Ewald and Particle Mesh Ewald and Cell Multipole method

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Complexity of Force Calculations

- Complexity is defined as how a computer algorithm scales with the number of degrees of freedom (particles)
- Number of terms in pair potential is $N(N-1)/2 \approx O(N^2)$
- For short range potential you can use neighbor tables to reduce it to $O(N)$
  - *(Verlet) neighbor list for systems that move slowly*
  - *bin sort list (map system onto a mesh and find neighbors from the mesh table)*
- Long range potentials with Ewald sums are $O(N^{3/2})$ but Fast Multipole Algorithms are $O(N)$ for very large N.

Comparison of timing for various non-bond computation methods

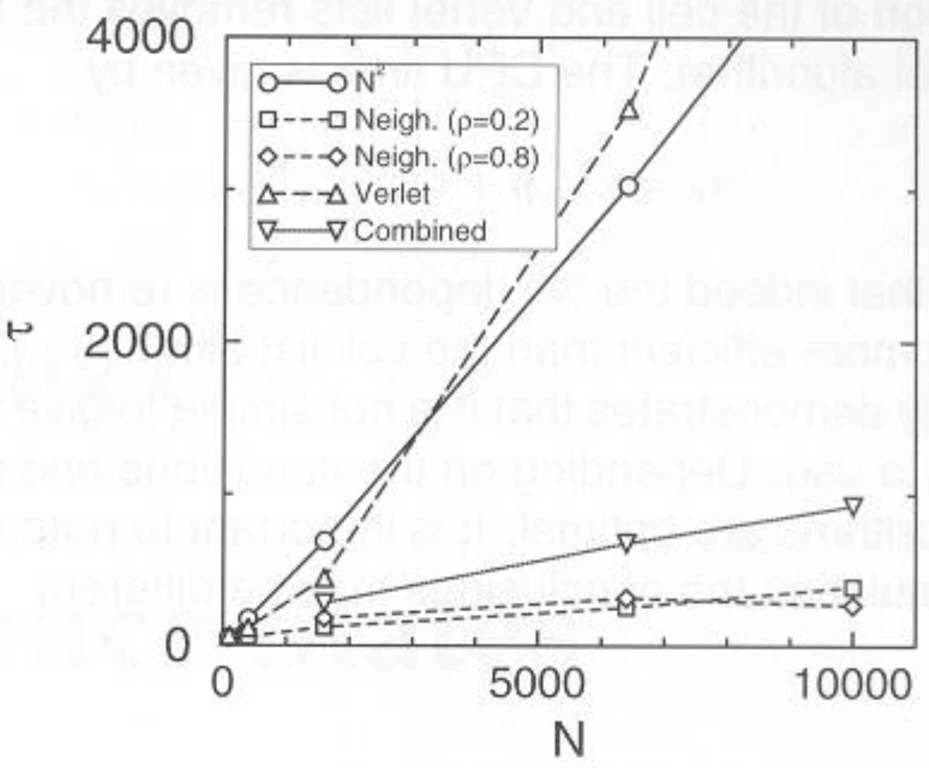


Figure from Frenkel and Smit

Comparison of various schemes to calculate the energy, time vs Number of particles N: r_c=2.5σ and Verlet Radius r_v=3.0σ

Radial Distribution Function

Radial distribution function, g(r)

- *key quantity in statistical mechanics*
- *Gives the probability of finding a pair of atoms a distance r apart,relative to the probability expected for a completely random distribution at same density*

Definition

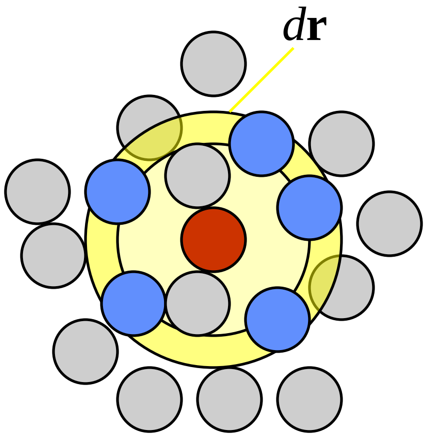
$$\boxed{g(r) = \frac{\boxed{\rho(r)d\mathbf{r}}}{\boxed{\rho^{id}(r)d\mathbf{r}}}}$$

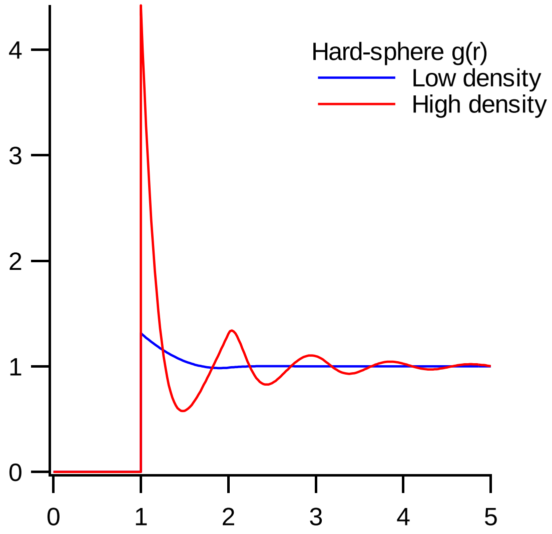
Number of atoms at r in actual system

Number of atoms at r for ideal gas

$$\rho^{id}(r)d\mathbf{r} = \frac{N}{V}d\mathbf{r}$$

$$g(r) = \frac{V}{N^2}\left\langle \sum_{i} \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle$$





Various thermodynamic quantities in terms of g(r)

Ensemble average of any pair function can be expressed in terms of g(r) as follows

$$\langle a(r_i, r_j) \rangle = \frac{1}{V^2} \int dr_i dr_j\, g(r_i, r_j) a(r_i, r_j)$$

For example we can write the energy as (assuming pair-wise additivity

$$E = \sum u_c(r_{ij}) + \frac{N\rho}{2} \int_{r_c}^{\infty} 4\pi r^2 u(r) g(r)$$

Simple Long-Range Correction

- Approximate distant interactions by assuming uniform distribution beyond cutoff: $g(r) = 1 \; r > r_{cut}$
- Corrections to thermodynamic properties
  - *Internal energy*

$$U_{lrc} = \frac{N}{2}\rho \int_{r_{cut}}^{\infty} u(r) 4\pi r^2 dr$$

  - *Virial*

$$P_{lrc} = \frac{1}{6}\rho^2 \int_{r_{cut}}^{\infty} r \frac{du}{dr} 4\pi r^2 dr$$

  - *Chemical potential*

$$\mu_{lrc} = \rho \int_{r_{cut}}^{\infty} u(r) 4\pi r^2 dr = 2\frac{U_{lrc}}{N}$$

