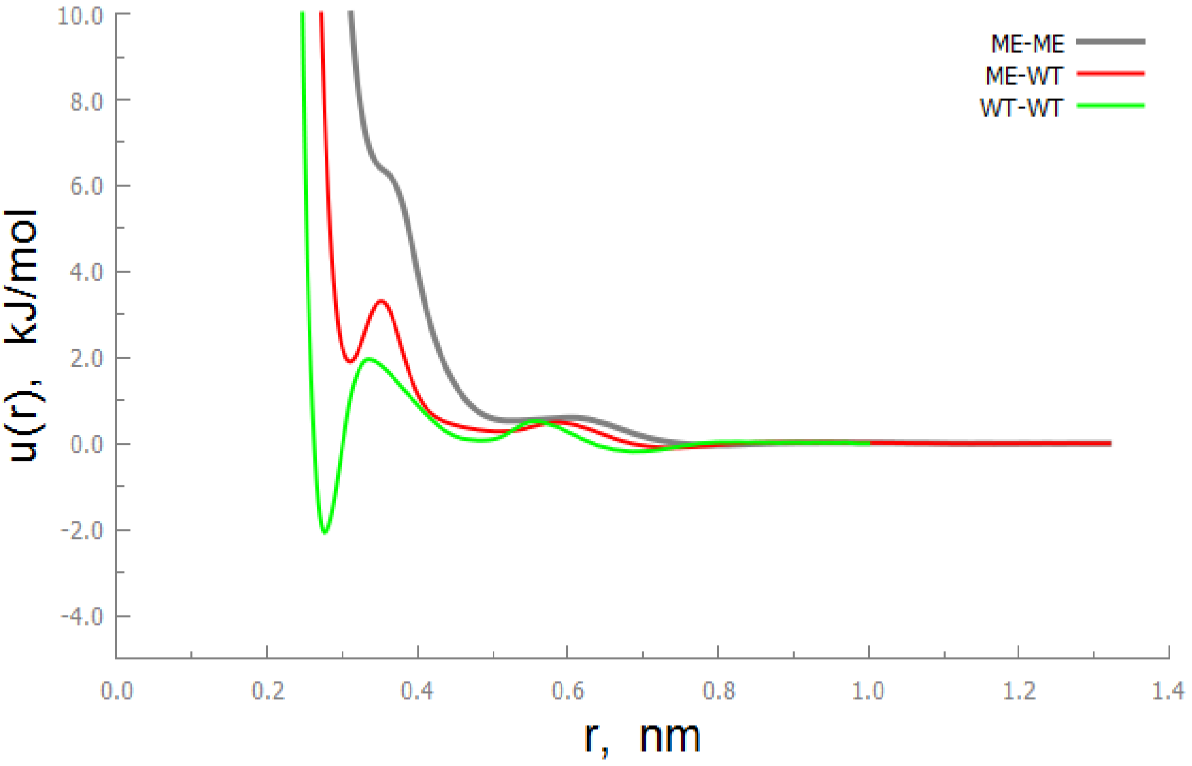
$r_{cut} = 1.00$, $\Delta r = 0.01$ nm

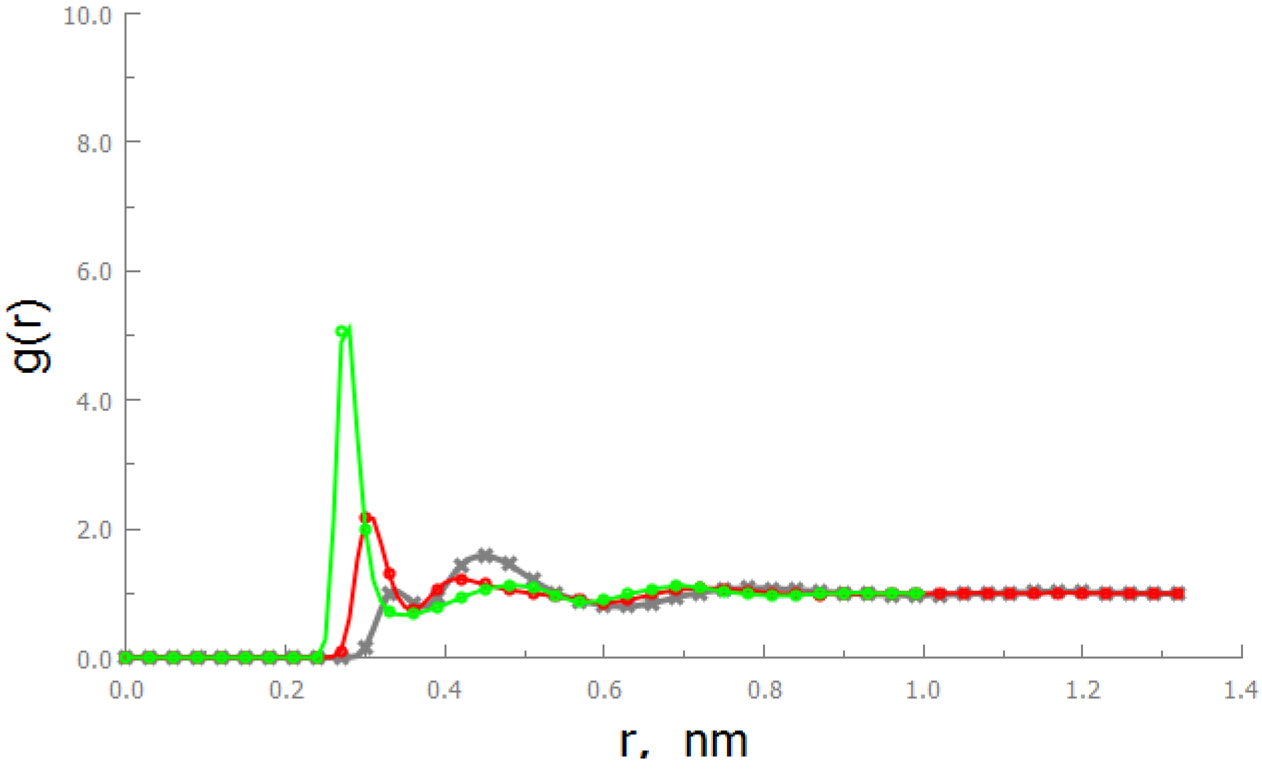
Coarse-graining water-methanol mixture: $X_m = 0.062$



