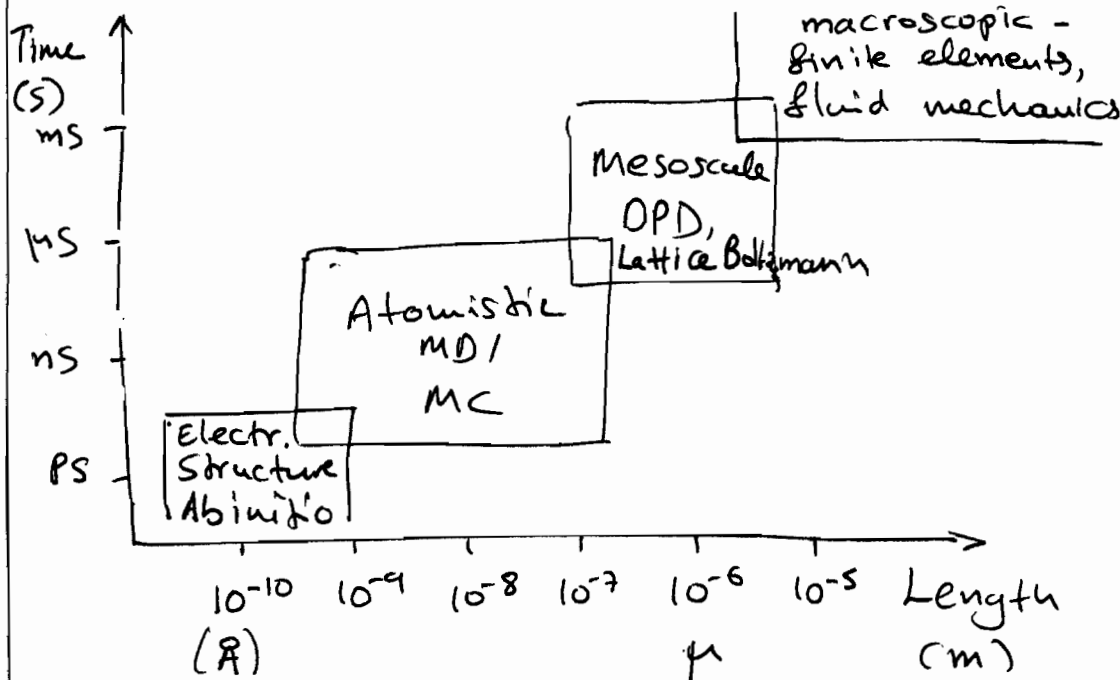


Refs: Ch. 17 in f+s

Peter + Kremer J. Chem. Soc. Faraday Trans.

144: 9-24 (2010)

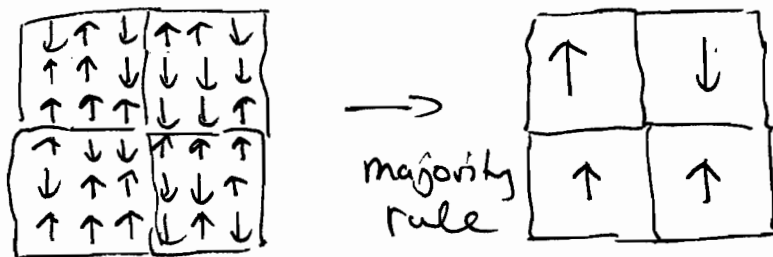
Length and Time Scales



* Separate or hybrid simulations?

* Mechanism for linking different scales?

