

CHEM-E4115

Computational Chemistry I (5op)

2nd part: molecular modelling

Electrostatics

- Computationally, electrostatics poses a major challenge
 - long-ranged and decays as $1/r$
 - In general, we define a long-range interaction as one for which $V(r) \sim 1/r^a$, where $a < d$, and d is the dimension of space
- Cut-off, reaction-field, Ewald-type methods, multipole expansions, ...

Effect of truncating electrostatic interactions in lipid bilayer: radial distribution function

Bare truncation of Coulomb interactions is likely to cause major error

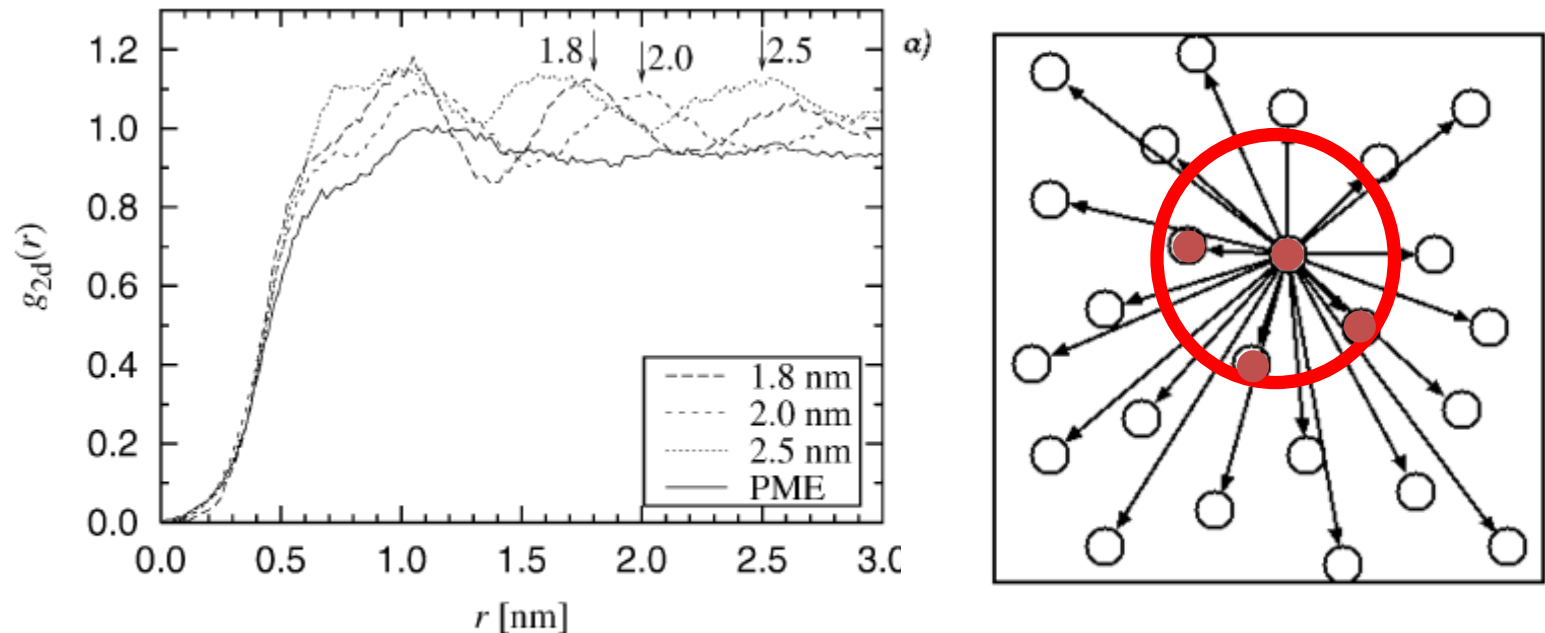


FIGURE 2 Radial distribution function $g_{2d}(r)$ for the center of mass positions of the DPPC molecules (Patra *et al.*, 2003).

