

# Effects of System Size and Time Scales in Molecular Dynamics Simulations of Bulk Water

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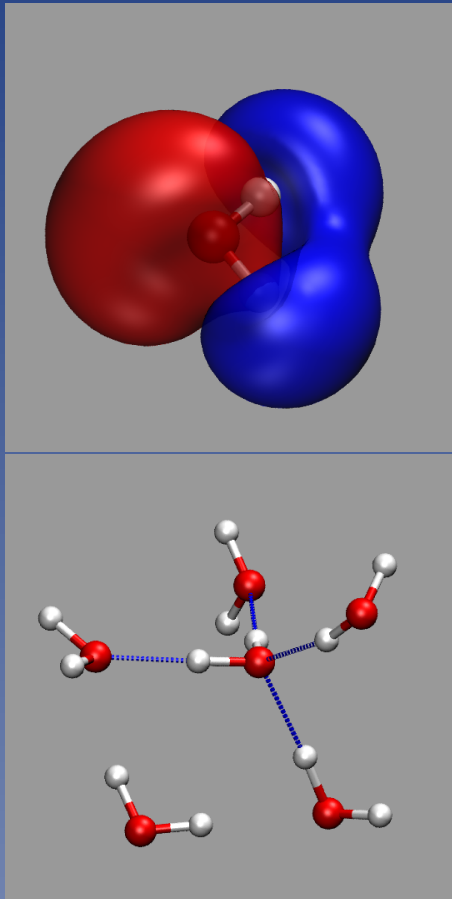
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# Outline

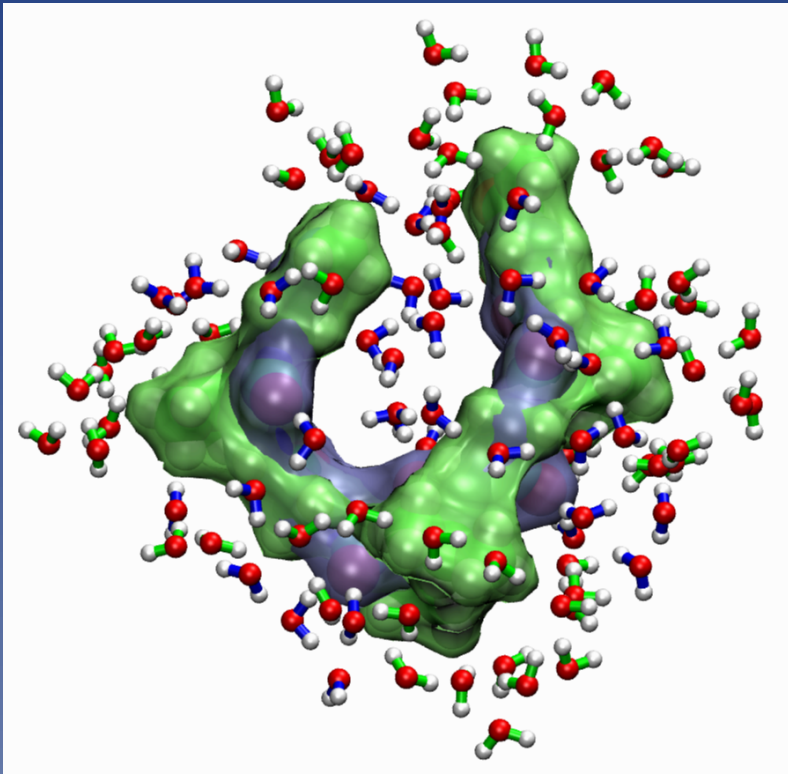
- Motivation, Models and Methods
- Radial-Distribution Functions
- Self-Diffusion Coefficients
- Dipole Auto-Correlations
- Dielectric Properties
- Summary and Outlook

# Motivation



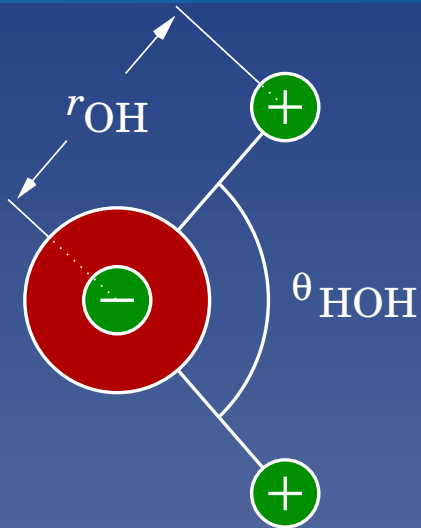
- Water plays integral role in bio- and electro-chemical processes
- Simple molecule, yet complex structure
- Benchmark some “common wisdoms” in Molecular Dynamics of water
- Large variation of data in literature
  - ⇒ explore causes of variations
  - ⇒ provide consistent reference data
  - ⇒ quantify error estimates

## Motivation Continued



- pure water as best case scenario  
⇒ minimal requirements for complex aqueous systems  
⇒ lots of studies on pure water already available
- small system, short time errors  
⇒ estimates for *ab initio* MD
- Lots of spare (single) cpu time

# Models and Methods

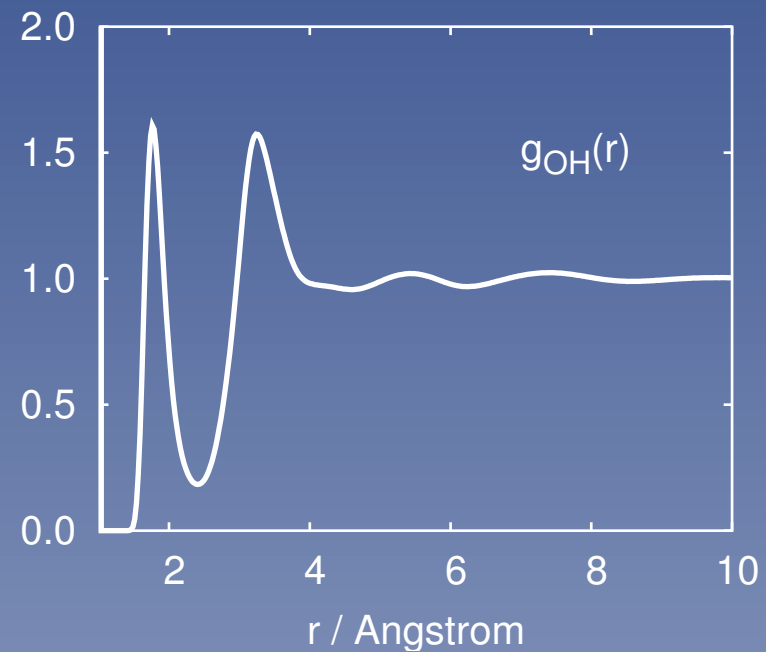
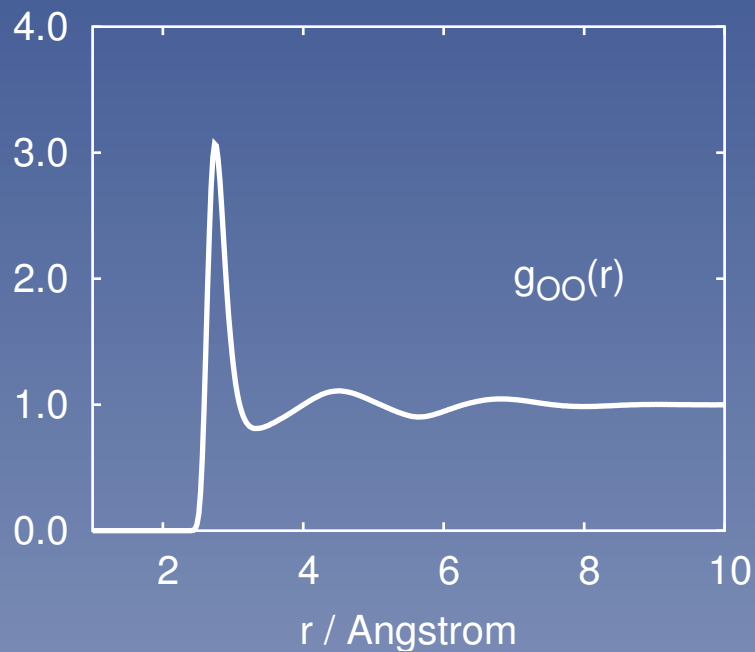


