3D-RISM Molecular Theory of Solvation

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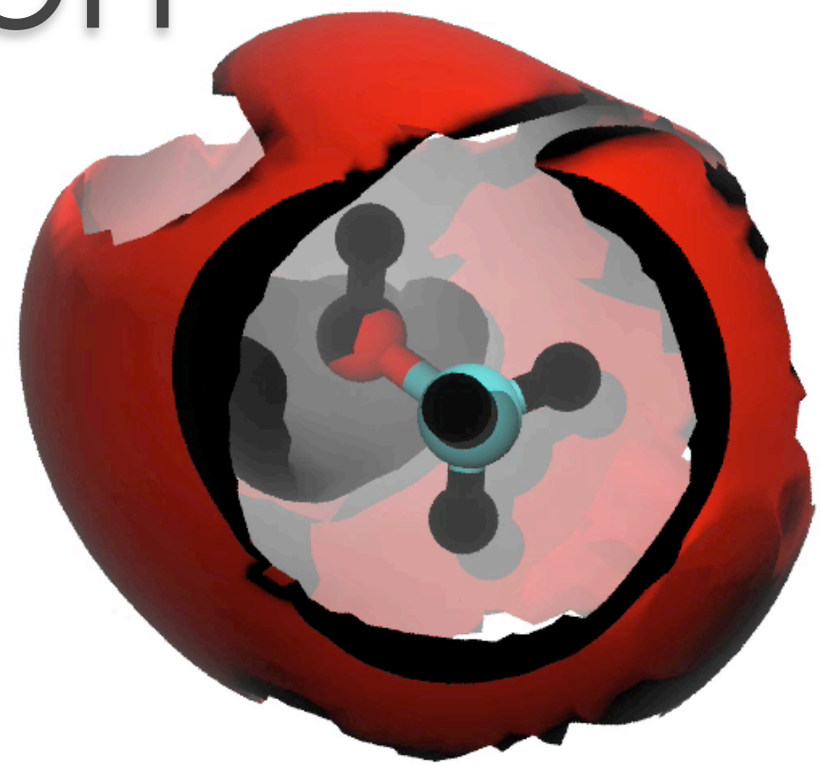
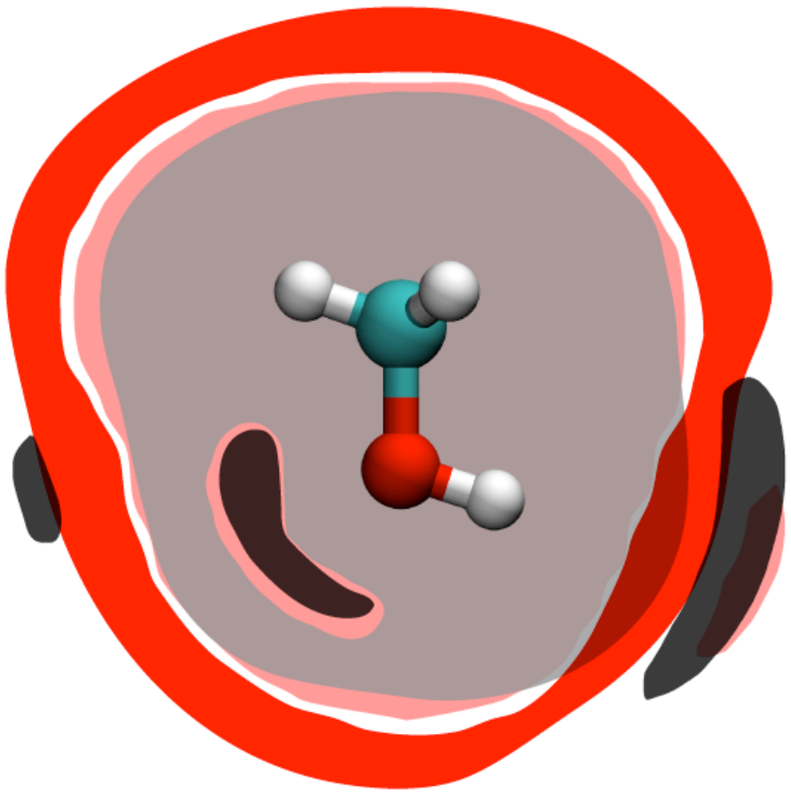
GPU Programming for Molecular Modeling Workshop, August 2010