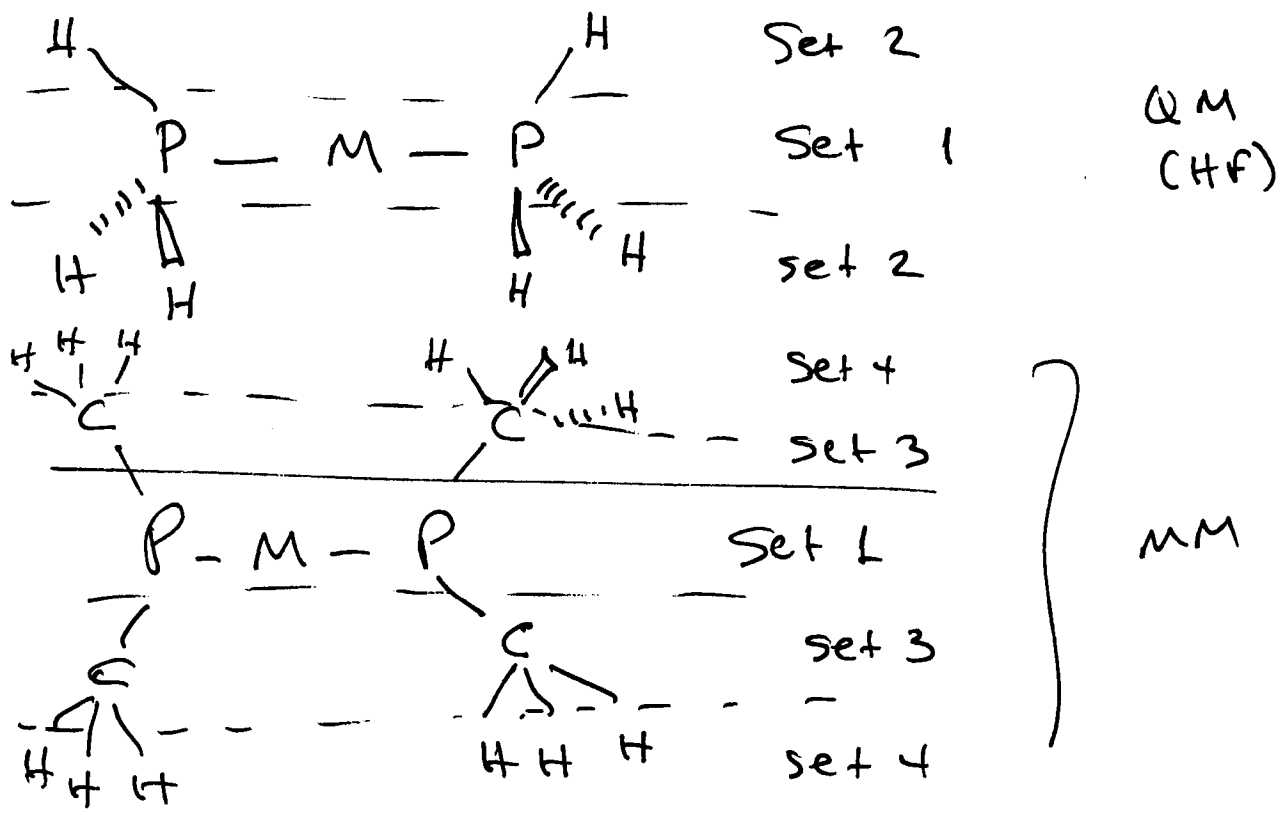
Renormalization group transformations



for exact correspondence, need more complex, longer-range interactions, multiple states

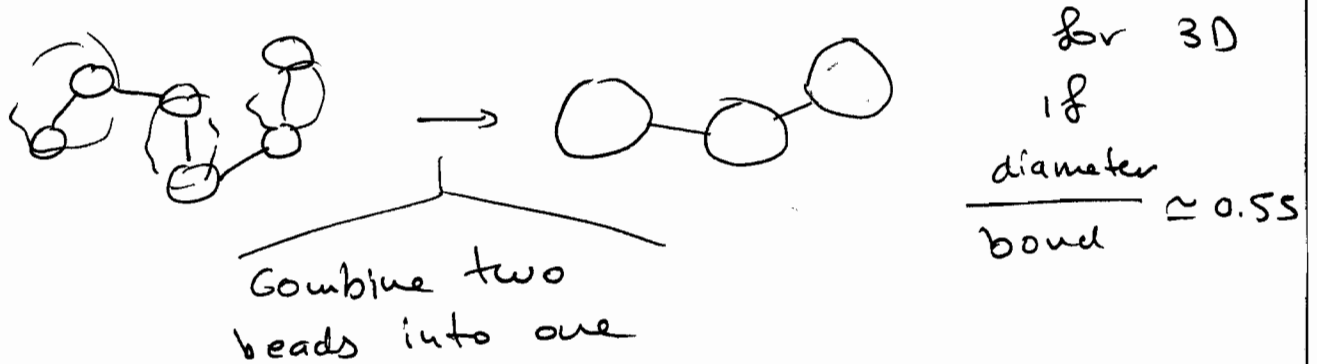
At the interface between QM / MM

Warshel and Levitt, 1976 2 Mol. Biol. 103:227
Chemistry Nobel (w/ite. karplus), 2013