Parameter	Value
$\theta_{\text{HOH}}$	$109.28^\circ$
$r_{\text{OH}}$	$1.00 \text{ \AA}$
$q_{\text{H}}$	$0.4236 e_0$
$q_{\text{O}}$	$-0.8472 e_0$
$\epsilon$	$0.6502 \text{ kJ/mol}$
$\sigma$	$3.166 \text{ \AA}$
$\mu$	$2.35 \text{ D}$

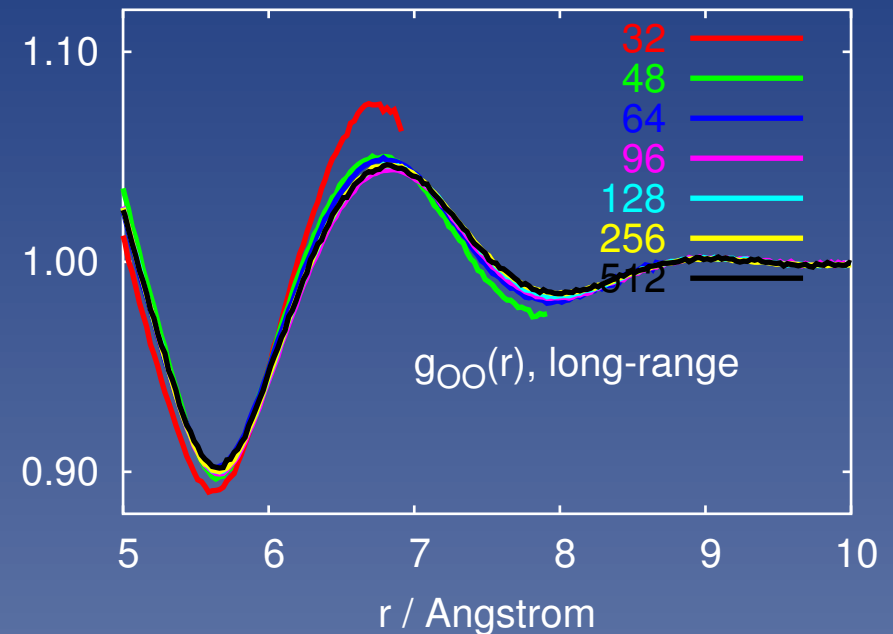
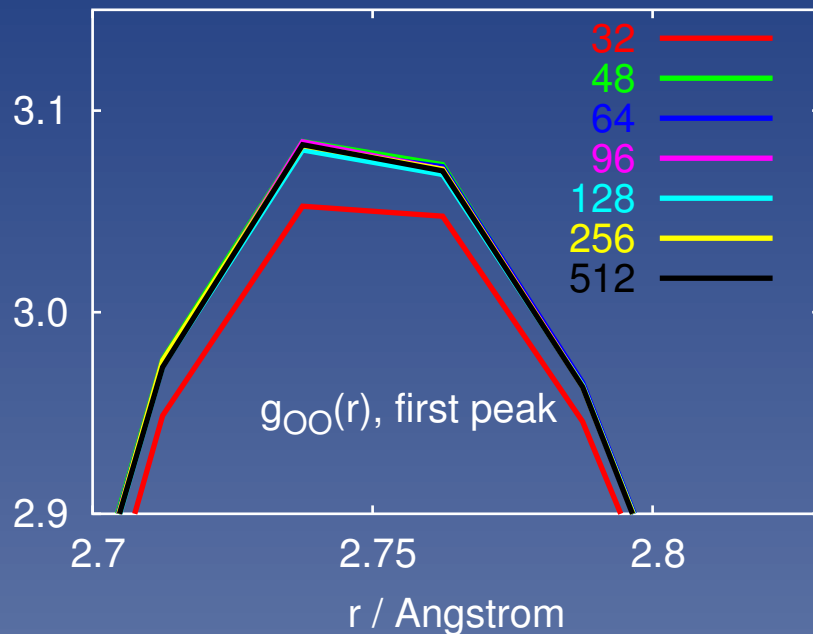
- classical Molecular Dynamics
- SPC/E water potential, simple, rigid
- 32, 48, 64, 96, 128, 256, 512, (512, 2048) water molecules
- cubic cell, constant volume, PBC
- 0.25 fs time step (2 fs time step, SHAKE) up to 110 ns simulation time (32–128 water)
- Temperature 298.15 K , Density:  $1.0 \text{ g cm}^{-3}$
- Ewald Summation, (Particle-Mesh Ewald)

# Radial-Distribution Functions (RDF)

- radial-distribution functions describe average structure
- atomic RDFs simplest form. ex.:  $g_{OO}(r)$  and  $g_{OH}(r)$