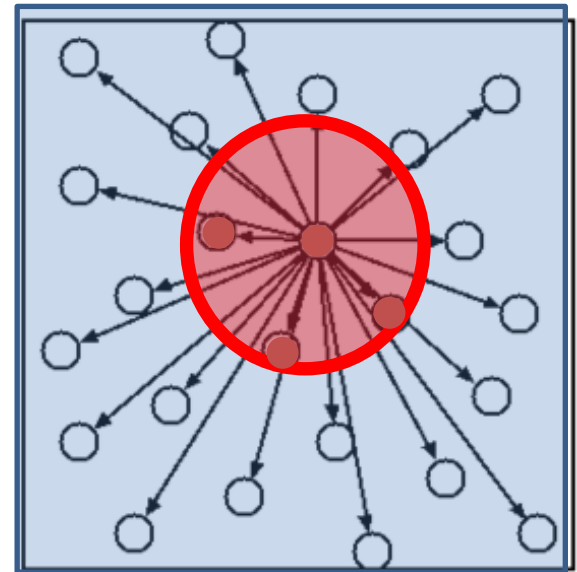
M. Patra et al., Biophys. J., 84:3636-3645, 2003

Reaction field electrostatics

- Explicit electrostatics with $r < r_{\text{cut}}$.
- For $r > r_{\text{cut}}$ the system is treated on a mean-field level and is thus completely described by its dielectric constant ϵ .

$$\mathcal{V}(r) = \frac{q_i q_j}{4\pi\epsilon_0 r} \left[1 + \frac{\epsilon - 1}{2\epsilon + 1} \left(\frac{r}{r_{\text{cut}}} \right)^3 \right] - \frac{q_i q_j}{4\pi\epsilon_0 r_{\text{cut}}} \frac{3\epsilon}{2\epsilon + 1},$$

for $r \leq r_{\text{cut}}$.



Ewald summation

- Ewald converted 1927 the slowly, conditionally convergent sum for the Coulomb potential in infinite lattice into two sums that converge rapidly and absolutely, one in real space another in reciprocal space