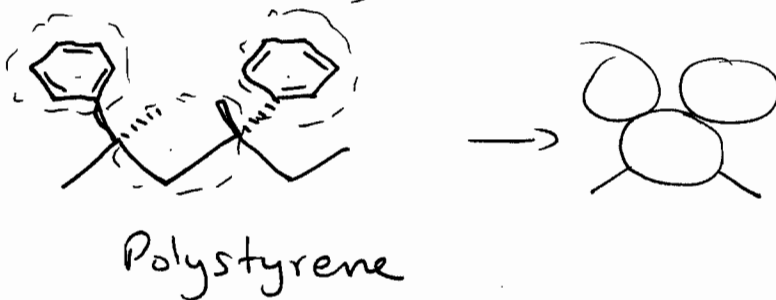
- Input coordinates for Set 1, 2 atoms
- use ab initio methods to calculate energy + gradients for set 1+2 atoms
- Set 3 coordinates functions of set 1+2
- carry out MM optimization for "dependent" atoms (set 4)
- Set 4 could be solvent molecules.

Certain properties can be made invariant under the transformation - e.g. end-to-end distance

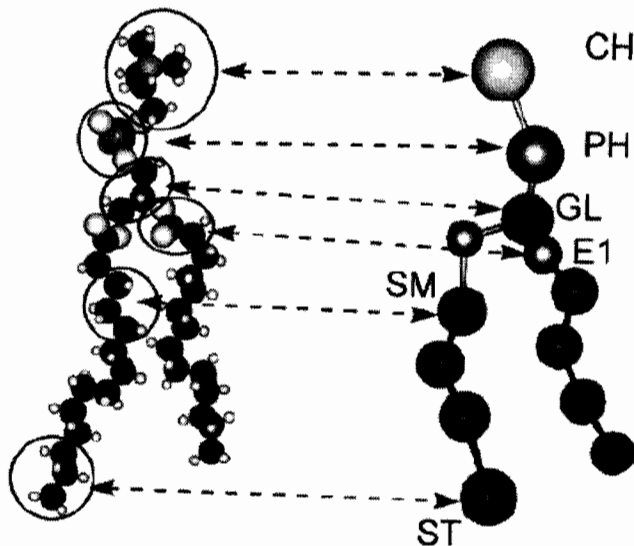


General criteria used for coarse-graining:

- * Structure (gcr)
 - * Forces / potential
 - * Thermodynamics (e.g. phase behavior) → hard!
- } commonly used



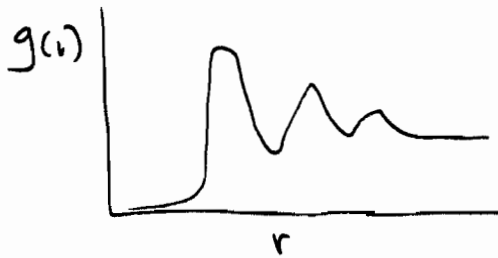
J. Phys. Chem. B. Vol. 105, No. 19, 2001 4465



Klein group
model for
DMPC lipid
(dimyristoylphosphatidyl-
choline)

Structure matching from

a) Iterative Boltzmann inversion of distribution functions



$$w(r) = -\ln(g(r))$$



(b) Reverse Monte Carlo

Perform perturbation on intermolecular potential model parameters, accept/reject based on reproduction of desired structure

Issues with static coarse-graining

- * Interactions are state dependent (change with density, temperature, composition in a mixture etc)
- * Properties not taken into account while coarse-graining are not well reproduced
- * Thermodynamics / phase transitions usually not well represented