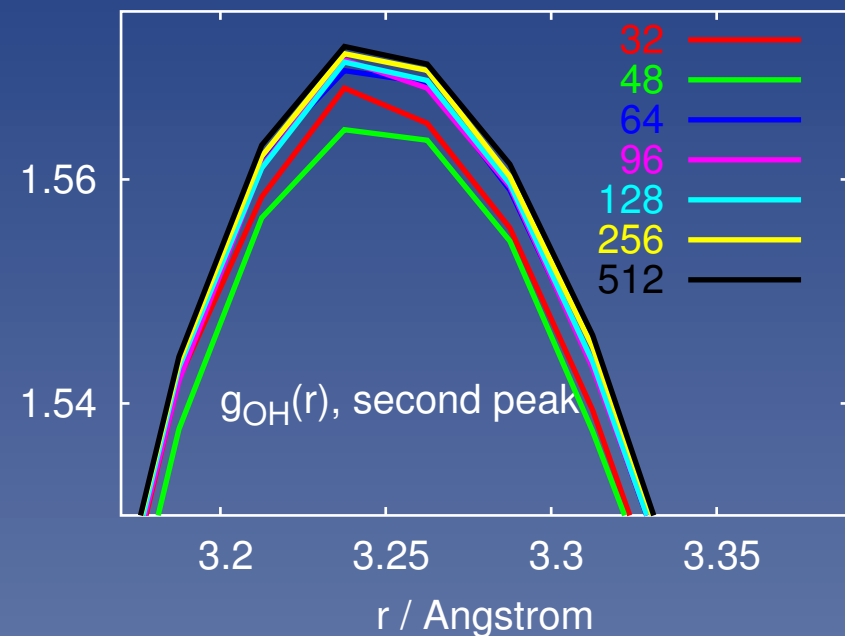
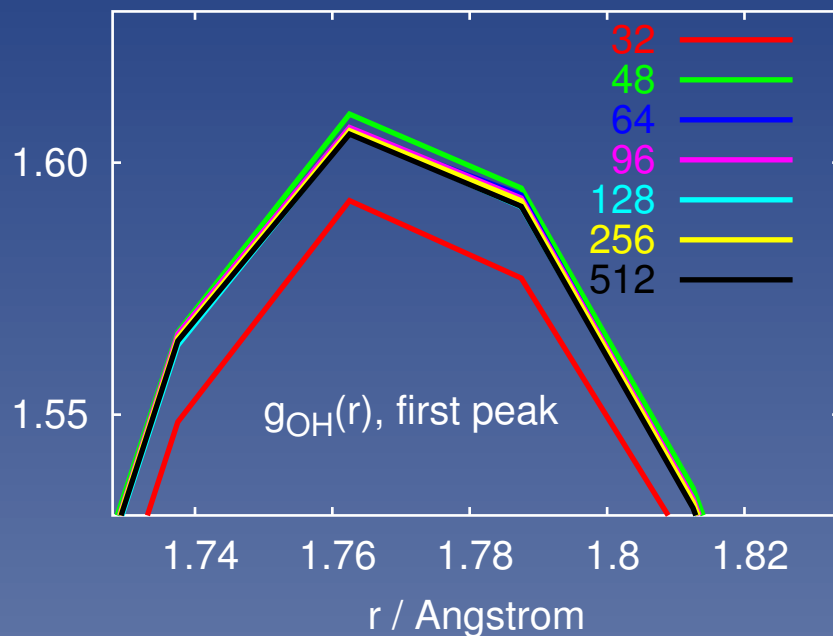


# Influence of System size on $g_{OO}(r)$



- only 32 water RDF differs significantly at first peak
- deviation from large system RDF, when Ewald 'kicks in'
- deviation smaller for larger systems

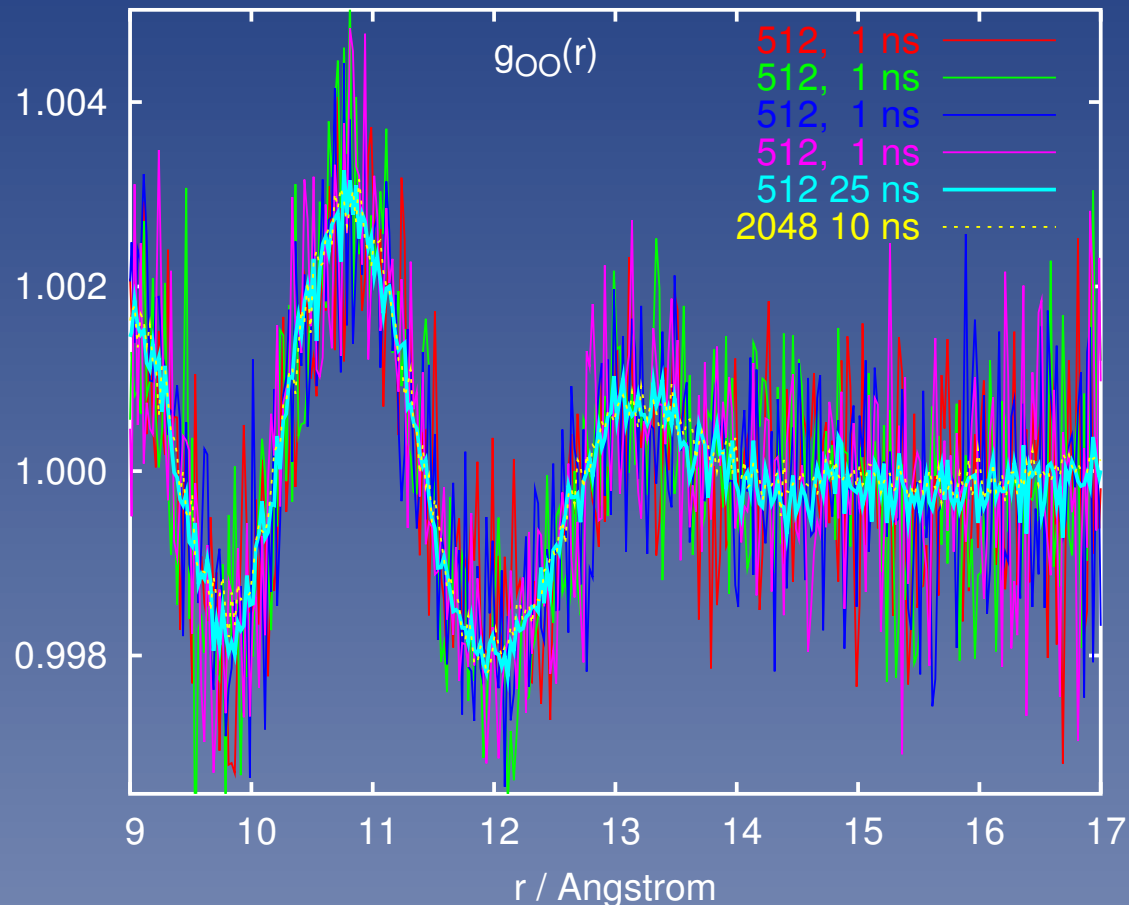
# Influence of System size on $g_{OH}(r)$



- only 32 water RDF differs significantly at first peak
- at second peak also 48 water RDF deviates



# Influence of Simulation Time on RDFs



- RDFs show standard statistical behavior
- peak positions up to  $r = 14$  Å already available with 1 ns simulation time
- RDFs no good benchmark for required system size