Solvent Distribution

- Grid based calculation
- Orientations of an explicit solvent model are averaged
- Mean solvent distribution calculated

$$g_{\gamma}^{\mathrm{UV}}(\mathbf{R})$$





Luchko et al. J. Chem. Theory. Comput. 2010 vol. 6 (3) pp. 607-624

3D-RISM

- Real space

$$h_\gamma^{\mathrm{UV}}(\mathbf{R}) = \sum_\alpha \int d\mathbf{R}' \, c_\alpha^{\mathrm{UV}}(\mathbf{R}' - \mathbf{R}) \chi_{\alpha\gamma}^{\mathrm{VV}}(R')$$

$$\chi_{\alpha\gamma}^{\mathrm{VV}}(R) = w_{\alpha\gamma}^{\mathrm{VV}}(R) + \rho_\alpha h_\gamma^{\mathrm{VV}}(R)$$

- K-space

$$h_\gamma^{\mathrm{UV}}(\mathbf{k}) = c_\alpha^{\mathrm{UV}}(\mathbf{k}) w_{\alpha\gamma}(k) + \rho^{\mathrm{V}} c_\alpha^{\mathrm{UV}}(\mathbf{k}) h_{\alpha\gamma}^{\mathrm{VV}}(k)$$

- Coupled with a closure

$$g = \exp\left[-\beta u + h - c + b\right]$$

$h \rightarrow$ total correlation function

$g \rightarrow$ pair distribution function

$c \rightarrow$ direct correlation function

$\omega \rightarrow$ intramolecular correlation

Kovalenko, A.; Hirata, F. Chem. Phys. Lett. 1998, 290, 237–244.

Kovalenko, A.; Hirata, F. J. Chem. Phys. 1999, 110, 10095–10112.

Thermodynamics

$h \rightarrow$ total correlation function

$g \rightarrow$ pair distribution function

$c \rightarrow$ direct correlation function

$b \rightarrow$ bridge function

- From $g(\mathbf{R})$ we can get:
  - Partial molar volume

$$\bar{V} = k_B T \chi_T \left(1 - \rho \sum_{\gamma} \int c_\gamma d\mathbf{r} \right)$$

  - Solvation free energy

$$\Delta\mu_{\mathrm{ex}} = \frac{\rho}{\beta} \int \left[h^2/2 - c + b - hc/2 + h \left(b - \int_0^1 b \, d\lambda \right) \right] d\mathbf{r}$$

  - Entropy and energy

$$\Delta S = \frac{\Delta(\Delta\mu_{\mathrm{ex}})}{\Delta T}, \; \Delta E = \Delta\mu_{\mathrm{ex}} + T\Delta S$$