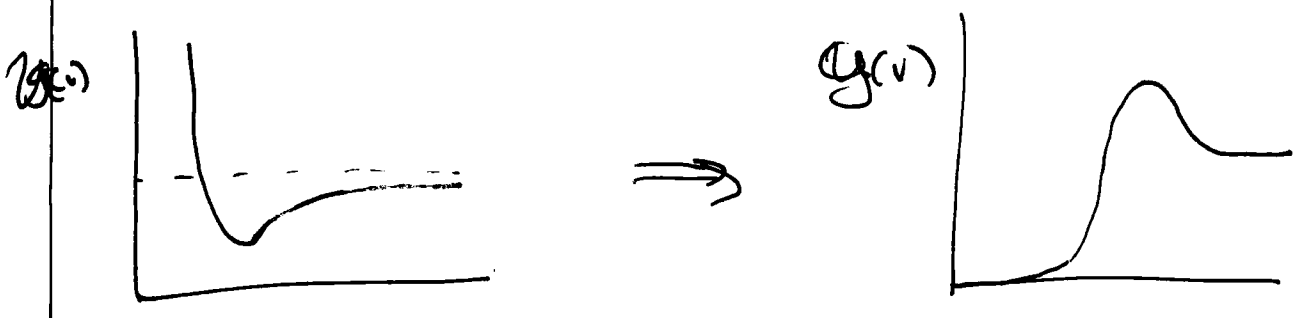
Iterative Boltzmann

Reith + Müller-Plathe, J. Comput. Chem., 24:1824 (2003)

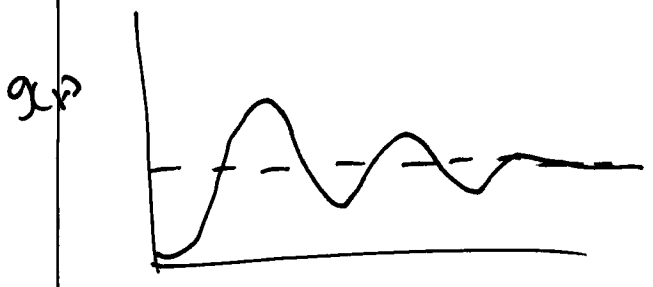
$$u_{i+1}(r) = u_i(r) - k_B T \ln \left(\frac{g_i(r)}{g(r)} \right) \quad (1)$$

\uparrow
 desired $g(r)$

At low ρ , $g(r) = e^{-u(r)}$, (exact)