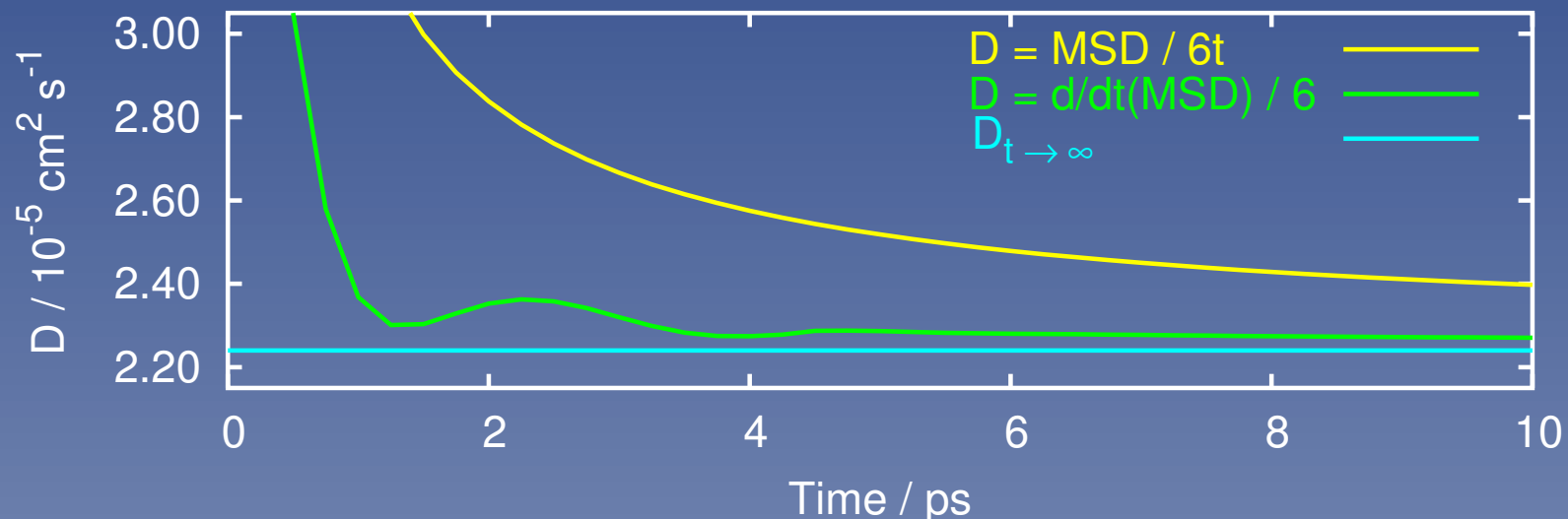
# Summary: Radial-Distribution Functions

- 64 water molecules sufficient for converged main peaks
- short trajectories sufficient for converged peak positions
- standard statistical behavior
- deviation from large system limit only close to cutoff
- long-range features up to 14 Å identifiable
- RDFs no good system size benchmark

# Self-Diffusion Coefficient (SDC)

Calculation from Mean Squared Displacement (MSD):

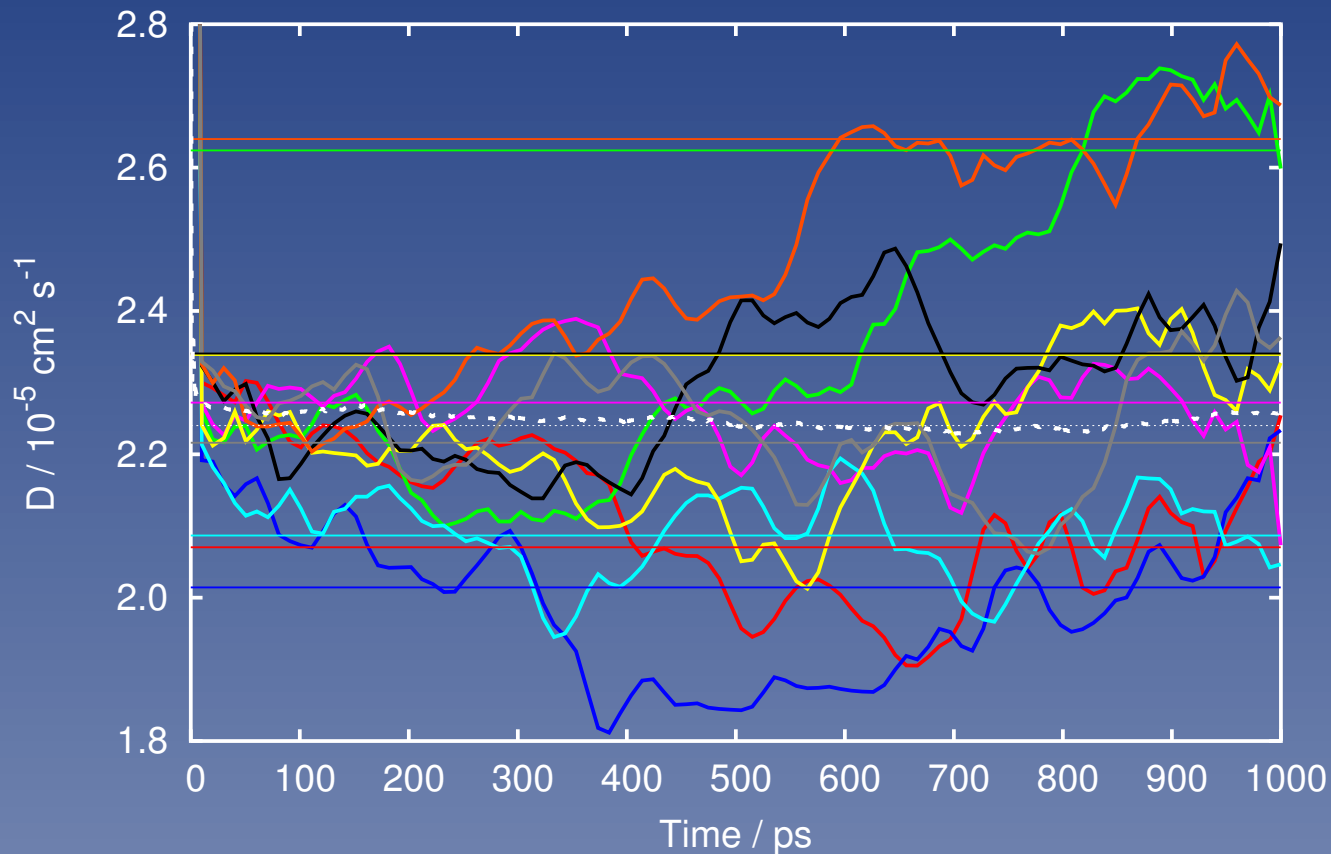
$$6 D t = \text{MSD} = \left\langle |\mathbf{r}_i(t + t_0) - \mathbf{r}_i(t_0)|^2 \right\rangle_{i,t_0} \quad \text{for } t \rightarrow \infty$$



⇒ Much better convergence for  $D = \frac{d}{dt} \frac{\text{MSD}}{6}$  instead of  $D = \frac{\text{MSD}}{6t}$