Expression for Lennard-Jones model

$$U_{lrc}^{LJ} = \frac{8}{9}\pi N \rho \sigma^3 \varepsilon \left[\left(\frac{\sigma}{r_c}\right)^9 - 3\left(\frac{\sigma}{r_c}\right)^3 \right]$$

$$P_{lrc}^{LJ} = \frac{32}{9}\pi \rho^2 \sigma^3 \varepsilon \left[\left(\frac{\sigma}{r_c}\right)^9 - \frac{3}{2}\left(\frac{\sigma}{r_c}\right)^3 \right]$$

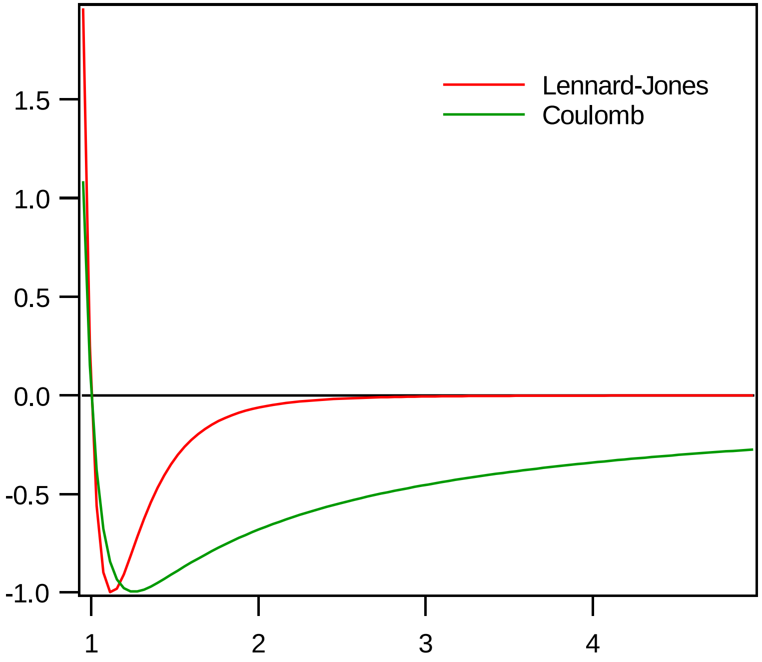
For $r_c/\sigma = 2.5$, these are about 5-10% of the total values

Coulombic Long-Range Correction

- Coulombic interactions must be treated specially
  - *very long range*
  - *1/r form does not die off as quickly as volume grows*

$$u^{tail} = \frac{N\rho}{2}\int_{r_c}^{\infty} dr\, u(r) 4\pi r^2$$

  - *Tail correction diverges unless u(r) decays faster than* r^{-3}
  - *So we can not use truncation plus long range correction for Coulombic and dipolar interactions*
- Methods
  - *Full lattice sum (Ewald summation)*
  - *Treat surroundings as dielectric continuum*



Ewald Sum (Frenkel + Smit, Ch 12)

Consider a system of N positively and negatively charged particles in a volume V ($V=L^3$).

Assume charge neutrality $\sum_i q_i = 0$

Coulomb energy of this N-particle system is given by

$$u_{Coul} = \frac{1}{2}\sum_{i=1}^{N} q_i \phi(r_i)$$

$\phi(r_i)$ is the electrostatic potential at the position of ion i

$$\varphi(r_i) = \sum_{j=1}^{N} \sum_{|n|}{}' \frac{q_j}{|r_{ij} + nL|}$$

For example image correspond to |n| =0 is n =(0,0,0); |n|=1 correspond to $n=(\pm L,0,0)$ $n=(0,\pm L,0)$ $n=(0,0,\pm L)$

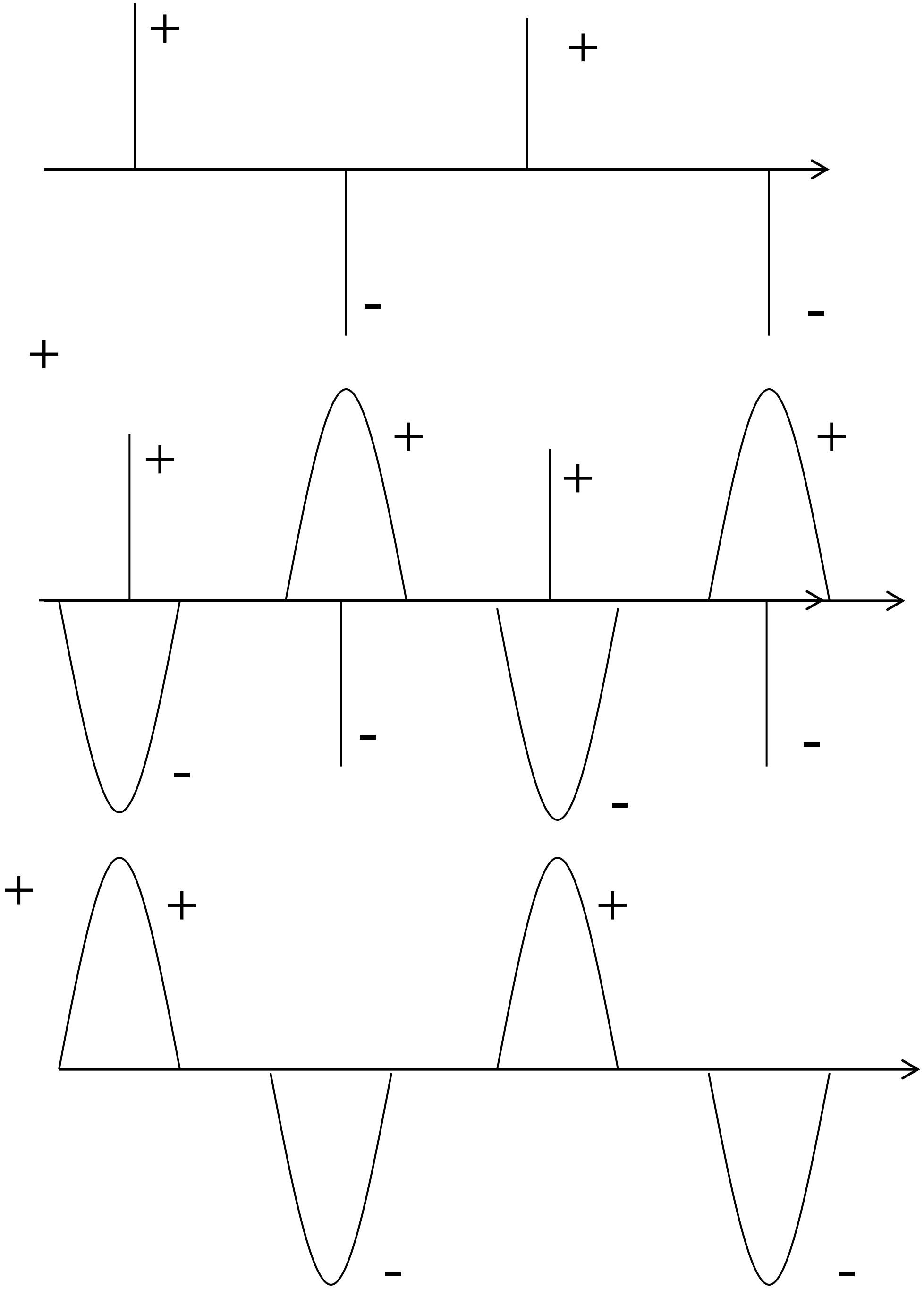
The prime on the summation indicates that the sum is over all periodic images n and over all particles j, except j =i if n=0. The sum is conditionally convergent. : it contains a mixture of positive and negative terms Separately both the positive and negative terms form a divergent series. The sum of a conditionally convergent series depents on the order in which its terms are considered.