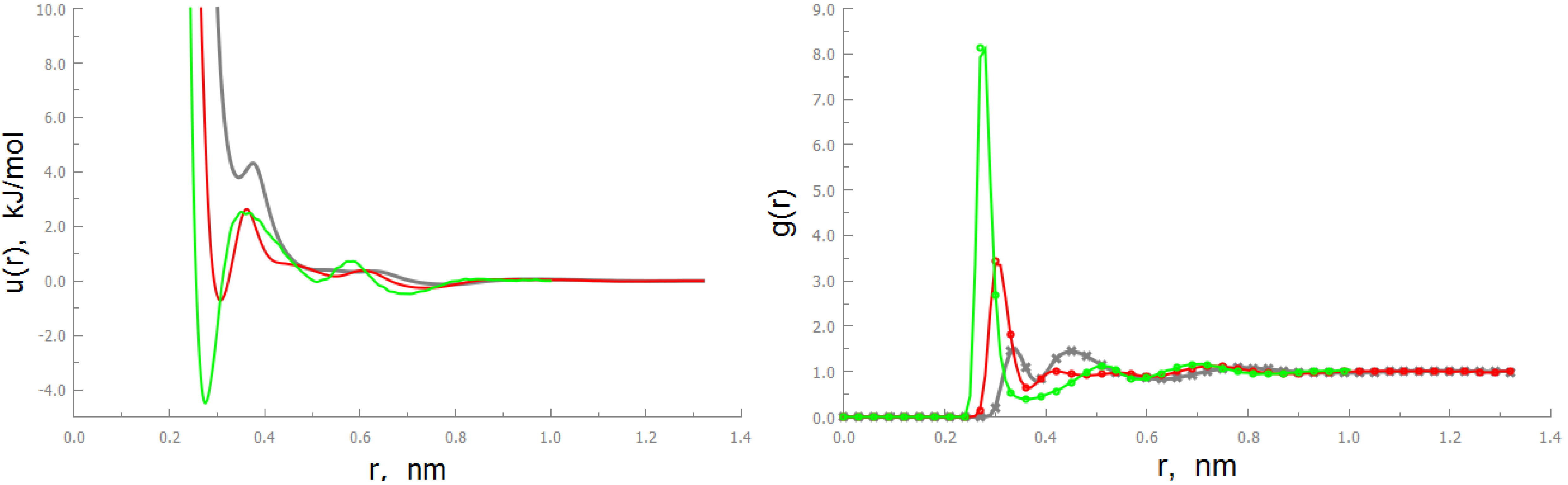


Coarse-graining water-methanol mixture: $X_m = 0.5$

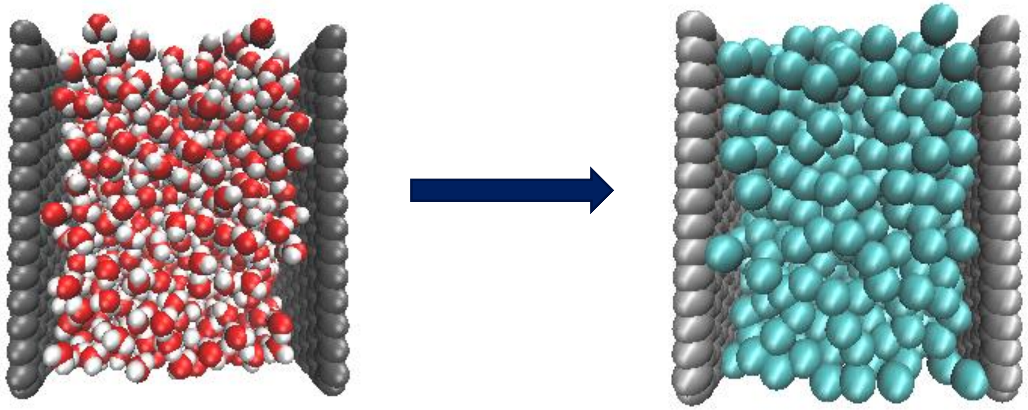