# Convergence of SDC

Self-Diffusion Coefficient, 128 SPC/E Water

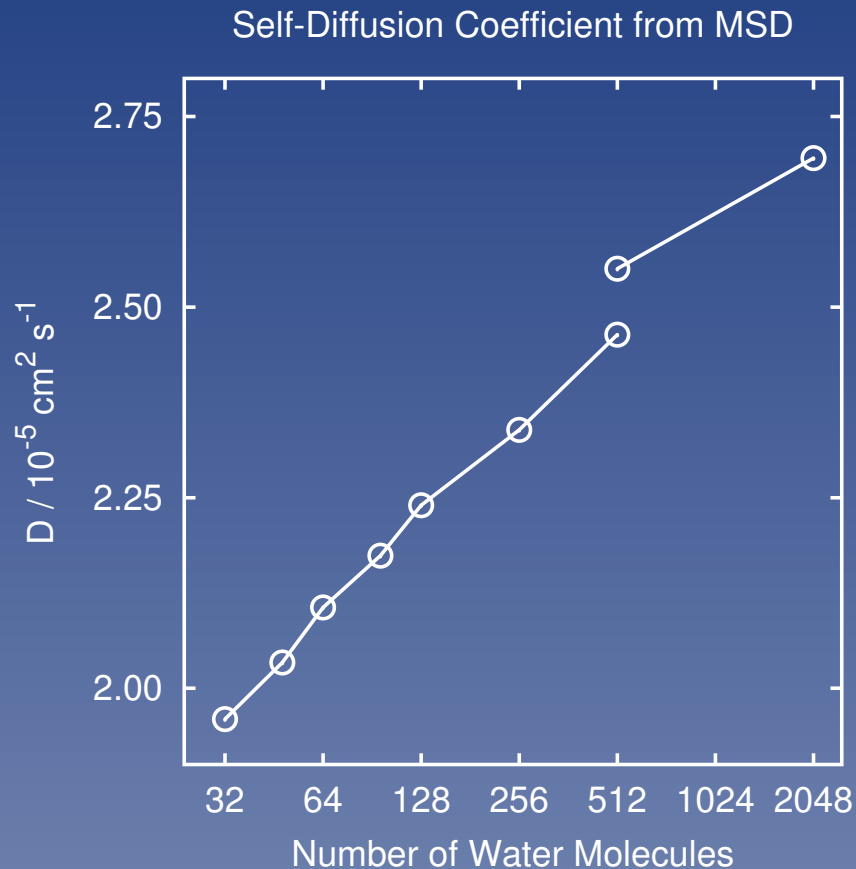


- solid lines:  
2 ns data
- dashed line:  
100 ns data
- thin lines:  
average over  
last third

⇒ very low frequency fluctuations (100s of picoseconds timescale)



# System Size Dependence of SDC



Lit.:  $D = 2.2 - 4.4$  for 216 – 512 SPC/E water

(van der Spoel *et al.*, J.Chem.Phys., 108(1998), 10220ff)

- SDC increases with system size
- slow convergence to bulk value
- is extrapolation possible?
- confirmation from much larger systems needed



## Summary: Self-Diffusion Coefficient

- Using  $D = \frac{\text{MSD}}{6t}$  overestimates SDC  
 $\Rightarrow D = \frac{d}{dt} \frac{\text{MSD}}{6}$  closer to  $t \rightarrow \infty$  value for small  $t$
- small system size underestimates SDC
- low statistical error, but large fluctuations  
 $\Rightarrow$  very long trajectories (10s of ns) needed
- data for even larger systems needed,  
to confirm current results, and/or derive extrapolation

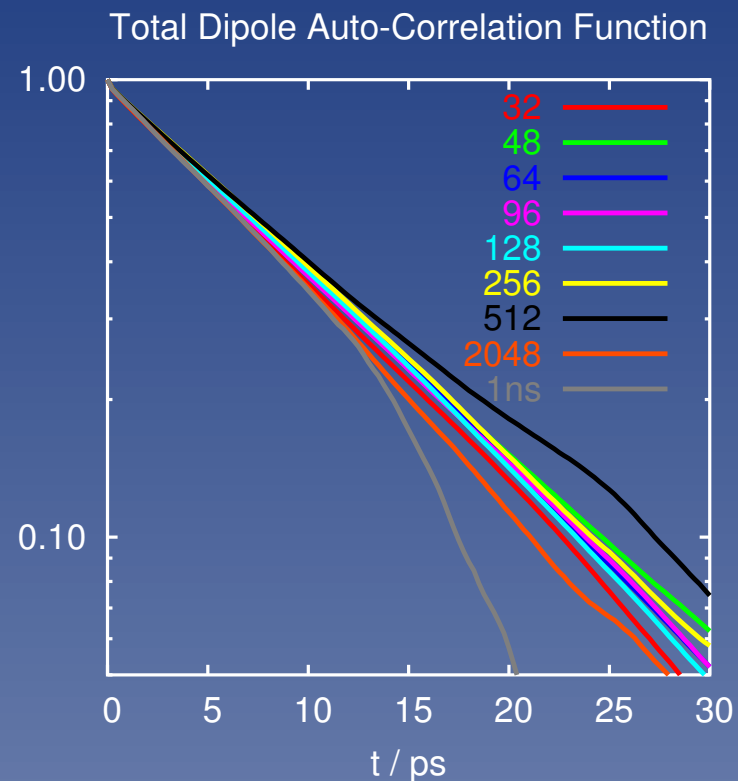
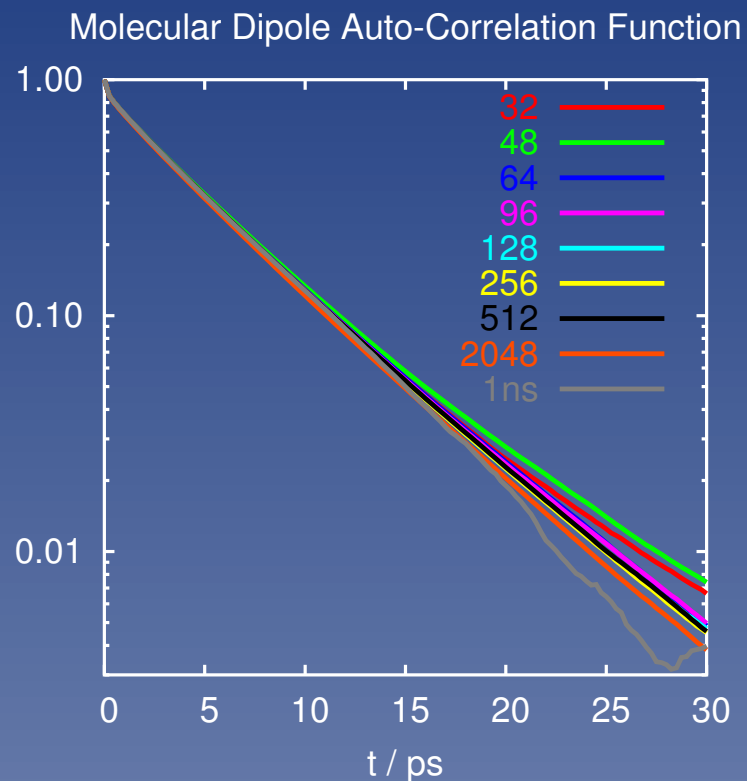
# Dipole Auto-Correlation Functions