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1 - f(r)}{r}$$

Ewald sum: periodicity

A.Y. Toukmaji, J.A. Board Jr. / Computer Physics Communications 95 (1996) 73–92

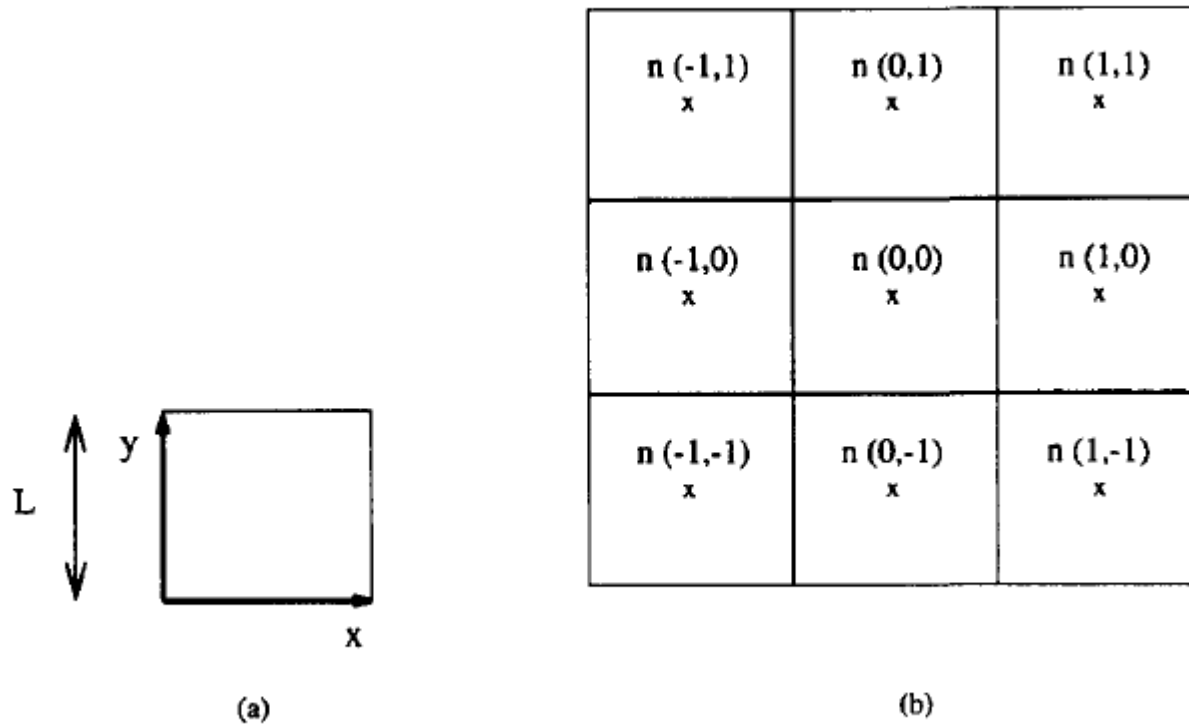


Fig. 1. In a 2D system (a) the unit cell coordinates and (b) a 3×3 periodic lattice built from unit cells.

Ewald sum

$\frac{n(-1,1)}{x}$	$\frac{n(0,1)}{x}$	$\frac{n(1,1)}{x}$
$\frac{n(-1,0)}{x}$	$\frac{n(0,0)}{x}$	$\frac{n(1,0)}{x}$
$\frac{n(-1,-1)}{x}$	$\frac{n(0,-1)}{x}$	$\frac{n(1,-1)}{x}$

$$U = \frac{1}{2} \sum_n \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{r_{ij,n}},$$

- $U_{\text{Ewald}} = U^r + U^m + U^0$
 - U^r Real space sum
 - U^m Reciprocal space sum
 - U^0 Constant term

$$U^r = \frac{1}{2} \sum_{i,j} \sum_n q_i q_j \frac{\text{erfc}(\alpha r_{ij,n})}{r_{ij,n}},$$

$$U^m = \frac{1}{2\pi V} \sum_{i,j} q_i q_j \sum_{\mathbf{m} \neq \mathbf{0}} \frac{\exp(-(\pi \mathbf{m} / \alpha)^2 + 2\pi i \mathbf{m} \cdot (\mathbf{r}_i - \mathbf{r}_j))}{m^2},$$