At high ρ , Eq. (1) tends to overcorrect, resulting in oscillations, use



$$u_{i+1}(r) = u_i(r) - \delta k_B T \ln \frac{g_i(r)}{g(r)}$$

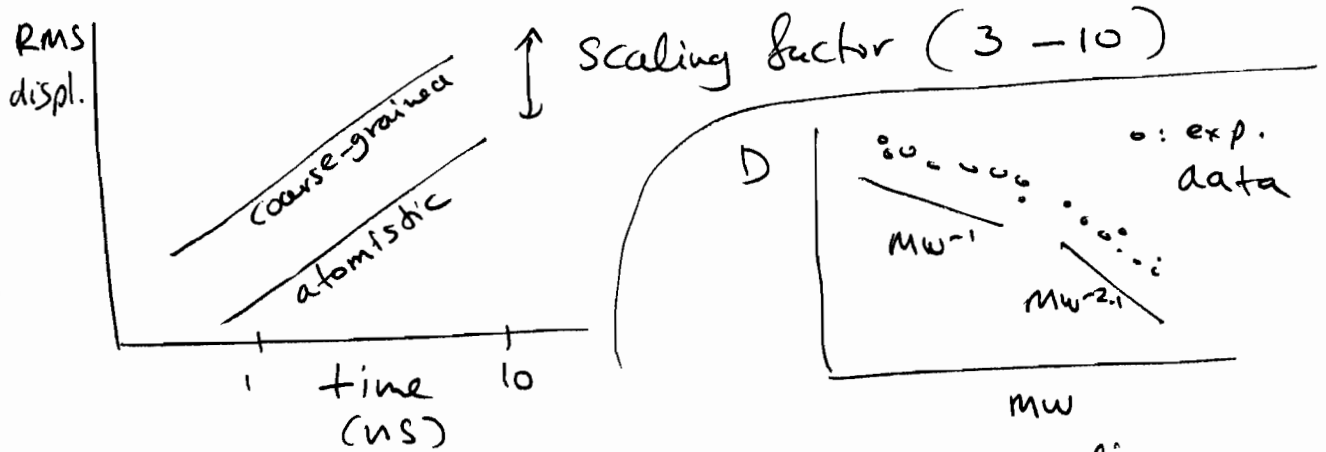
\uparrow

$$\delta < 1$$

National Brand

Dynamics

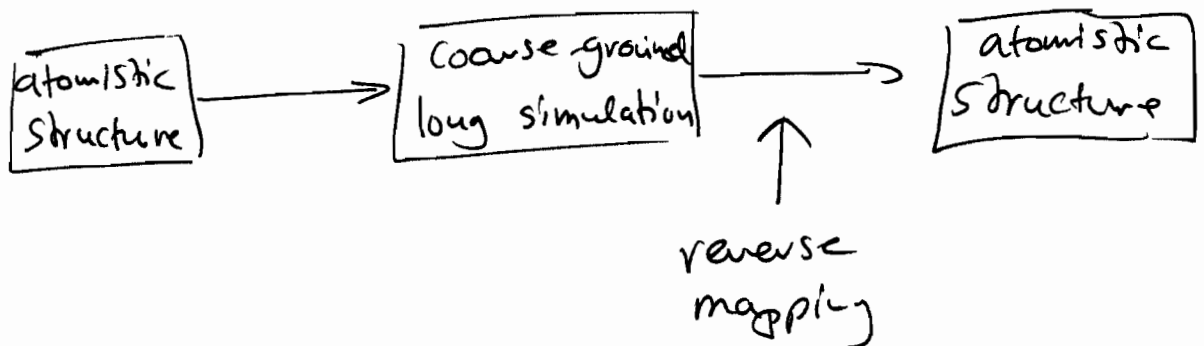
Coarse-grained models have intrinsically faster dynamics than ^{their} atomistic counterparts: (Smoother interactions, lower barriers)



good case: scaling over range of MW

Reverse Mapping

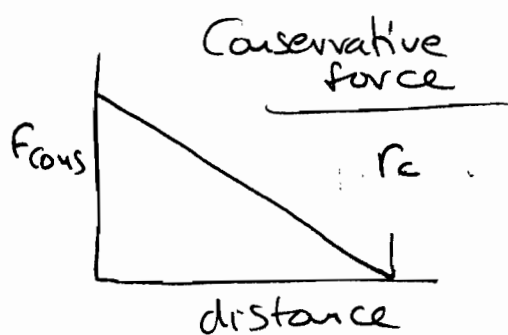
To address detailed structural questions over long time scales (e.g. for interpreting NMR data)



Dissipative Particle Dynamics

Essentially Molecular / Brownian Dynamics with a very soft potential

{ Hoogerbrugge + Koelman, Europhys. Lett., 19:155-160 }
 { Groot + Warren, JCP 107:4423-35 (1997) (1992) }



$$\text{Total force} = \sum_{j \neq i} \left(\vec{F}_{\text{cons}}(\vec{r}_{ij}) + \vec{F}_{\text{diss}}(\vec{r}_{ij}, \vec{v}_{ij}) + \vec{f}_{\text{random}}(\vec{r}_{ij}) \right)$$

Dissipative force

$$\begin{aligned} \vec{F}_{\text{diss}}(\vec{r}_{ij}, \vec{v}_{ij}) &= \\ &= -\gamma \omega^D(r_{ij}) (\vec{v}_{ij} \cdot \hat{r}_{ij}) \hat{r}_{ij} \end{aligned}$$

\uparrow friction coefficient \nwarrow distance dependence of γ

Random force

$$\vec{F}_{\text{random}}(\vec{r}_{ij}) = \sigma \omega^R(r_{ij}) \sum_{i,j} \hat{r}_{ij}$$

\nearrow magnitude of random force \uparrow dist. dependence \uparrow random # Gaussian Distr.