Calculation by standard auto-correlation function procedure:

$$c_{\mathcal{A}\mathcal{A}}(t) = \frac{C_{\mathcal{A}\mathcal{A}}(t)}{C_{\mathcal{A}\mathcal{A}}(0)} \quad \text{with} \quad C_{\mathcal{A}\mathcal{A}}(t) = \langle \mathcal{A}_i(t + t_0) \cdot \mathcal{A}_i(t_0) \rangle_{i,t_0}$$

- Calculated for molecular dipole moment vectors ( $\mathcal{A} = \vec{\mu}_i$ ) and total cell dipole moment ( $\mathcal{A} = \vec{M}$ ) vectors.
- Integration gives dipolar relaxation times  
(first part numerical, then extrapolation from exponential decay to  $t \rightarrow \infty$ )

# Dipole Auto-Correlation Functions

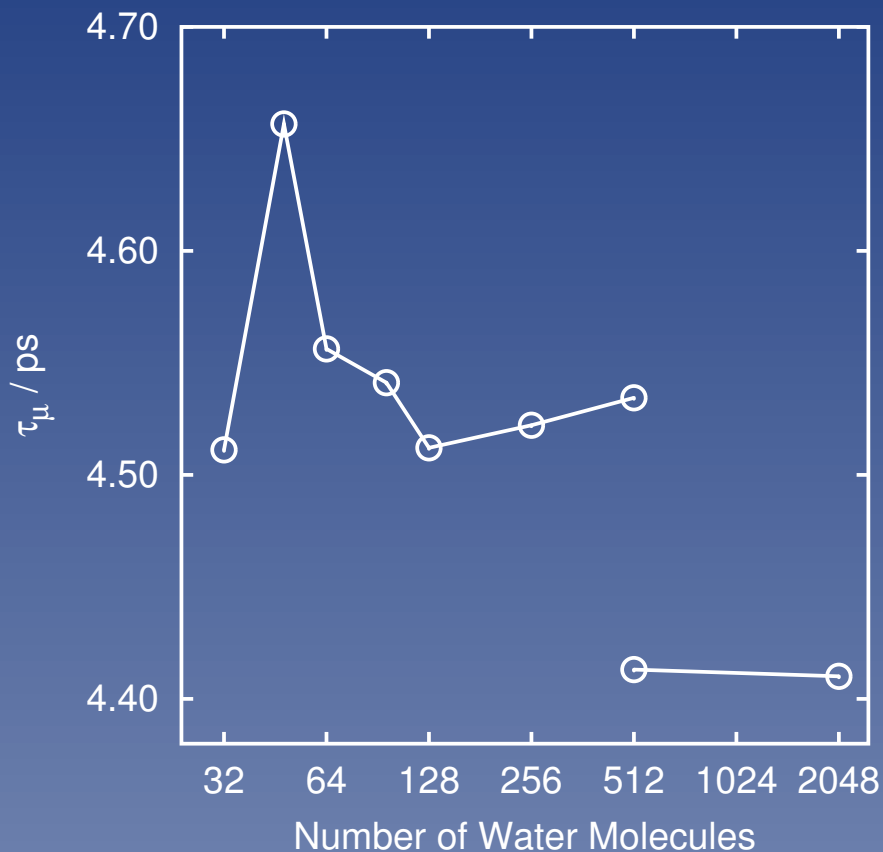


- small system size effect for  $c_{\mu\mu}^{\rightarrow\rightarrow}(t)$  in the (very) long-range part
- $c_{MM}^{\rightarrow\rightarrow}(t)$  difficult to converge



# System Size Dependence of Relaxation Times

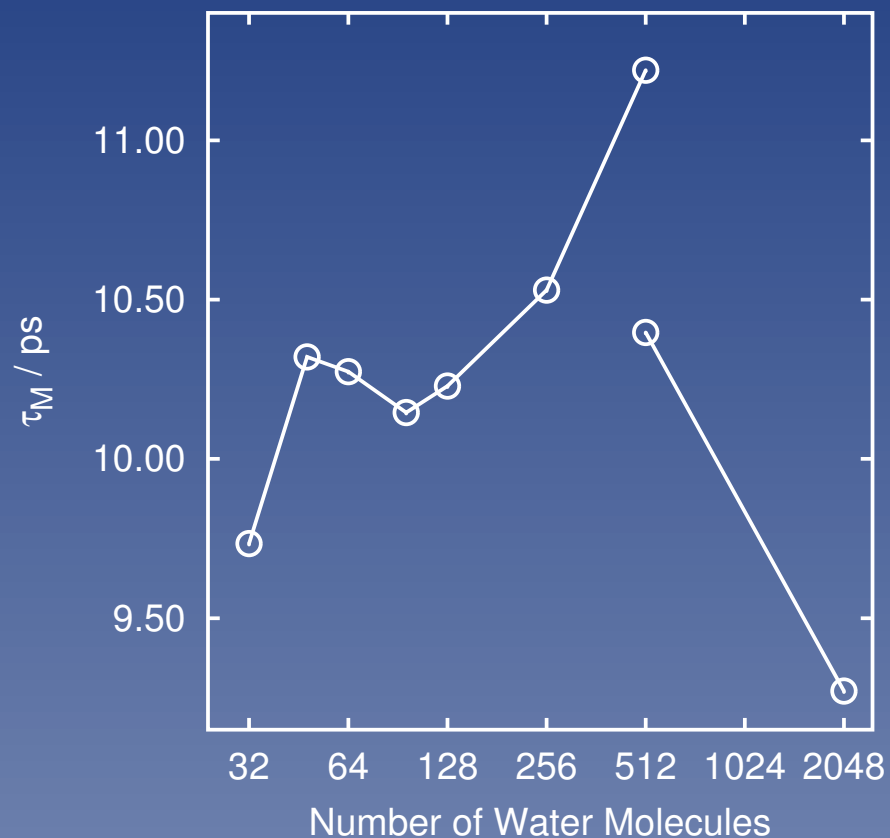
Molecular Dipole Relaxation Time



exp. value:  $\tau_{\mu} = 4.5$  ps

(Nabobov *et al.*, Mol. Phys., 65 (1988), 1473ff)

Total Dipole Relaxation Time



exp. value  $\tau_M = 8.4$  ps

(Buchner *et al.*, Chem. Phys. Lett., 306 (1999), 57ff)



## Summary: Dipole Auto-Correlation

- dipole auto-correlation difficult to converge beyond 10 ps
- better convergence for  $c_{\mu\mu}(t)$  due to better statistics
- consistent results with  $\geq 50$  ns and  $\geq 64$  water