A series $\sum_{n=0}^{\infty} a_n$ is said to **converge conditionally** if $\lim_{m\to\infty} \sum_{n=0}^{m} a_n$ exists and is a finite number (not ∞ or $-\infty$), but $\sum_{n=0}^{\infty} |a_n| = \infty.$

A classical example is given by

$$1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \cdots = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n}$$

which converges to $\ln(2)$ but is not absolutely convergent



Real Space

Reciprocal Space

Now we have three contribution

- Potential due to point charge q_i
- Potential due to Gaussian screening charge cloud with charge $-q_i$
- Potential due to compensating charge cloud with charge q_i

The contribution to the electrostatic potential at point r_i due to a set of screened charges can easily be computed by direct summation because the electrostatic potential due to screened charge is a rapidly decaying function of r. A Gaussian charge distribution of following form is Commonly used

$$\rho(r)=\frac{q_i\alpha^3}{\pi^{3/2}}\exp(-\alpha^2 r^2)$$

Review of Basic Electrostatics

- Force between charges $\mathbf{F} = \frac{q_1 q_2}{r^2}\hat{\mathbf{r}}$
- In terms of electric field $\mathbf{F}(\mathbf{r}) = q_1\mathbf{E}(\mathbf{r})$
- Static electric field satisfies

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = 4\pi\rho(\mathbf{r})$$

$$\nabla \times \mathbf{E}(\mathbf{r}) = 0$$

- Charge density ρ(**r**)
  - *for point charge q_2:* $\rho(\mathbf{r}) = q_2\delta(\mathbf{r})$
- Electrostatic potential
  - *zero curl implies **E*** can be written $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r})$
  - *potential energy of charge q_1 at* **r**, *relative to position at infinity*

$$u(\mathbf{r}) = q_1\phi(\mathbf{r})$$

- Poisson's equation
  - $\nabla^2\phi = -4\pi\rho$

For a single charge z at the origin the solution of this equation is the Coulomb potential

$$\phi(r) = \frac{z}{4\pi |r|}$$

For a collection of N point charges we can define a charge density

$$\rho_p(r) = \sum_{i=1}^{N} q_i \delta(r - r_i)$$

Potential at point r can be written as

$$\phi(r) = \sum_{i=1}^{N} \frac{q_i}{4\pi |r - r_i|}$$

Fourier transform allows us to cast these equations in a different form.Let us consider a periodic system with a cubic box of length and volume V. Any function f(r) that depends on the coordinates can be written as a Fourier series

$$f(r)=\frac{1}{V}\sum_{l=-\infty}^{\infty}\tilde{f}(k)e^{ik\cdot r}$$

Where k=(2π/L)l with l=(l_x,l_y,l_z) are the lattice vectors in Fourier space.The Fourier coefficients f(k) are calculated using

$$\tilde{f}(k)=\int 4\pi r^2 dr f(r)e^{-ik\cdot r}$$

Poisson's equation in Fourier space takes the following form

$$-\nabla^2\phi(r)=-\nabla^2\left(\frac{1}{V}\sum_k\tilde{\phi}(k)e^{ik\cdot r}\right)$$
$$=\frac{1}{V}\sum_k k^2\tilde{\phi}(k)e^{ik\cdot r}$$

If take the following form for Fourier space charge density

$$\rho(r)=\frac{1}{V}\sum_k\tilde{\rho}(k)e^{ik\cdot r}$$

Poisson equation in Fourier space takes the following simple form

$$k^2\tilde{\phi}(k) = 4\pi\tilde{\rho}(k)$$

For example, to find the solution for Poisson's equation for a point charge of strength z at the origin, we have to perform the Fourier transform of a delta function

$$\begin{aligned}\tilde{\rho}(k) &= \int_V dr z \delta(r) e^{-ik\cdot r} \\ &= z\end{aligned}$$

Remember the following representation of the delta function

$$\delta(r) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ik\cdot r} dk$$

So the solution for Poisson's equation becomes

$$\tilde{\phi}(k) = \frac{4\pi z}{k^2}$$

Solution for a unit charge (often called Green's function)

$$\tilde{g}(k) = \frac{4\pi}{k^2}$$

Now for a collection of point charges with charge density given by

$$\rho(r) = \sum_{i=1}^{N} q_i \delta(r - r_i)$$

the electrostatic potential is given by

$$\tilde{\phi}(k) = \tilde{g}(k)\rho(k)$$

with

$$\rho(k) = \int_V dr \sum_{i=1}^{N} q_i \delta(r - r_i) e^{-ik \cdot r}$$

$$= \sum_{i=1}^{N} q_i e^{-ik \cdot r}$$

So in Fourier space solution of Poisson's equation is obtained by multiplying g(k) with ρ(k)

Convolution Theorem (Arfken Chapter 15)

If we have a function $f_1(x)$ which is the convolution (*) of two other functions $f_2(x)$ and $f_3(x)$

$$f_1(x) = f_2(x) * f_3(x) \equiv \frac{1}{\sqrt{2\pi}} \int f_2(x') f_3(x - x') dx'$$

Then the Fourier coefficients of these functions are related by a simple multiplication

$$f_1(k) = f_2(k) f_3(k)$$

This is useful when we have a charge distribution that does not consist of simple point charges, but a more diffusive distribution

$$\rho(r) = \sum_i q_i \gamma(r - r_i) = \int dr' \gamma(r') \rho_p(r - r')$$

$\gamma(r)$ is the shape of the single charge distribution

The solution of Poisson’s equation for such charge distribution becomes

$$\phi(k) = g(k)\gamma(k)\rho_p(k)$$

Ewald Sum

○ We want to sum the interaction energy of each charge in the central volume with all images of the other charges

