Some theoretical considerations of the Adaptive Resolution Simulation (AdResS)

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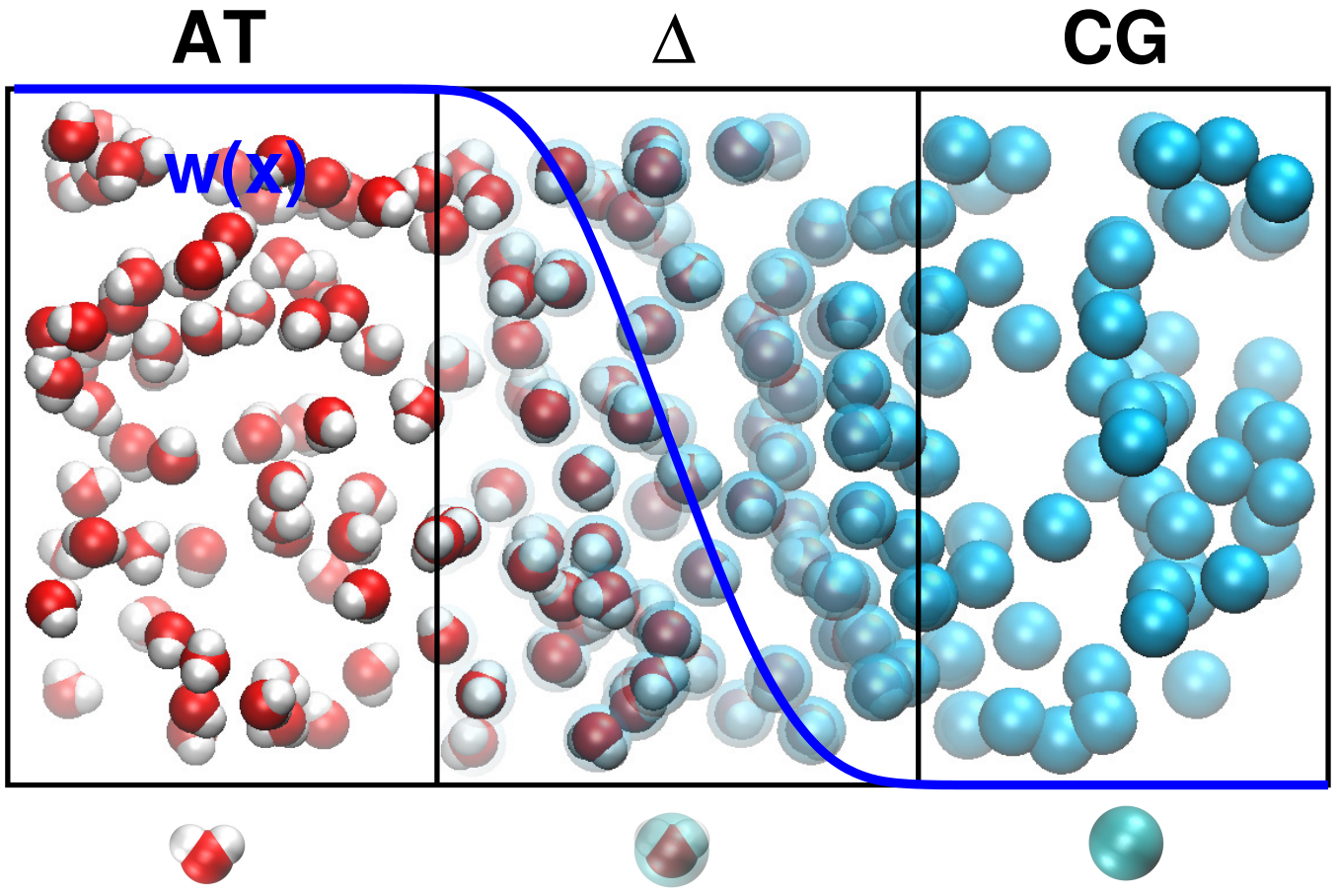
AdResS, Basic concepts



$$\mathbf{F}_{\alpha\beta} = w(x_\alpha)w(x_\beta)\mathbf{F}^{AT}_{\alpha\beta} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}^{CG}_{\alpha\beta}$$