# Static Dielectric Constant $\epsilon(0)$

Derivation of static Dielectric Constant via  $G_k$

$$\langle \vec{M}^2 \rangle_t - \langle \vec{M} \rangle_t^2 \approx \langle \vec{M}^2 \rangle_t = \sum_i^N \langle \vec{\mu}_i \cdot \vec{M} \rangle_t = N\mu^2 G_k.$$

( $\vec{M}$  = total dipole,  $\vec{\mu}$  molecular dipole,  $N$  = # of molecules)

and the dipolar strength  $y$ :

$$y = \frac{4\pi\rho\mu^2}{9k_B T}, \quad \text{with } \rho = \frac{N}{V}, \quad V = \text{Volume}$$



## $\epsilon(0)$ from MD Simulations

Considering the dielectric boundary conditions in an MD simulation leads to (Neumann, Mol. Phys. 50(1983), 841ff):

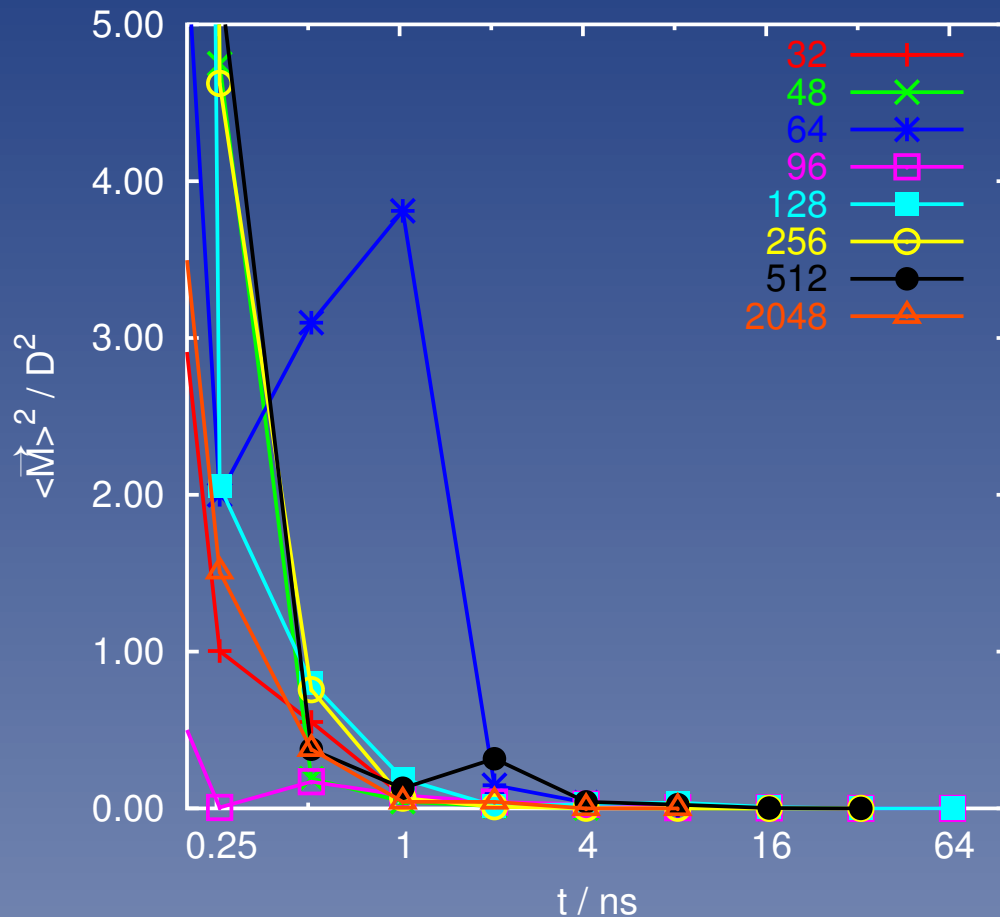
$$\frac{\epsilon(0) - 1}{\epsilon(0) + 2} \left[ 1 - \frac{\epsilon(0) - 1}{\epsilon(0) + 2} \cdot \frac{2(\epsilon_{\text{RF}} - 1)}{2\epsilon_{\text{RF}} + 1} \right]^{-1} = yG_k$$

For a conventional Ewald-Summation is  $\epsilon_{\text{RF}} = \infty$ .

Therefore we get:

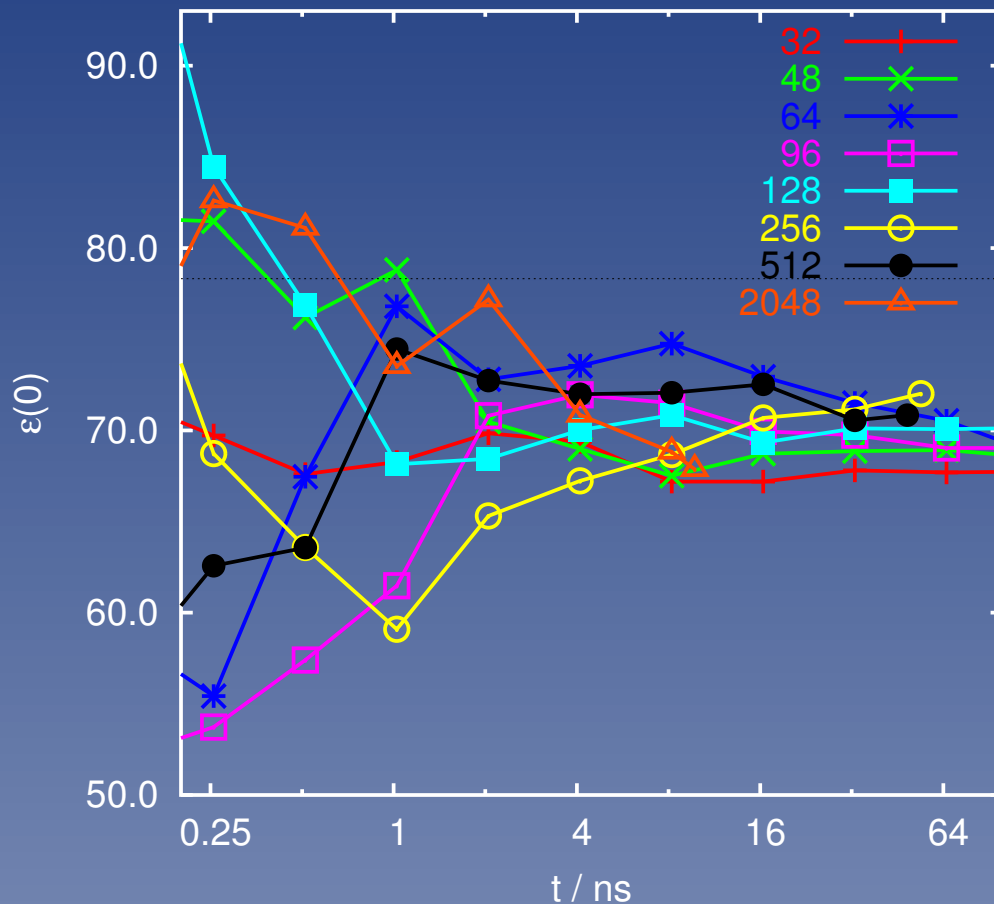
$$\frac{\epsilon(0) - 1}{3} = yG_k \quad \Leftrightarrow \quad \epsilon(0) = 3yG_k + 1$$