- *express in terms of electostatic potential*

$$U_q = \tfrac{1}{2} \sum_{\substack{\text{charge i}\\ \text{in central}\\ \text{volume}}} q_i \phi(\mathbf{r}_i)$$

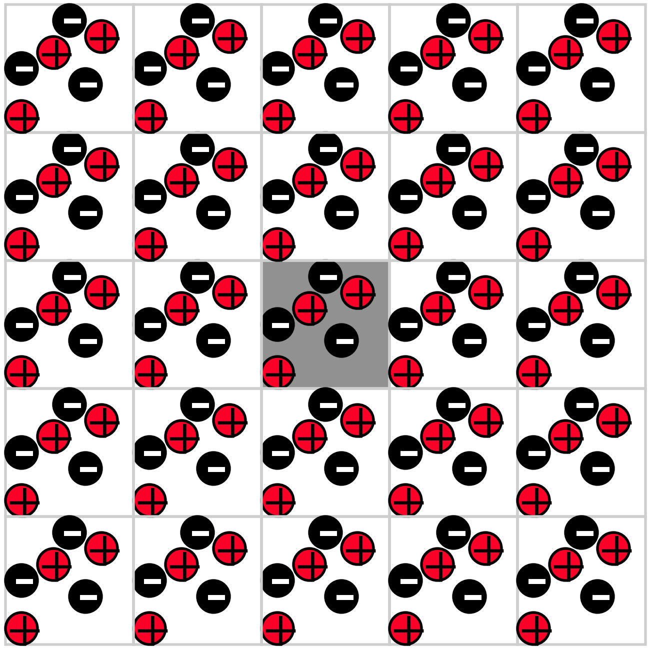
- *the charge density creating the potential is*

$$\rho(\mathbf{r}) = \sum_{\substack{\mathbf{n}\text{,image}\\ \text{vectors}}} \sum_{j \text{ in } \mathbf{n}} q_j \delta(\mathbf{r})$$

$$= \sum_{\mathbf{n}} \sum_{j} q_j \delta\left(\left|\mathbf{r} - (\mathbf{r}_j + \mathbf{n}L)\right|\right)$$

- *this is a periodic function (of period L), but it is very sharp*

Fourier representation would never converge



Ewald Sum: Fourier 1.

- Compute field instead by smearing all the charges

$$\rho(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{j} q_j (\alpha/\pi)^{3/2} \exp\left[-\alpha \left| \mathbf{r} - (\mathbf{r}_j + \mathbf{n}L) \right|^2 \right]$$

include $\mathbf{n} = 0$

Large α takes ρ back
to δ function

- Electrostatic potential via Poisson equation
  - *direct space form* $\nabla^2 \phi(\mathbf{r}) = -4\pi\rho(\mathbf{r})$
  - *reciprocal space* $k^2 \phi(\mathbf{k}) = 4\pi\rho(\mathbf{k})$
- Fourier transform the charge density

$$\rho(\mathbf{k}) = \tfrac{1}{V} \int_V d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})$$

$$= \tfrac{1}{V} \sum_j q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j} e^{-k^2/4\alpha}$$

$$a_n = \tfrac{1}{L} \int_{-L/2}^{+L/2} f(x) \cos(2\pi n x/L) dx$$

$$b_n = \tfrac{1}{L} \int_{-L}^{+L} f(x) \sin(2\pi n x/L) dx$$

Charge density in the Fourier space

$$\rho(k) = \int_V dr e^{-ik\cdot r} \rho(r)$$

$$= \int_V dr e^{-ik\cdot r} \sum_{j=1}^{N} \sum_{n} q_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\left[-\alpha \left| r-(r_j+nL) \right|^2\right]$$

$$= \int dr e^{-ik\cdot r} \sum_{j=1} q_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\left[-\alpha \left| r-r_j \right|^2\right]$$

$$= \sum_{j=1}^{N} q_j e^{-ik\cdot r_j} \exp\left(-\frac{k^2}{4\alpha}\right)$$

With the above charge density in Fourier space Poisson's equation becomes

$$k^2 \phi(k) = 4\pi\rho(k)$$

$$\phi(k) = \frac{4\pi}{k^2} \sum_{j=1}^{N} q_j e^{-ik\cdot r_j} \exp\left(-\frac{k^2}{4\alpha}\right)$$

○ Invert transform to recover real-space potential

$$\phi(\mathbf{r}) = \sum_{k\neq 0} \phi(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= \frac{1}{V} \sum_{k\neq 0} \sum_{j} \frac{4\pi q_j}{k^2} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_j)} e^{-k^2/4\alpha}$$

- *in principle requires sum over infinite number of wave vectors* **k**
- *but reciprocal Gaussian goes to zero quickly if* α *is small*

- The electrostatic energy can now be obtained
  - *for point charges in potential of smeared charges*

$$U_q = \tfrac{1}{2}\sum_i q_i \phi(\mathbf{r}_i)$$

$$= \tfrac{1}{2}\sum_{\mathbf{k}\neq 0} \frac{4\pi V}{k^2} e^{-k^2/4\alpha} \boxed{\sum_{i,j} \frac{q_i q_j}{V^2} e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)}}$$

product of identical sums

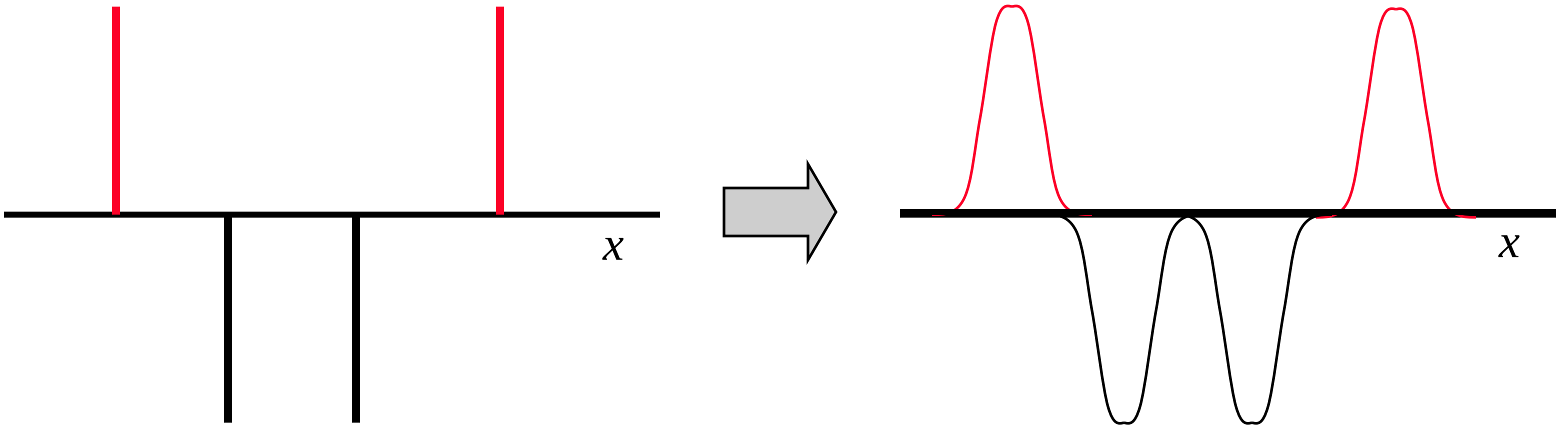
$$= \tfrac{1}{2}\sum_{\mathbf{k}\neq 0} \frac{4\pi V}{k^2} e^{-k^2/4\alpha} \left|\rho(\mathbf{k})\right|^2$$