$$U^0 = \frac{-\alpha}{\sqrt{\pi}} \sum_{i=1}^N q_i^2.$$

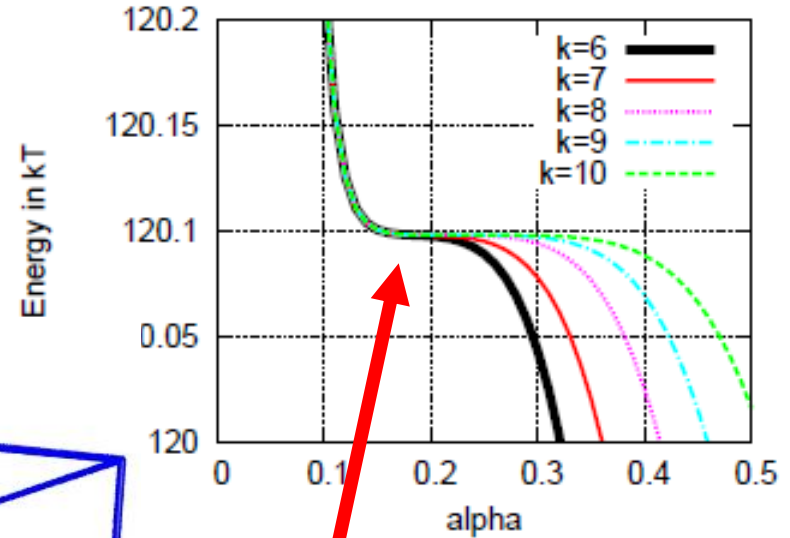
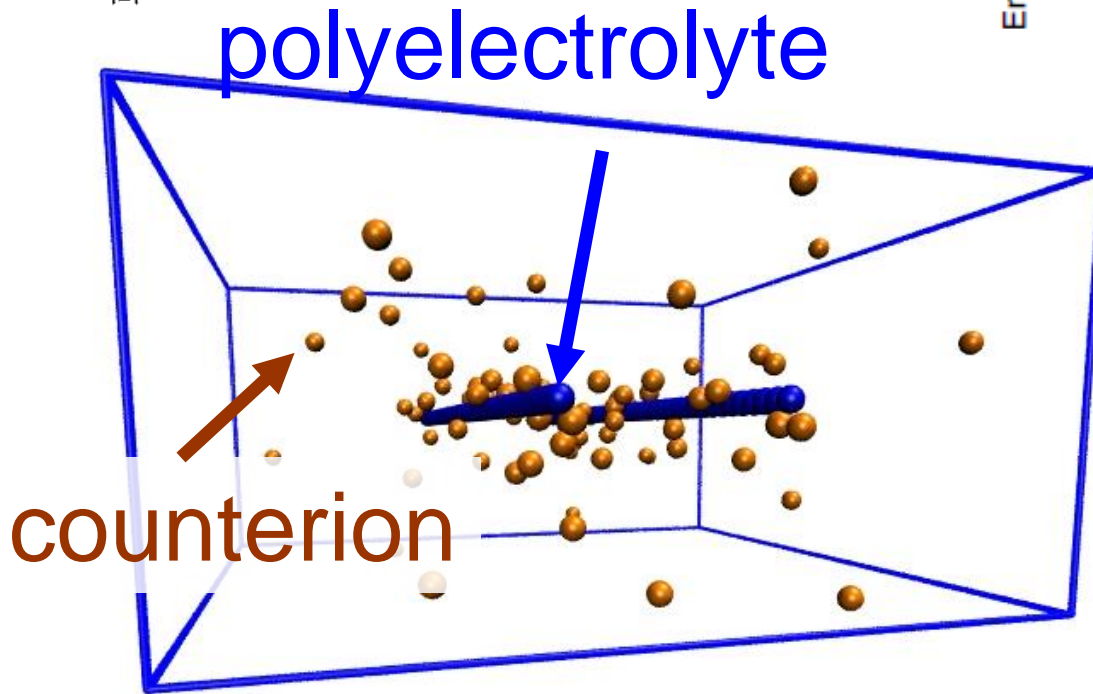
V is the volume of the simulation box, $\mathbf{m} = (l, j, k)$ is a reciprocal-space vector, and \mathbf{n} was defined earlier. The self-term U^0 is a correction term that cancels out the interaction of each of the introduced artificial counter-charges with itself as will be explained in Section 2.2. The complimentary error function decreases monotonically as x increases and is defined by $\text{erfc}(x) = 1 - \text{erf}(x) = 1 - (2/\sqrt{\pi}) \int_0^x e^{-u^2} du$. The theory of Ewald summation is described in more detail by Kittel [33] and Tosi [51].

Ewald summation convergence: Example

$$U^r = \frac{1}{2} \sum_{i,j}^{N'} \sum_{\mathbf{n}} q_i q_j \frac{\text{erfc}(\alpha r_{ij,n})}{r_{ij,n}},$$

$$U^m = \frac{1}{2\pi V} \sum_{i,j}^N q_i q_j \sum_{\mathbf{m} \neq \mathbf{0}} \frac{\exp(-(\pi \mathbf{m} / \alpha)^2 + 2\pi i \mathbf{m} \cdot (\mathbf{r}_i - \mathbf{r}_j))}{m^2},$$

$$U^o = \frac{-\alpha}{\sqrt{\pi}} \sum_{i=1}^N q_i^2.$$



Convergence
Region (plateau)