Coupling the two resolutions

Representability problem

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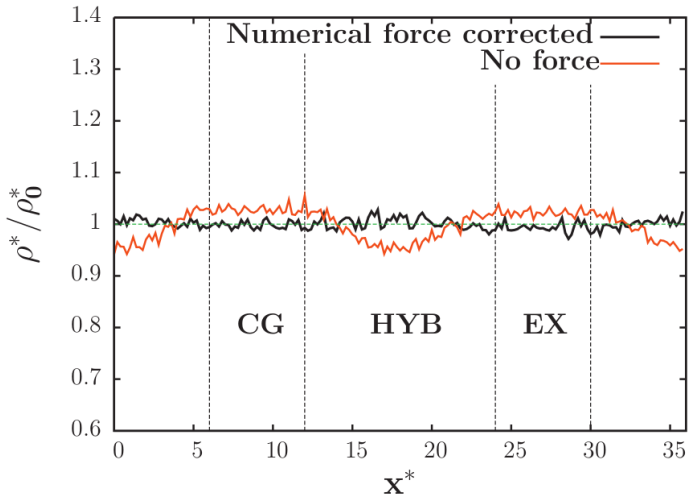
- wrong density profile in hybrid region...



S. Poblete, et. al., J. Chem. Phys. **132**, 114101 (2010)

With courtesy of Luigi Delle Site

Coupling the two resolutions

Effective grand-canonical approach [1]

- Use the structurally correct coarse-grained model (fit $g(r)$):
  $-P_{AT}V \neq -P_{CG}V$; $\rho \neq \rho_0$;
  $g_{AT}(r) = g_{CG}(r)$; $\kappa_{AT} = \kappa_{CG}$

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- The "thermodynamic force":

$$-\left[P_{AT} + \frac{\rho_0}{M_\alpha}\int_\Delta \mathbf{F}^{\mathrm{th}}(x)\,\mathrm{d}x\right]V = -P_{CG}V;$$

$$\mathbf{F}_\alpha = \sum_\beta \mathbf{F}_{\alpha\beta} + \mathbf{F}^{\mathrm{th}}(x_\alpha).$$

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- Is AdResS a grand canonical simulation:

$$p(\mathbf{x}, N) = \frac{1}{\mathcal{Z}} e^{\beta\mu_{AT}N - \beta\mathcal{H}^{AT}(\mathbf{x})} \quad (?)$$

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Proof

- Notation:
  atomistic $\mathbf{x}_1; N_1$, hybrid $\mathbf{x}_2; N_2$, coarse-grained $\mathbf{x}_3; N_3$.
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- Firstly, fix the number of molecules in atomistic region:

$$p(\mathbf{x}_1, N_1) = p(\mathbf{x}_1|N_1)\, p(N_1)$$

  we should prove:

$$p(\mathbf{x}_1|N_1) = \frac{1}{Z_{N_1}} e^{-\beta\mathcal{H}^{AT}(\mathbf{x}_1)}$$

$$p(N_1) = \frac{1}{\mathcal{Z}_1} e^{\beta\mu_{AT} N_1} Z_{N_1}$$

Proof

- The atomistic region is a sub system embedded in the hybrid region.

$$p(\mathbf{x}_1|N_1) = \sum_{N_2} \int p(\mathbf{x}_1|N_1;\mathbf{x}_2,N_2)\, p(\mathbf{x}_2,N_2|N_1)\,\mathrm{d}\mathbf{x}_2$$