$$\rho(\mathbf{k}) = \frac{1}{V}\sum_j q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}$$

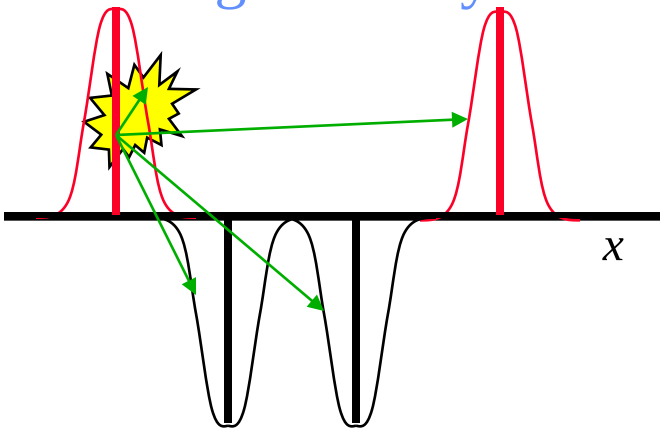
- Two corrections are needed
  - *self interaction*
  - *correct for smearing*

Ewald Sum. Self Interaction 1.

- In Ewald sum, each point charge is replaced by smeared Gaussian centered on that charge
  - *this is done to estimate the electrostatic potential field*



- All point charges interact with the resulting field to yield the potential energy
  - *This means that the point charge interacts with its smeared representation*
  - *We need to subtract this*



Ewald Sum. Self Interaction 2.

- We work in real space to deal with the self term
  - *Poisson's equation for the electrostatic potential due to a single smeared charge*

$$\nabla^2\phi(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \qquad\qquad \rho(\mathbf{r}) = q_j(\alpha/\pi)^{3/2}\exp\left[-\alpha\left|\mathbf{r}-\mathbf{r}_j\right|^2\right]$$

In Spherical coordinate with the Gaussian charge density

$$-\frac{1}{r}\frac{\partial^2 r\phi(r)}{\partial r^2} = 4\pi\rho(r)$$

Integration by parts

$$-\frac{\partial\, r\phi(r)}{\partial r} = \int_\infty^r dr 4\pi r\rho(r)$$

$$= -2\pi q_i\left(\frac{\alpha}{\pi}\right)^{3/2}\int_r^\infty dr^2\exp(-\alpha r^2)$$

$$= -2q_i\left(\frac{\alpha}{\pi}\right)^{3/2}\exp(-\alpha r^2)$$

Second partial integration gives

$$r\phi(r) = 2q_i\left(\frac{\alpha}{\pi}\right)^{3/2}\int_0^r dr\ \exp(-\alpha r^2)$$
$$= q_i\, erf\left(\sqrt{\alpha} r\right)$$

Where the error function is defined as

$$erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-u^2)du$$

So the potential at point r due to the Gaussian charge is

$$\phi(r) = \frac{q_i}{r} erf\left(\sqrt{\alpha} r\right)$$

φ(r) at r=0 is the self-term to be subtracted

$$\phi(r=0) = 2q_i\sqrt{\frac{\alpha}{\pi}}$$

Ewald Sum. Self Interaction 2.

So the self-interaction contribution to the total energy is

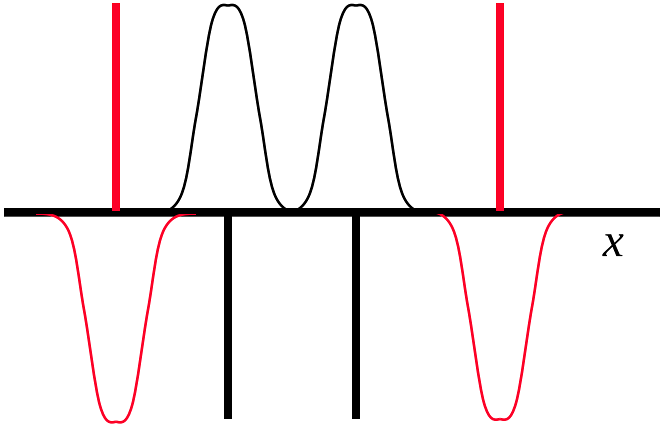
$$\begin{aligned} U_{self} &= \tfrac{1}{2}\sum_j q_j \phi(0) \\ &= \left(\tfrac{\alpha}{\pi}\right)^{1/2} \sum_j q_j^2 \end{aligned}$$

independent of configuration

Ewald Sum. Real space contribution

- We add the correct field and subtract the approximate one to correct for the smearing

$$\begin{aligned}\Delta\phi_j(\mathbf{r}) &= \phi_j^p(\mathbf{r}) - \phi_j^G(\mathbf{r}) \\ &= \frac{q_j}{\left|\mathbf{r}-\mathbf{r}_j\right|} - \frac{q_j}{\left|\mathbf{r}-\mathbf{r}_j\right|} erf\left(\sqrt{\alpha}\left|\mathbf{r}-\mathbf{r}_j\right|\right) \\ &= \frac{q_j}{\left|\mathbf{r}-\mathbf{r}_j\right|} erfc\left(\sqrt{\alpha}\left|\mathbf{r}-\mathbf{r}_j\right|\right)\end{aligned}$$



- This field is short ranged for large α (narrow Gaussians)
  - *can view as point charges surrounded by shielding countercharge distribution*

Ewald Sum. Smearing Correction 2.