  - Mean solvation force

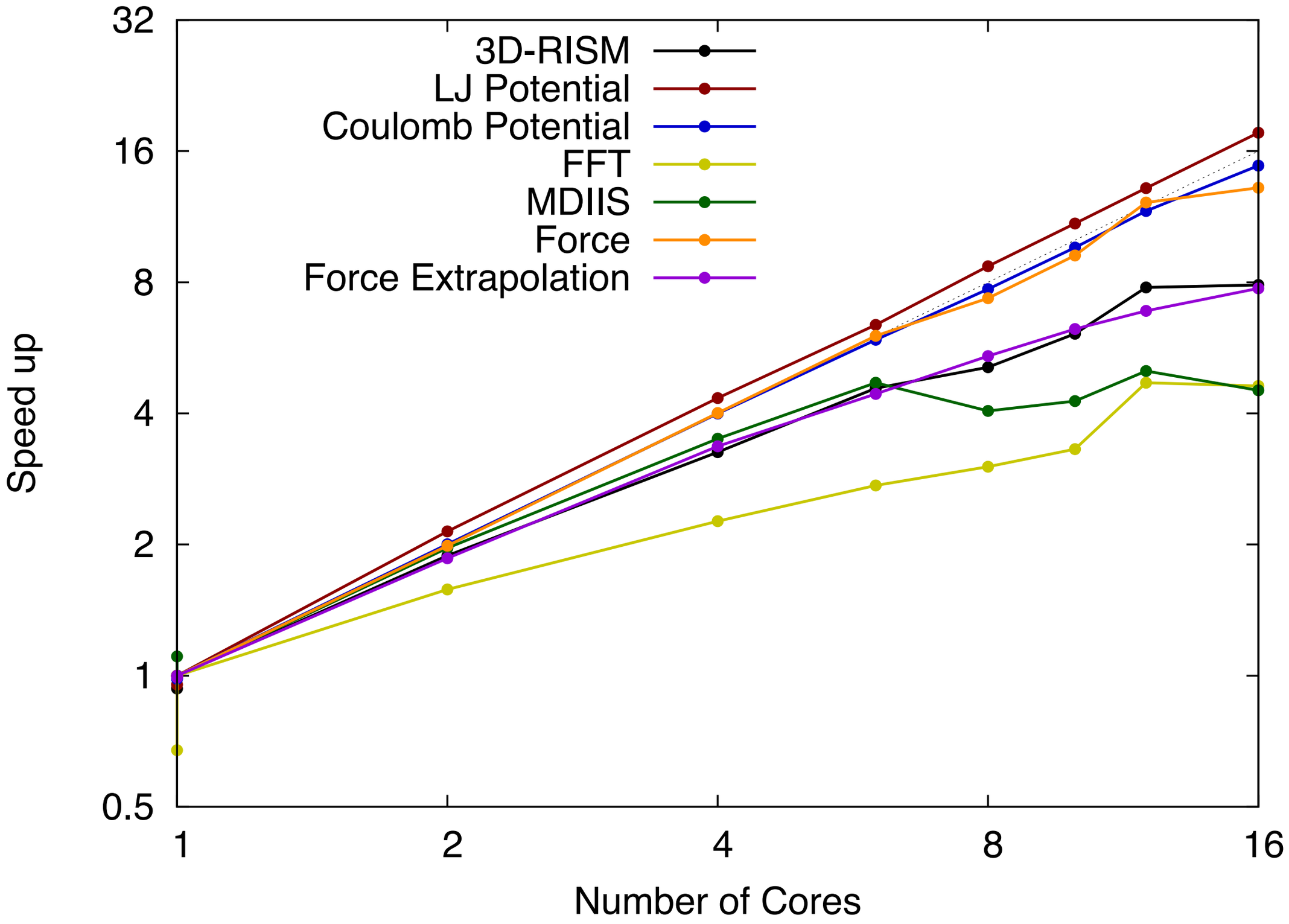
$$\mathbf{f}^{\mathrm{UV}}(\mathbf{r}_i) = -\frac{\partial \Delta\mu_{\mathrm{ex}}}{\partial \mathbf{r}_i} = -\sum_{\alpha} \rho_\alpha \int d\mathbf{R} g_\alpha^{\mathrm{UV}}(\mathbf{R}) \frac{\partial u_\alpha^{\mathrm{UV}}(\mathbf{R} - \mathbf{r}_i)}{\partial \mathbf{r}_i}$$

Computational Characteristics

- 3D arrays with 0.5 Å grid spacing

$$N = N_{\mathrm{box}} \left[\underbrace{4}_{asymptotics} + N_{\mathrm{solv}} \left\{ \underbrace{2N_{\mathrm{MDIIS}}}_{c,\mathrm{residual}} + \underbrace{2}_{g,h} \right\} \right]$$

- 24 base-pair DNA (~1500 atoms) in cTIP3P-Na^+Cl^-
  - 70 Å X 70 Å X 125 Å
  - ~ 3 GB RAM
  - ~1.5 CPU hours (Intel Core 2 Duo)
- MPI version uses distributed memory


3D-RISM
LJ Potential
Coulomb Potential
FFT
MDIIS
Force
Force Extrapolation
Speed up
32
16
8
4
2
1
0.5
1
2
4
8
16
Number of Cores

MPI Scaling

Computational Considerations

- Largely consists of BLAS, FFT and LAPACK operations
- Typically 50% FFT, 25% MDIIS and 25% other
- Fortran 95