Coarse-graining water-methanol mixture: $X_m = 0.938$



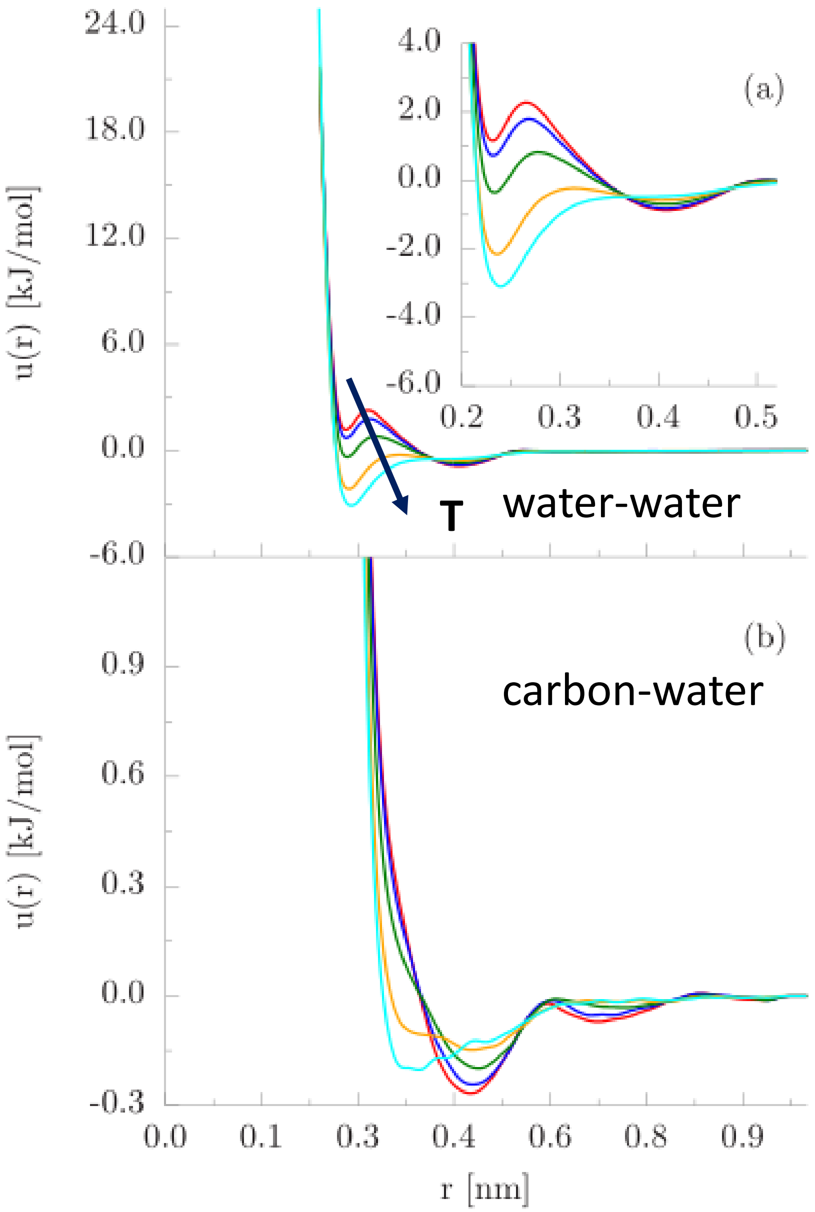
Coarse-graining water in graphene slit channels:

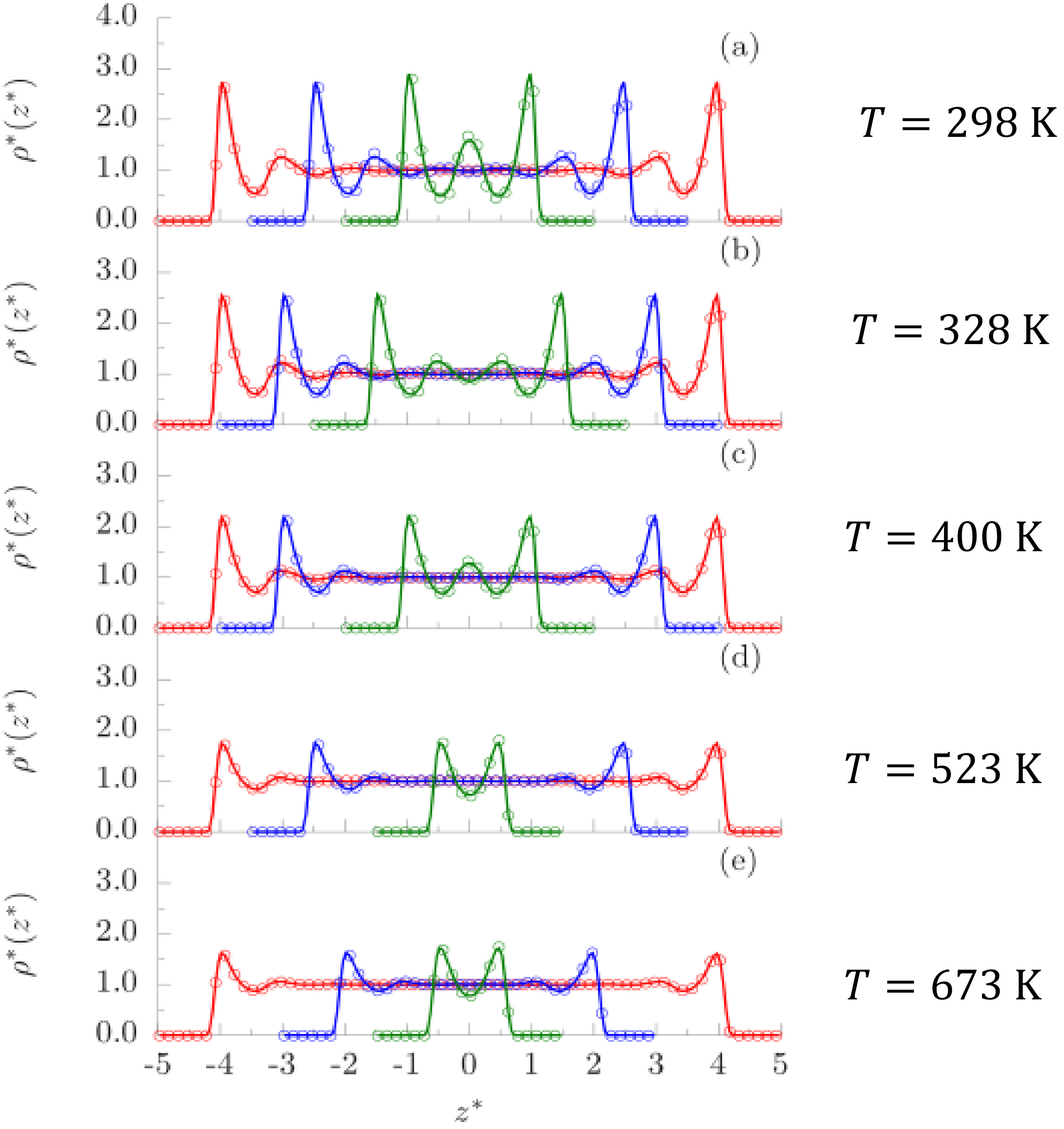


State	T [K]	ρ [gm/cm^3]
I	298	1.0
II	328	0.985
III	400	0.935
IV	523	0.8
V	673	0.66

$$r_{\mathrm{cut}} = 1.0 \text{ nm}$$

$$\Delta r = 0.02 \text{ nm}$$





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Transferability / scaling of CG potentials of water confined in graphene slit channels.

2-point linear interpolation

$$u(r,T) = C_{\mathrm{L}} \times u(r,T_{\mathrm{L}}) + C_{\mathrm{U}} \times u(r,T_{\mathrm{U}})$$