○ Sum interaction of all charges with field correction

- *convenient to stay in real space*
- *usually α is chosen so that sum converges within central image*

$$\Delta U = \tfrac{1}{2}\sum_{\mathbf{n}}\sum_{i\neq j} q_i \Delta\phi_j(r_{ij})$$

$$= \tfrac{1}{2}\sum_{\mathbf{n}}\sum_{i\neq j} \frac{q_i q_j}{r_{ij}} erfc\left(\sqrt{\alpha}\, r_{ij}\right)$$

○ Total Coulomb energy

$$U_c = U_q(\alpha) - U_{self}(\alpha) + \Delta U(\alpha)$$

- *each term depends on α, but the sum is independent of it*

  if enough lattice vectors are used in the reciprocal- and real-space sums

Choice of parameters

Real space part of the energy involves evaluating
(consider $\alpha^{1/2} = \alpha$

$$\Delta U = \tfrac{1}{2} \sum_{\mathbf{n}} \sum_{i \neq j} q_i \Delta\phi_j(r_{ij})$$

$$= \tfrac{1}{2} \sum_{\mathbf{n}} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} erfc\left(\sqrt{\alpha}\, r_{ij}\right)$$

To ensure convergence of the real space part we need to choose α such that erfc is small at the real-space cutoff R. Suppose we specify small to be exp(-p). So p controls the accuracy. For large values of argument erfc behaves as exp(- $\alpha^2 r^2$). SO we demand

$$\alpha^2 r^2 = p$$

$$\text{or } \alpha = p^{1/2}/R \qquad (1)$$

In Fincham notation $\alpha = \alpha^2$

Fincham, Mol. Simulation, 13,1-9 (1994)

For reciprocal space we need to compute the following

$$\begin{aligned}U_q &= \tfrac{1}{2}\sum_i q_i \phi(\mathbf{r}_i)\\ &= \tfrac{1}{2}\sum_{\mathbf{k}\neq 0}\frac{4\pi V}{k^2}e^{-k^2/4\alpha}\sum_{i,j}\frac{q_i q_j}{V^2}e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\\ &= \tfrac{1}{2}\sum_{\mathbf{k}\neq 0}\frac{4\pi V}{k^2}e^{-k^2/4\alpha}\left|\rho(\mathbf{k})\right|^2\end{aligned}$$

The rate of convergence is controlled by the factor exp($-k^2/4\ \alpha^2$). Like before if we require the terms to have the value exp(-p) at the reciprocal cutoff K, then we have

$$p=K^2/\ 4\ \alpha^2$$

$$or\quad K = 2\alpha^{p1/2}=2p/R \qquad\qquad (2)$$

Equ. 1 and 2 specify the choice of parameters α and reciprocal cutoff K once the accuracy parameter p and real space cutoff R have been chosen

Time estimate for Ewald summation

The number of ions within the cutoff sphere is

$4\pi/3R^3n$, n is the number density

Each of the N ions interacts with the other ions in the surrounding cutoff sphere , but each pair interactions needs to be considered only once. Thus

$$T_R=1/2\ N\ 4\pi/3R^3nt_R$$

The value of reciprocal space within a cutoff K is

$$\frac{4\pi}{3}K^3=\frac{4\pi}{3}\frac{8p^3}{R^3}$$

The reciprocal-space points are given by k=2π/L(l,m,n), where l, m, n are integers. The volume of each reciprocal point is $(2\pi/L)^3$. The number of reciprocal points with the cutoff K is given by

$$\frac{4\pi}{3}\frac{8p^3}{R^3}\frac{L^3}{8\pi^3}=\frac{4\pi}{3}\left(\frac{p}{\pi}\right)^3\frac{N}{nR^3}$$

Where $n = N/L^3$

This grows as N as the density of points in k-space increases with system

For each k-points a sum over over N ions needs to be performed and the execution time is

$$T_F = \frac{1}{2}\frac{4\pi}{3}\left(\frac{p}{\pi}\right)^3 \frac{N^2}{nR^3} t_F$$

So the total execution time for real space and k-space summation is given by

$$T = \frac{1}{2}\frac{4\pi}{3}\left[NnR^3 t_R + \left(\frac{p}{\pi}\right)^3 \frac{N^2}{nR^3} t_F \right]$$

For fixed p and R, T_R varies as N and T_F varies as N^2

To find the optimal value of R which minimizes the total execution time T we have $dT/dR=0$, which gives

$$R_{OPT} = \left(\frac{p}{\pi}\right)^{1/2} \left[\frac{t_F}{t_R}\right]^{1/6} \frac{N^{1/6}}{N^{1/3}}$$

This choice of optimal real-space cutoff gives the following optimal time

$$T_{OPT} = 2T_R = 2T_F = \frac{4\pi}{3} N^{3/2} \left(\frac{p}{\pi}\right)^{3/2} \left(t_R t_F\right)^{1/2}$$

When optimized it is equally divided between real and reciprocal space parts calculation and it grows as $N^{3/2}$

Now introduce the following dimensionless parameter

$$\bar{R} = \frac{R}{L} \qquad \bar{\alpha} = p^{1/2}/\bar{R}$$

$$\bar{\alpha} = \alpha L$$

$$\bar{K} = \frac{KL}{2\pi} \qquad \bar{K} = \frac{p}{\pi \bar{R}} = \frac{p^{1/2}}{\pi} \bar{\alpha}$$

Factor of 2π is included in the definition of $\bar{K}$ so that $\bar{K}$ corresponds to integer cutoff i.e. maximum value of $(l^2+m^2+n^2)^{1/2}$

With the above definition optimized value of cutoff becomes

$$\overline{R}_{OPT} = \left(\frac{p}{\pi}\right)^{1/2} \left[\frac{t_F}{t_R}\right]^{1/6} N^{-1/6}$$

To get an estimate we assume p = π^2. This gives exp(-p) = 5.2x10^{-5} .This gives

$$\overline{\alpha} = \pi / \overline{R}$$
$$\overline{K} = \overline{\alpha}$$

Particle-Mesh Ewald Method

Break the sum in two parts each of which should converge rapidly

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

❑The first part should f(r)/r goes to zero very fast beyond some cutoff *R* so that the summation up to the cutoff is a good approximation to this contribution to the electrostatic potential

❑The second part (1-f(r))/r is a slowly varying function for all r, so that its Fourier transform can be be represented by only few k-vectors within the cutoff K. This permits an efficient computation of this part in reciprocal space

Particle Mesh based approaches rely on the use of fixed cutoff on the direct space sum together with an FFT based approximation of the reciprocal space sum that scales as *N log(N)*

We have reciprocal part of the electrostatic energy

$$U(k)=\frac{1}{2V}\sum_{k\neq 0}\frac{4\pi}{k^2}\exp\left(-\frac{k^2}{4\alpha}\right)\left|\tilde{\rho}(k)\right|^2$$

Fourier space charge density $\tilde{\rho}(k)=\int_V dr e^{-ik\cdot r}\rho(r)=\sum_{j=1}^{N} q_j e^{ik\cdot r_j}$