# $\langle \vec{M} \rangle^2$ Convergence



- contribution of  $\langle \vec{M} \rangle_t^2$  negligible after a few ns.  
 $\Rightarrow$  assumption  
 $\langle \vec{M}^2 \rangle_t - \langle \vec{M} \rangle_t^2 \approx \langle \vec{M}^2 \rangle_t$   
 valid
- convergence also not size dependent

# $\epsilon(0)$ Convergence



- very slow convergence

- $\epsilon(0)$  not size dependent

(Madden *et al.*, Adv. Chem. Phys., 56(1984), 467ff)

- convergence also not size dependent

- result:  $\epsilon(0) = 69 \pm 1$

Lit.:  $\epsilon(0) = 53 - 81$  for 216 - 820 SPC/E

(van der Spoel *et al.*, JCP, 108(1998), 10220ff)

- exp. value: 78.32

(Buchner *et al.*, Chem. Phys. Lett., 306(1999), 57ff)

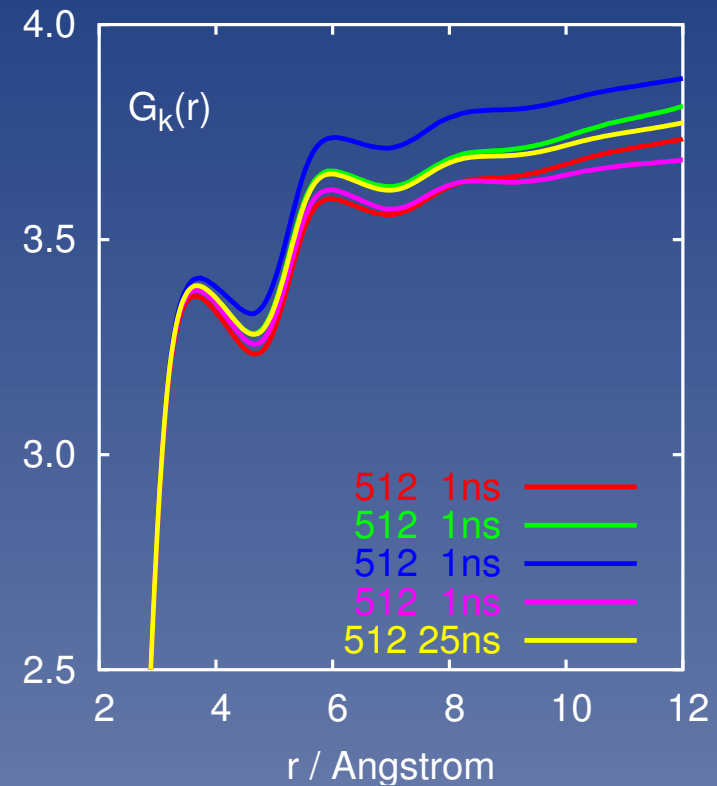
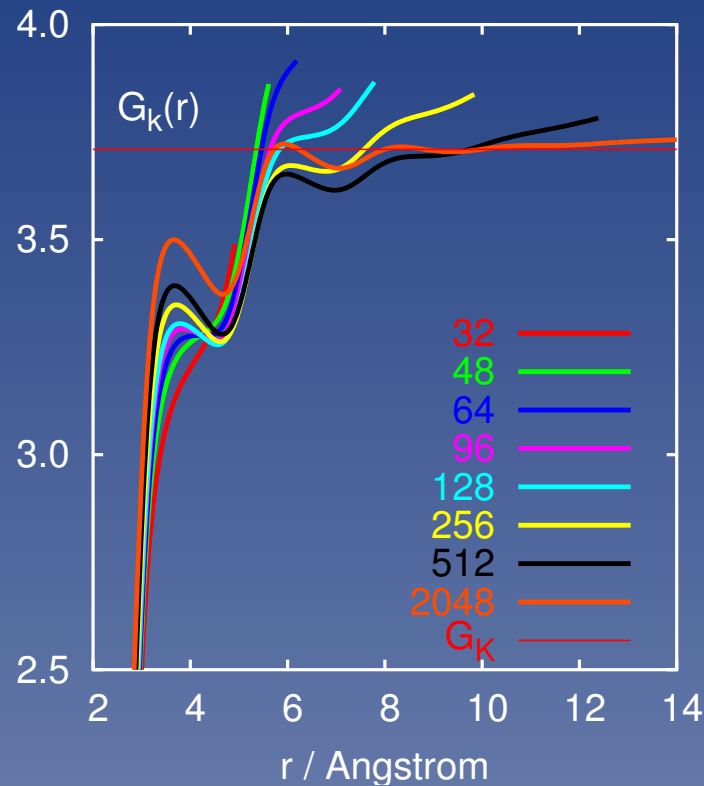
## Size Dependent Kirkwood G Factor

Angular correlation between a dipole and the net dipole of the sphere of size  $R$  surrounding the center of the dipole (including the dipole itself!).

$$G_k(R) = \left\langle \frac{\vec{\mu}_i^0}{|\mu_i|} \sum_{j, r_{ij} \leq R} \frac{\vec{\mu}_j^0}{|\mu_j|} \right\rangle_{i,t} \quad \text{with} \quad \vec{\mu}_k^0 = \frac{\vec{\mu}_k}{|\mu_k|}$$

For isolated system:  $\lim_{R \rightarrow \infty} G_k(R) = G_k$ .

# Size Dependent Kirkwood G Factor



- surprisingly large system size effect for  $3 \text{ \AA} < R < 5 \text{ \AA}$   
 $\Rightarrow$  for large system mid- to longrange effects cancel. cf.  $\epsilon(0)$ .





## Summary

- effects of system size and simulation time depend on property
- radial-distribution functions need medium system size, but only short trajectories
- self-diffusion coefficients need large systems and long simulation times, statistical error misleading
- dipole auto-correlation difficult to converge, but extrapolation via exponential decay works
- $\varepsilon(0)$  needs long simulation time, but independent from system size (even with 32 water molecules!).



## Summary Continued / Outlook

- preliminary results, but already many insights
- this study can give error estimates
- can explain variation of results in literature
- can explain good agreement for SDC from short simulations (cancellation of systematic errors)
- more examination needed to quantify errors
- still room for further simulations (smaller, larger, longer)
- are there other properties to look at?



# Thanks

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