$$C_{\mathrm{L}} = \frac{T_{\mathrm{U}} - T}{T_{\mathrm{U}} - T_{\mathrm{L}}}$$

$$C_{\mathrm{U}} = \frac{T - T_{\mathrm{L}}}{T_{\mathrm{U}} - T_{\mathrm{L}}}$$

For $T = 310$ K, $\mathrm{T_L}$ =298 and $\mathrm{T_U}$ =328 K

For $T = 473$ K, $\mathrm{T_L}$ =400 and $\mathrm{T_U}$ =523 K

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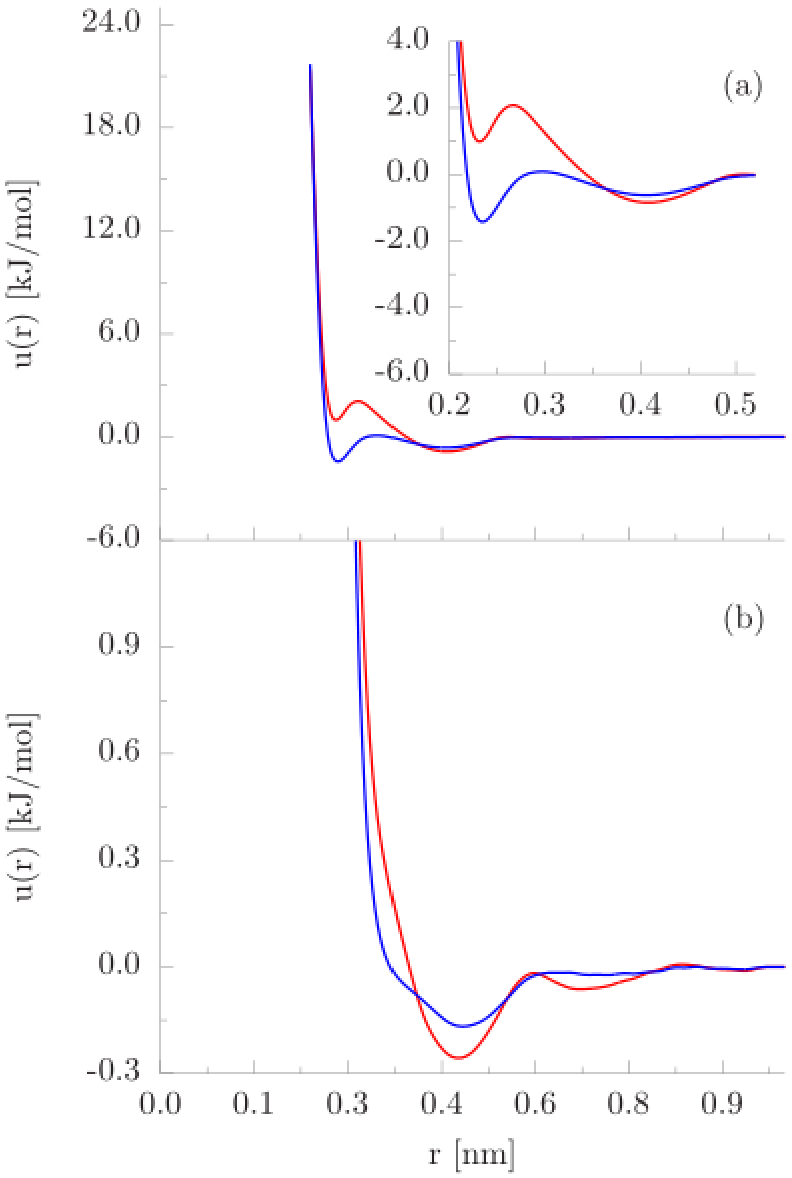