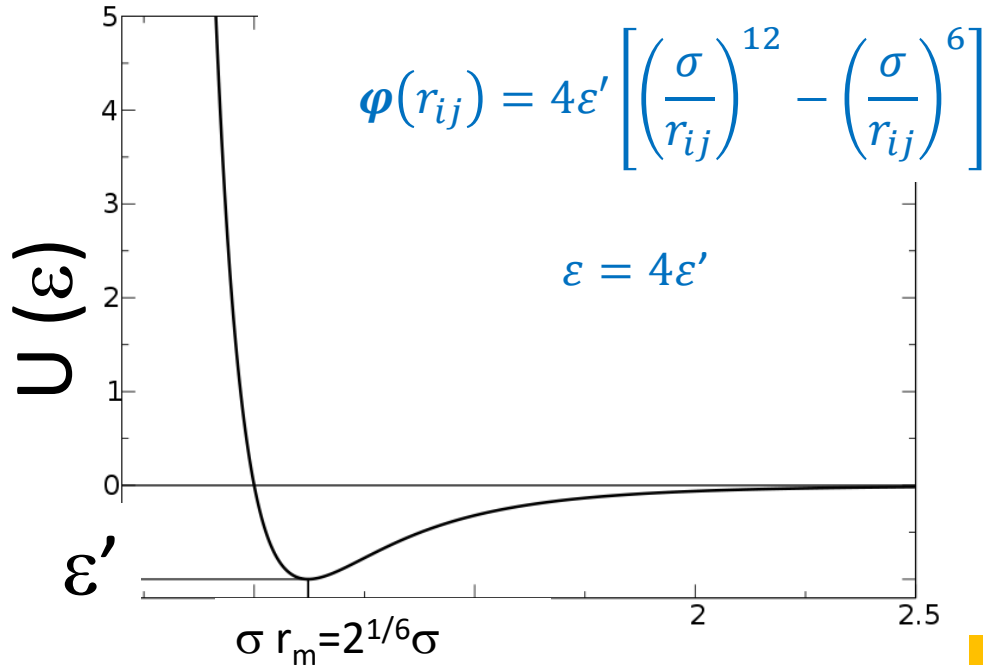
Miscellaneous topics

Dimensionless units

- Advantages
 - numerical values ~ 1 , instead of typically very small values associated with atomic scale
 - simplification of equations of motion (absorption of parameters defining the model into units)
 - possibility of scaling results of single simulation for a whole class of systems described by same model

Dimensionless units

Example: Lennard-Jones 12-6



Property	Reduced Form