Recall that Fourier transformed Green's function $\tilde{g}(k)=\frac{4\pi}{k^2}$

$$\tilde{\gamma}(k)=\exp(-k^2/4\alpha^2)$$

In terms of these reciprocal part of the energy is written as

$$U_q = \frac{1}{2}\sum_j q_j \left(\frac{1}{V} \sum_{k \neq 0} \tilde{g}(k)\tilde{\gamma}(k)\tilde{\rho}(k) e^{ik \cdot r_j} \right) = \frac{1}{2}\sum_j q_j \varphi^{(k)}(r_j)$$

where $$\phi^{(k)}(r_i) = \left(\frac{1}{V} \sum_{k \neq 0} \tilde{g}(k)\tilde{\gamma}(k)\tilde{\rho}(k) e^{ik \cdot r_i} \right)$$ is the electrostatic potential due to the 2nd term in the identity

Fourier transform of which is given by

$$\tilde{\phi}^{(k)}(k) = \tilde{g}(k)\tilde{\gamma}(k)\tilde{\rho}(k)$$

As discussed earlier, products in reciprocal space correspond to convolutions in real space. So the reciprocal component of the electrostatic potential is due to the original charge distribution ρ(r) convoluted by a Gaussian smearing function γ(r)

PME implementations

Performing Fourier transformation in the reciprocal space by FFT routines involves following complicacy

- ☐Charge assignment: The point charge with continuous coordinates have to be replaced by a grid based charge density, since FFT is a discrete and finite transformation.
- ☐Solving Poisson’s equ: Poisson's equation for the discrete charge distribution has to be solved by FFT. However, It is not obvious nor true that the best grid approximation to the continuum solution of the Poisson equation is achieved by using the continuum Green function.
- ☐Force assignment: Once the electrostatic energy has been obtained from the solution of Poisson's equation the forces have to be calculated and assigned back to the particles in our system. The procedure of assigning the forces calculated on the mesh back to the actual particles can -under certain circumstances-lead to unwanted violations of Newton’s third law.

Charge assignment

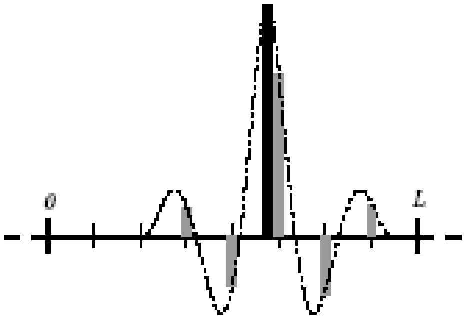
The purpose of the charge assignment is to substitute the actual charge density of point particles with a mesh based charge density. Consider first 1-d case: Define an even function W(x) such that the fraction of charge which is assigned to the mesh point x_p due to unit charge at position x is given by $W(x-x_p)$. If the charge density of the system is $\rho(x)$, then the mesh based charge density ρ_M can be written as convolution

$$\rho_M(x_p) = \frac{1}{h}\int_0^L dx W(x_p - x)\rho(x)$$

$h=L/N_M$ is the spacing of grid points and N_M is the number of grid points, x_p are the mesh points with $p = 0, 1, \ldots N_{M-1}$

Three dimensional charge assignment function W(r) can be written as

$$W(r) = W(x)W(y)W(z)$$



Sketch of the 1-d charge assignment. A suitable fraction of a charge residing at some position within the interval [0:L] is assigned to its five nearest grid points of an 8-mesh. The fractions (gray) are determined by a charge assignment functions(dashed curve).

In three dimension mesh charge density can be written as

$$\rho_M(r_p) = \frac{1}{h^3}\int_{L^3} d^3 r\, W(r_p - r)\rho(r)$$

$$= \frac{1}{h^3}\sum_{i=1}^{N} q_i W(r_p - r_i)$$

Function *W* should have the following properties:

- Charge conservation: the fractional charges of one particle, which have distributed to the surrounding grid points, sum up to the total charge of the particle.
- Finite and if possible small, support (essentially the range of values for which the function is non-zero), since the computational cost increases with the number of mesh points among which the charge of each particle is distributed.
- Localization of discretization errors: inaccuracies in the force between two particles due to the discretization should become small with increasing particle separation.
- Large degree of smoothness: the fractional charge of particle I which is assigned to some mesh point x_p should be smoothly varying function of the position of the particle i.
- Minimization of aliasing errors: the charge assignment function should decay sufficiently rapidly in the Fourier space

Solving Poisson Equation

Recall the Fourier space contribution to the electrostatic energy

$$U_q = \frac{1}{2}\sum_j q_j \left(\frac{1}{V} \sum_{k \neq 0} \tilde{g}(k)\tilde{\gamma}(k)\tilde{\rho}(k) e^{ik \cdot r_j} \right) = \frac{1}{2}\sum_j q_j \varphi^{(k)}(r_j)$$

In PME implementation it is assumed that the above equation is valid for the discrete case also with the charge density ρ(k) replaced by the Fourier transform of the mesh based charge density

$$\rho_M(r_p) = \frac{1}{h^3}\int_{L^3} d^3 r W(r_p - r)\rho(r)$$

$$= \frac{1}{h^3}\sum_{i=1}^{N} q_i W(r_p - r_i)$$

Fourier transforming gives

$$\tilde{\rho}_M(k) = h^3 \sum_{r_p \in M} \rho_M(r_p) e^{-ik \cdot r_p}$$

$r_p \in M$ is the sum over three dimensional mesh in real space and the k-vectors are from the corresponding Fourier space mesh. In this scheme continuum Coulomb Green function is best accompanied by a Lagrange interpolation scheme for the charge assignment.