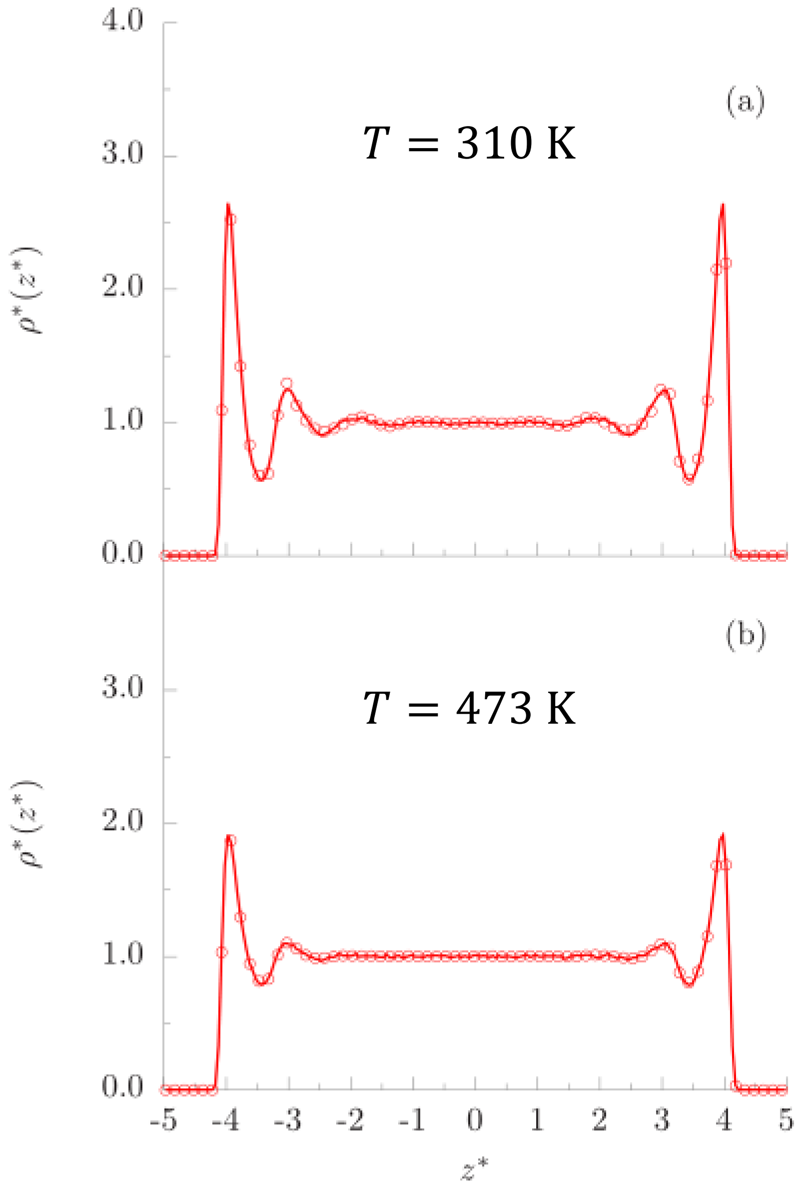

S. Y. Mashayak and Aluru N. R., JCP (2012)

Conclusions

1. Relative entropy is a generic systematic CG method.
2. It can be used effectively to optimize structure-based CG potentials.
3. Structure-reproducing CG potentials for:
   1. SPC/E bulk water: RDF
   2. Water-methanol mixtures: RDF
   3. Water in graphene channels: Local density profiles

Thank you for listening!