Length	$r^* = r/\sigma$
Time	$t^* = t/\tau = t(\epsilon/m\sigma^2)^{1/2}$
Temperature	$T^* = k_B T/\epsilon$
Force	$f^* = f\sigma/\epsilon$
Energy	$\phi^* = \phi/\epsilon$
Pressure	$P^* = P\sigma^3/\epsilon$
Number density	$N^* = N\sigma^3$
Density	$\rho^* = \sigma^3 \rho/m$
Surface tension	$\gamma^* = \gamma\sigma^2/\epsilon$

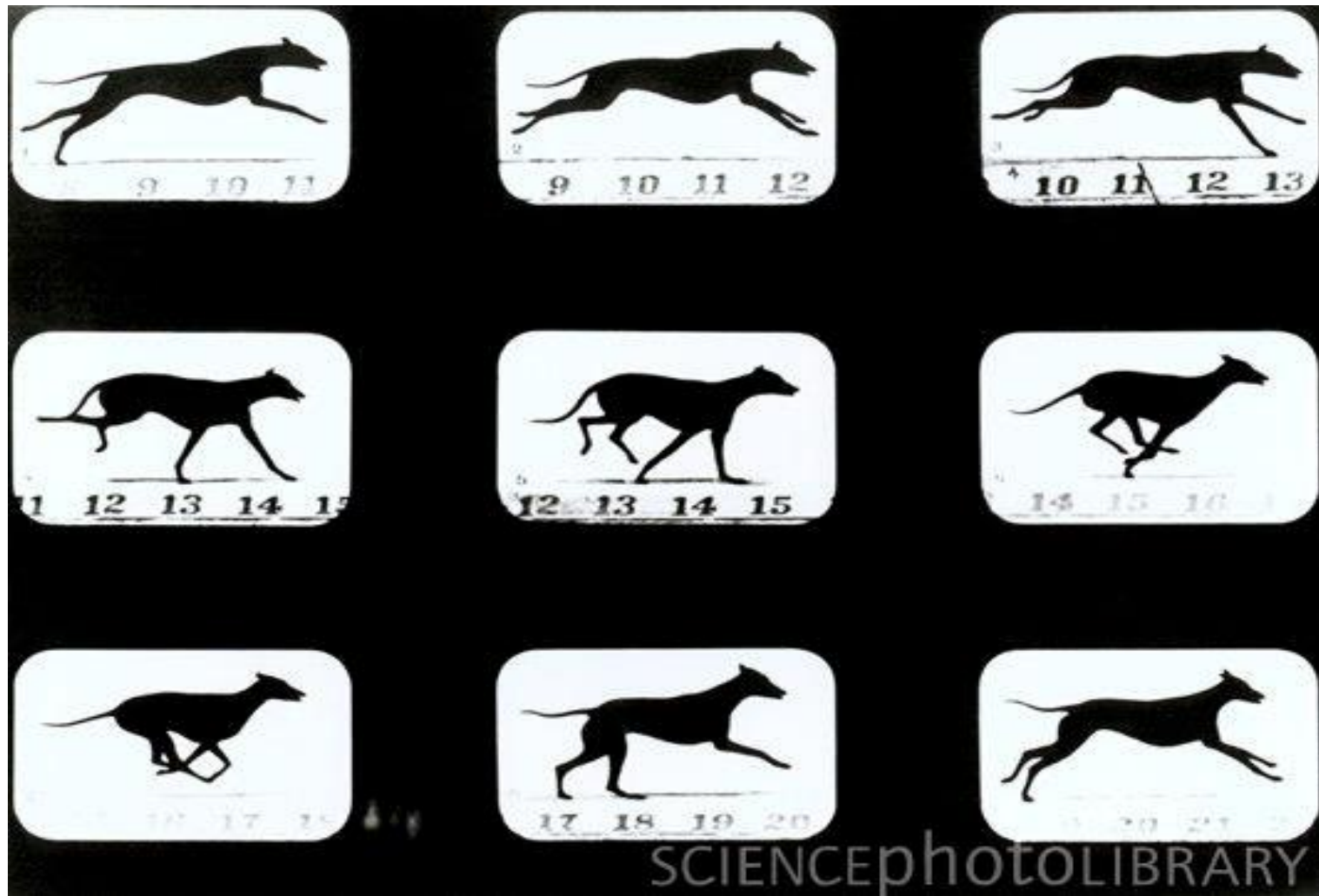
$$\varphi^*(r^*) = \left[\left(\frac{1}{r^*} \right)^{12} - \left(\frac{1}{r^*} \right)^6 \right]$$