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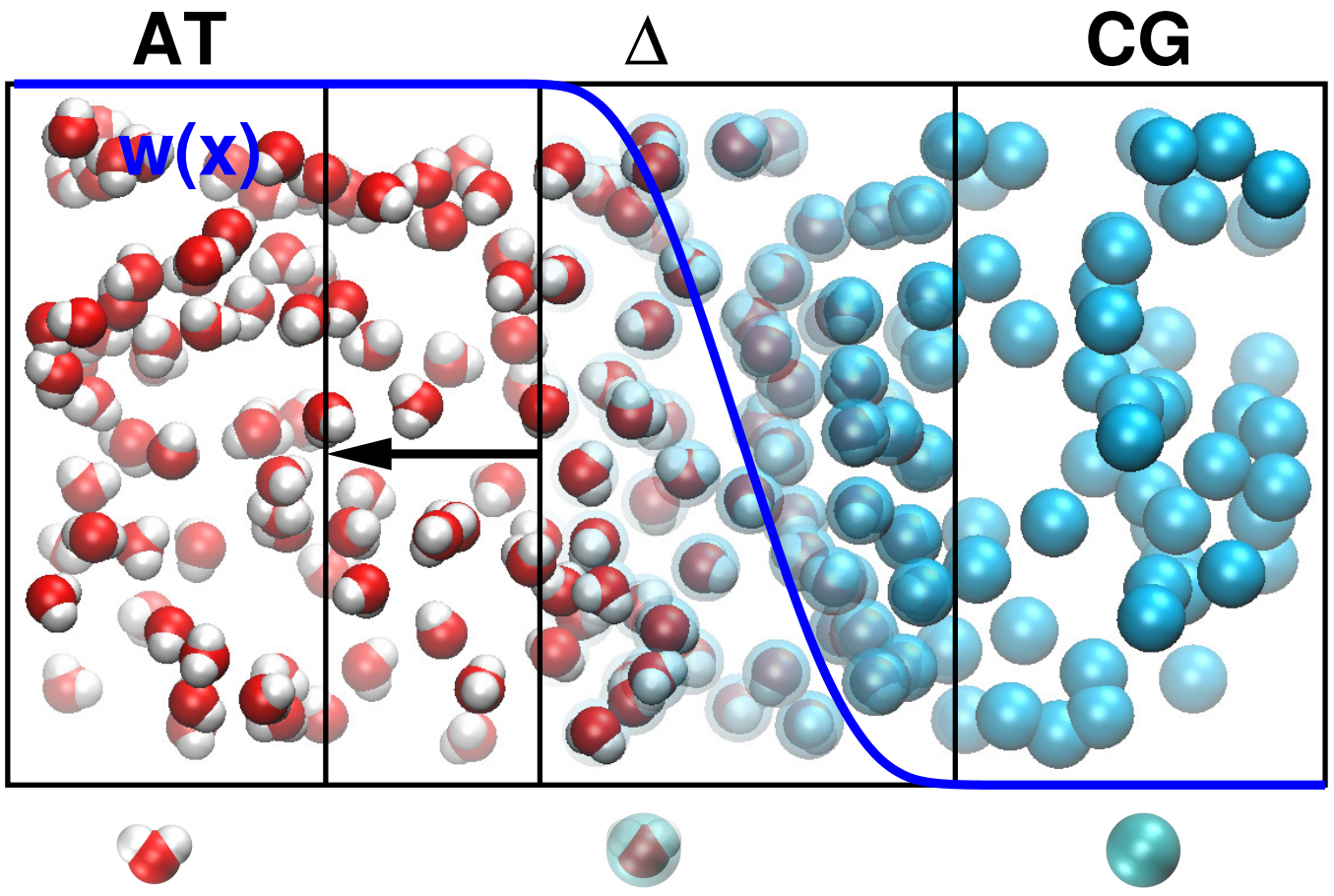
- Fortunately, we have

$$p(\mathbf{x}_1|N_1;\mathbf{x}_2,N_2) \propto e^{-\beta\mathcal{H}^{AT}(\mathbf{x}_1;\mathbf{x}_2,N_2)} \quad \text{AT probability!!}$$

$$\mathcal{H}^{AT}(\mathbf{x}_1;\mathbf{x}_2,N_2) = \sum_{j=1}^{N_1} \frac{1}{2} m_i \mathbf{v}_i^2 + \sum_{i,j=1}^{N_1} \frac{1}{2} U^{AT}(\mathbf{r}_i - \mathbf{r}_j) + \sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N_2} U^{AT}(\mathbf{r}_i - \mathbf{r}_j)$$

Extension of the hybrid region



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- The thermodynamic force approach gives the right $\rho(x)$.
- The extension of hybrid region gives the right $g(r)$.

Proof of molecule number probability

- the probability of N_1:

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  - additive Hamiltonian of AT and CG regions:

$$\mathcal{H}(\mathbf{x}_1, N_1; \mathbf{x}_3, N_3) = \mathcal{H}^{AT}(\mathbf{x}_1, N_1) + \mathcal{H}^{CG}(\mathbf{x}_3, N_3); \qquad N_1 + N_3 = N$$

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- we prove:
  - First order accuracy: $\mu_{AT} = \mu_{CG} \leftarrow$ thermodynamics force.
  - Second order accuracy: $\kappa_{AT} = \kappa_{CG} \leftarrow g_{AT}(r) = g_{CG}(r)$.

Thanks!