In order for the configurations of the system to appear with the correct Boltzmann weight, the following condition must be satisfied:

$$w^D(r_{ij}) = [w^R(r_{ij})]^2 \quad \left(\begin{array}{l} \text{often used: } (1-r)^2 r < 1 \\ w^D(r_{ij}) = \begin{cases} (1-r)^2 r < 1 \\ 0 & r \geq 1 \end{cases} \end{array} \right)$$

γ and σ are related to the temperature:

$$\sigma^2 = 2k_B T \gamma$$

DPD is similar to Brownian Dynamics, but unlike BD, DPD frictional (dissipative) + random forces conserve momentum \rightarrow

DPD obeys "hydrodynamic" (Navier-Stokes) behavior at long time + length scales

Soft, penetrable spheres \rightarrow "blobs" of fluid \rightarrow

\Rightarrow } much larger time steps can be used with respect to -e.g.- LJ simulations

Implementation Issues

I. Integration method: forces on a particle depend on its velocity

Pagonabarraga et al. Europhys. Lett., 42: 377-82 (1998) argue convincingly that a time reversible algorithm is necessary:

Leap-frog:
$$v(t + \Delta t/2) = v(t - \Delta t/2) + \Delta t \frac{F(t)}{m} \quad (1)$$

$$r(t + \Delta t) = r(t) + \Delta t v(t + \Delta t/2)$$

In DPD, force at time t depends on velocities at time $t \rightarrow$ approximate $v(t)$ as

$$v(t) = \frac{v(t + \Delta t/2) + v(t - \Delta t/2)}{2} \quad (2)$$

(2) implies that in (1) $v(t + \Delta t/2)$ appears on both sides of the equation \rightarrow solve self-consistently by iteration

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EUROPHYSICS LETTERS

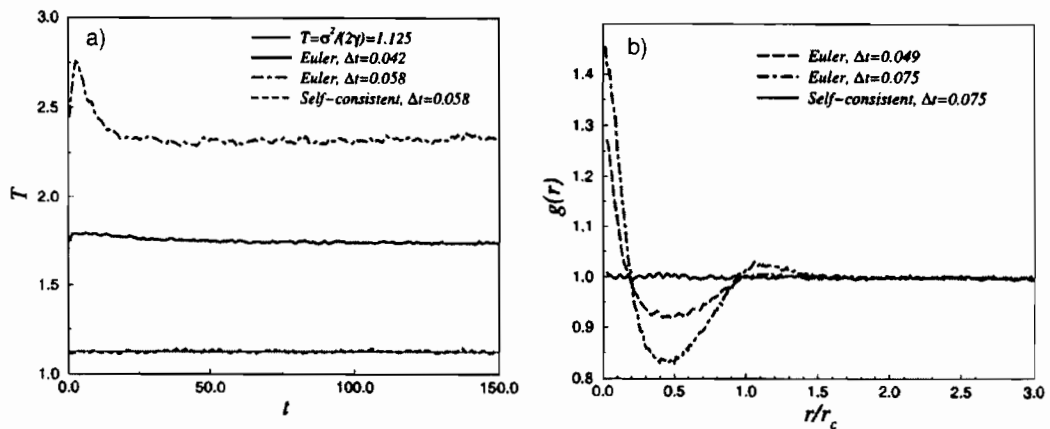


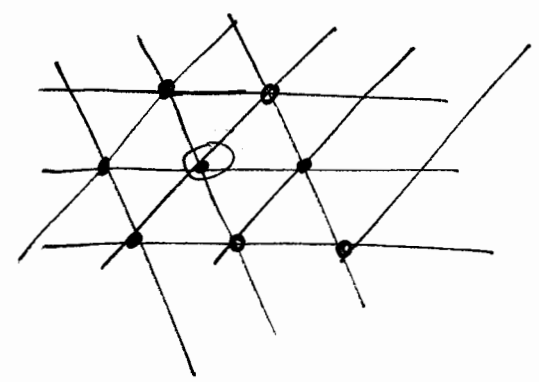
Fig. 1. - Comparison of the equilibrium properties of an ideal 2D DPD gas with the self-consistent and the Euler algorithms, for $\sigma=1.5$, $\gamma = 1$, $n = 25$, $L = 10r_c$, $r_c = 4$. a) Measured and imposed temperature; t is the time in units of $r_c \frac{m}{(2k_B T)}$. b) Radial distribution function.

Lattice-Boltzmann (LB) method

Cellular automata

Frisch et al. PRL

56(14): 1505 (1986)



* Time and space discretized

* Particles move along "links" to nearest-neighbor sites

* In LB method, particle density on a site is a continuous variable (real).

* Collision rules to preserve momentum + energy

* Recovers Navier-Stokes equations (hydrodynamics) for large systems