Initial velocities for MD simulations

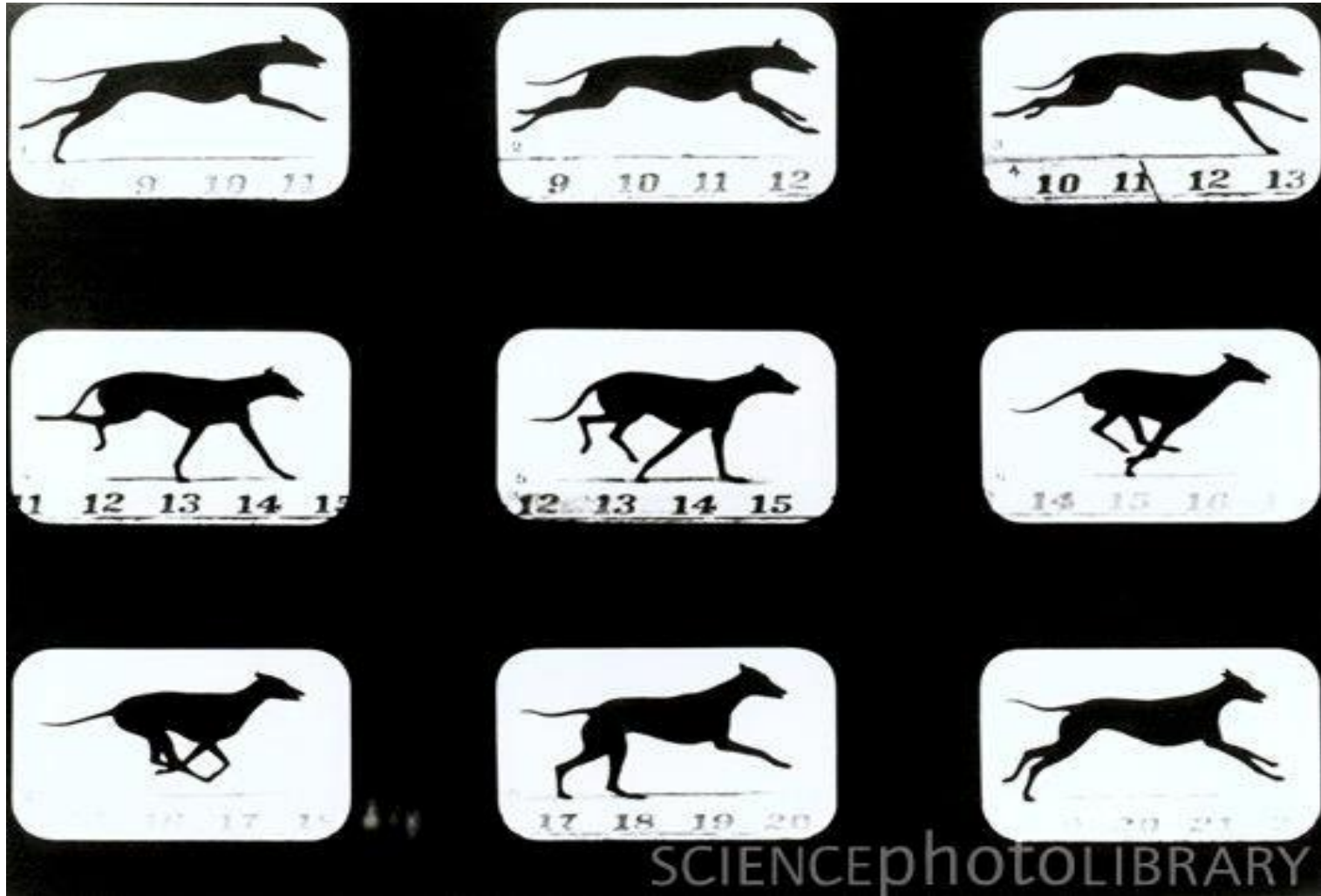
- Random initial velocities such that total momentum vanishes average conforms to desired temperature
- Initial distribution of velocity components may be
 - Uniform between $-v_{\min}$ and $+v_{\max}$
 - Gaussian:

$$\rho(v_{i,x}) = \sqrt{\frac{m_i}{2\pi k_B T}} \exp\left\{-\frac{1}{2} m_i v_{i,x}^2 / (k_B T)\right\}$$

Molecular dynamics in brief: sequence of static images



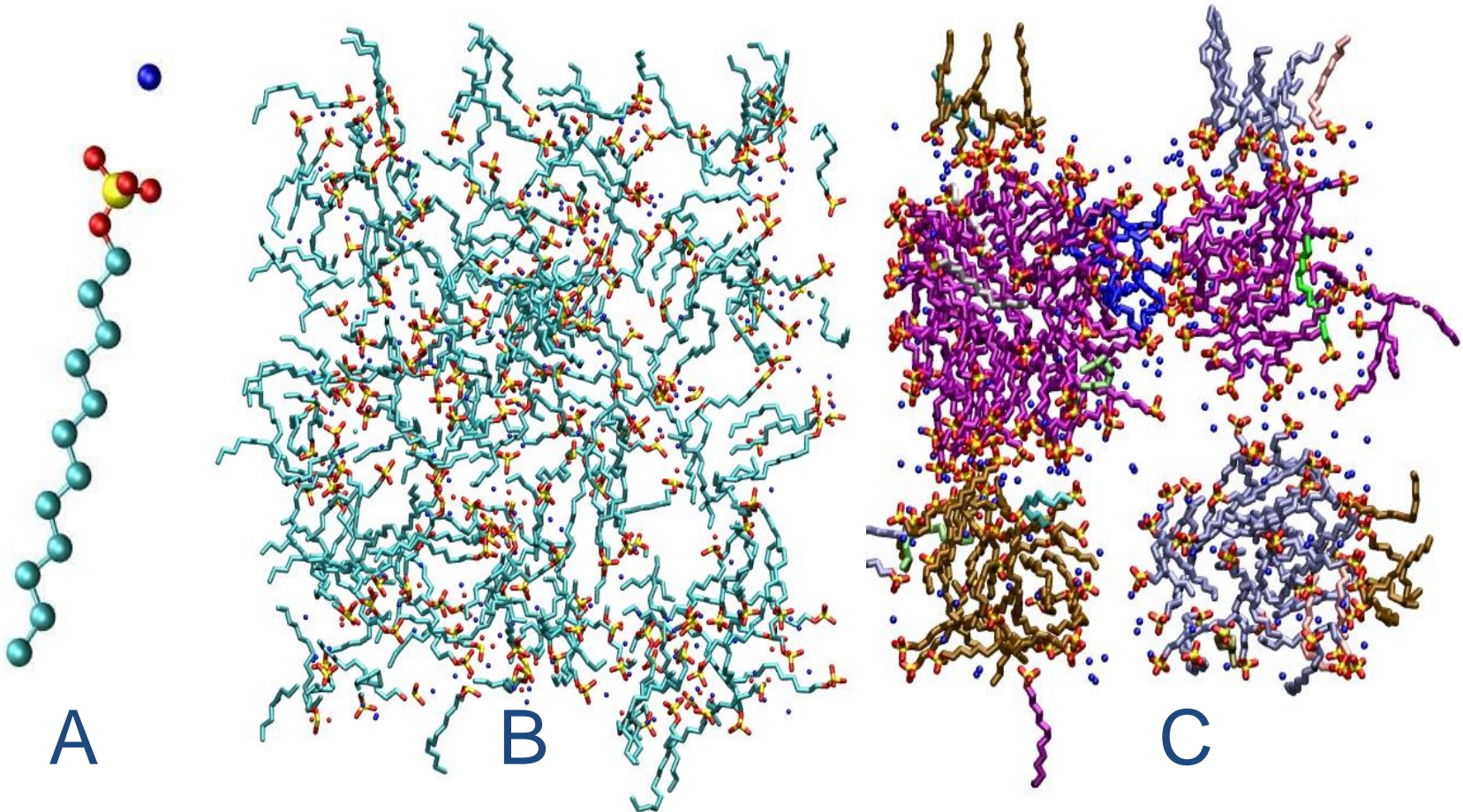
Note: Average may not be representative



Movies for visualizing molecular modelling

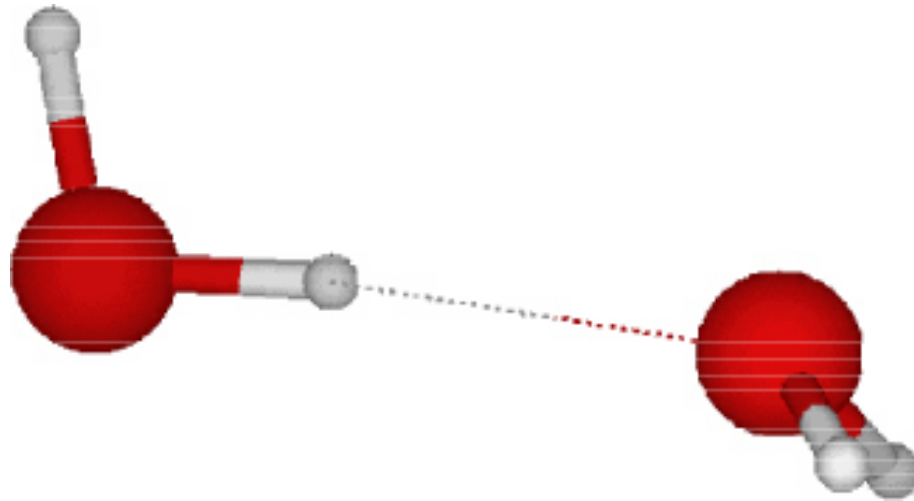
- Materials simulations (metals, surfaces, shear flows, liquids, some molecular materials...)
 - <http://lammps.sandia.gov/movies.html>
- Biomolecules
 - <http://www.ks.uiuc.edu/Gallery/Movies/>

Example: Sodium dodecyl sulfate



Cut-offs

- Same neighbor list commonly used for different interactions (van der Waals cut-off, electrostatics real space cut-off,...)
- Water dimer



Estimating errors in simulations

- Same set of initial conditions -> same results
- But there is both systematic & statistical error
 - Simulation model
 - Algorithm
 - Time steps, truncation, shifts & algorithm modifications
 - Rounding error (numerical error)
- Even if all systematic error is eliminated, statistical error remains!!!

Estimating errors in simulations

- Standard deviation and method of blocks