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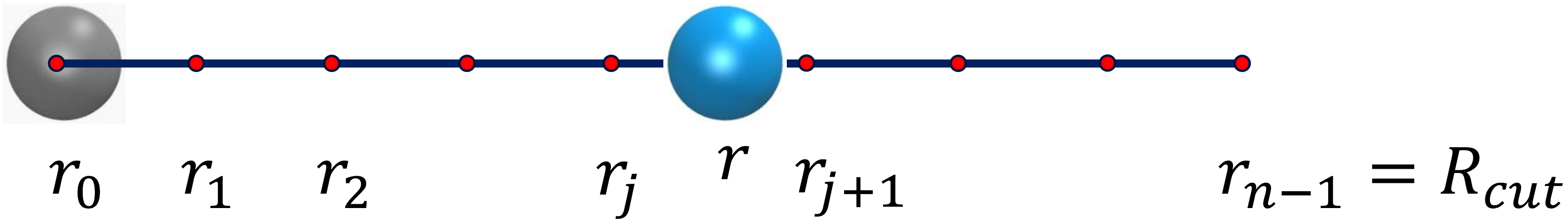
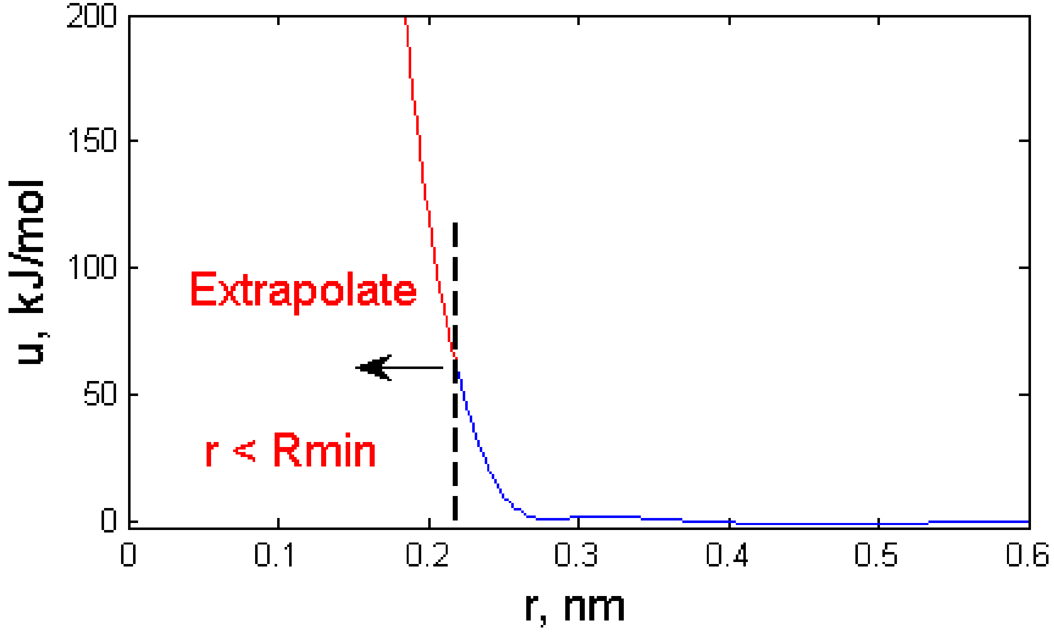
Uniform cubic B-spline functional form





$$u_{\mathrm{SP}}(r) = \begin{bmatrix} 1 & t & t^2 & t^3 \end{bmatrix} \frac{1}{6} \begin{bmatrix} 1 & 4 & 1 & 0 \\ -3 & 0 & 3 & 0 \\ 3 & -6 & 3 & 0 \\ -1 & 3 & -3 & 1 \end{bmatrix} \begin{bmatrix} c_j \\ c_{j+1} \\ c_{j+2} \\ c_{j+3} \end{bmatrix}$$

$$\Delta r = \frac{R_{\mathrm{cut}}}{n-1}, \quad r_j \le r < r_{j+1}, \quad t = \frac{r - r_j}{\Delta r}$$