Charge assignment scheme by Essmann et. al

Consider a single term in the Fourier sum $q_i e^{-ik\cdot r_i}$

This term can not be used in a discrete Fourier transform because r does not, in general correspond to a mesh point. However, we can interpolate $e^{-ik\cdot r_i}$ in terms of values of the complex exponential at mesh points

As in the earlier case consider 1-d sysetm: x varies between 0 and L and there are M equidistant Mesh points in this interval. The particle coordinates x_i is located between mesh points $[Mx_i/L]$ and $[Mx_i/L]+1$ where […] denotes the integer part of the real number. Let us denote $u_i = Mx_i/L$.

$$e^{-ik_x x_i} \approx \sum_{j=-\infty}^{\infty} W_{2p}(u_i - j) e^{-ik_x Lj/M}$$

Then we can write order-2p interpolation of the exponential as

$$e^{-ik_x x_i} \approx \sum_{j=-\infty}^{\infty} W_{2p}(u_i - j) e^{-ik_x Lj/M}$$

W_{2p} are the interpolation coefficients. Strictly speaking the sum over j contains only M terms. To account for the periodic boundary conditions, we have written it as -∝<j< ∝. For an interpolation of order *2p* only the *2p* mesh points nearest to x_i contributes to the sum. For all other points, W_{2p} vanish. Fourier transform of the total charge density now becomes

$$\rho_k \approx \sum_{i=1}^{N} q_i \sum_{j=-\infty}^{\infty} W_{2p}(u_i - j) e^{-ik_x Lj/M}$$
$$= \sum_j e^{-ik_x Lj/M} \sum_{i=1}^{N} q_i W_{2p}(u_i - j)$$

$$\rho_k \approx \sum_{i=1}^{N} q_i \sum_{j=-\infty}^{\infty} W_{2p}(u_i - j) e^{-ik_x Lj/M}$$

$$= \sum_{j} e^{-ik_x Lj/M} \sum_{i=1}^{N} q_i W_{2p}(u_i - j)$$

Above expression can be viewed as a discrete FT of a meshed charge density

$$\rho(j) = \sum_{i=1}^{N} q_i W_{2p}(u_i - j)$$

W_{2p} act as charge assignment coefficients

With the Lagrangian interpolation the exponential can be written as

$$\exp\left(2\pi i \frac{m_\alpha}{K_\alpha} u_\alpha\right) \approx \sum_{k=-\infty}^{\infty} W_{2p}(u_\alpha - k) \cdot \exp\left(2\pi i \frac{m_\alpha}{K_\alpha} k\right). \tag{3.5}$$

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Reciprocal part of the Coulomb energy is given by

$$
\begin{aligned}
E_{\mathrm{rec}} \approx \tilde{E}_{\mathrm{rec}} = & \frac{1}{2\pi V} \sum_{\mathbf{m}\neq 0} \frac{\exp(-\pi^2 \mathbf{m}^2/\beta^2)}{\mathbf{m}^2} \\
& \times F(Q)(m_1, m_2, m_3) F(Q)(-m_1, -m_2, -m_3) \\
= & \frac{1}{2} \sum_{m_1=0}^{K_1-1} \sum_{m_2=0}^{K_2-1} \sum_{m_3=0}^{K_3-1} F^{-1}(\psi_{\mathrm{rec}})(m_1, m_2, m_3) \\
& \times F(Q)(m_1, m_2, m_3) \cdot K_1 K_2 K_3 \cdot F^{-1}(Q)(m_1, m_2, m_3) \\
= & \frac{1}{2} \sum_{m_1=0}^{K_1-1} \sum_{m_2=0}^{K_2-1} \sum_{m_3=0}^{K_3-1} Q(m_1, m_2, m_3) \\
& \cdot (\psi_{\mathrm{rec}} \star Q)(m_1, m_2, m_3), \qquad (3.10)
\end{aligned}
$$

B-spline interpolation

$$\exp\left(2\pi i\,\frac{m_i}{K_i}\,u_i\right)\approx b_i(m_i)\sum_{k=-\infty}^{\infty} M_n(u_i-k)\cdot\exp\left(2\pi i\,\frac{m_i}{K_i}\,k\right), \qquad (4.3)$$

where $b_i(m_i)$ is given by

$$b_i(m_i)=\exp(2\pi i(n-1)m_i/K_i)\times\left[\sum_{k=0}^{n-2} M_n(k+1)\exp(2\pi i m_i k/K_i)\right]^{-1}. \qquad (4.4)$$

Back-interpolation

Back interpolation is done in a similar way as the distribution of charges to the mesh via some assignment function W. The force on a particle i is given by

$$F_i = q_i \sum_{r_p \in M} E(r_p) W(r_i - r_p)$$

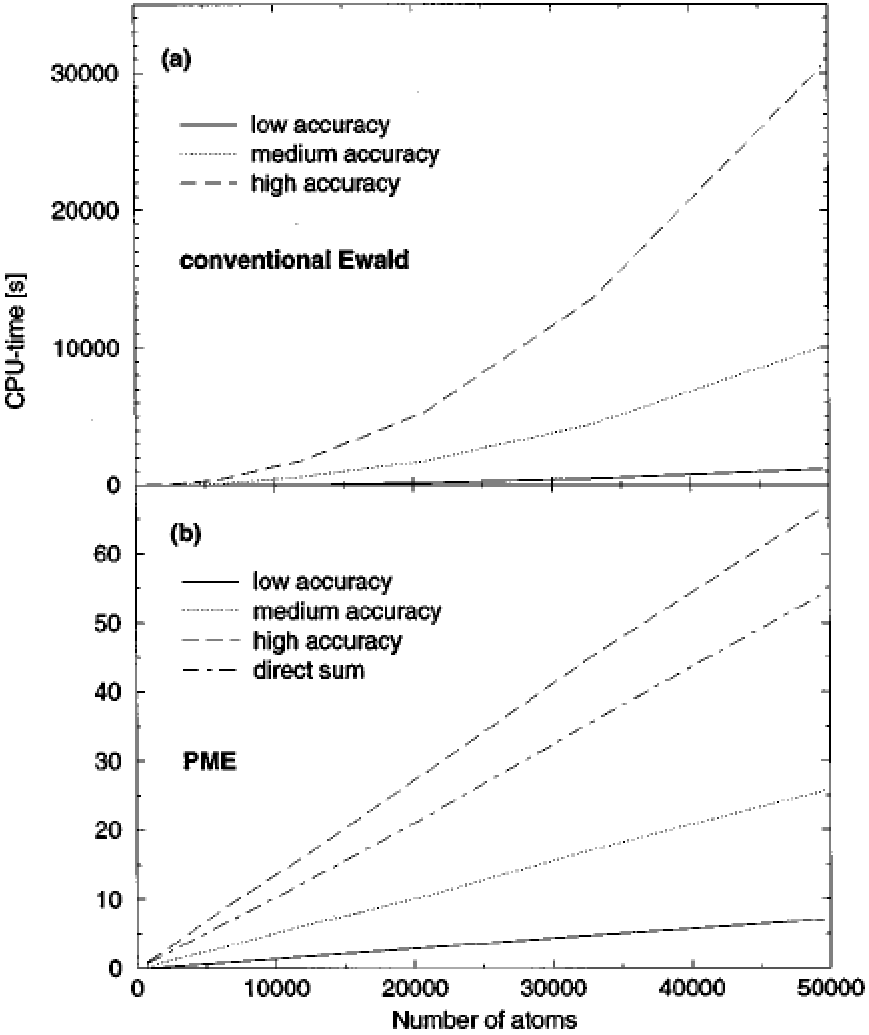


FIG. 2. Comparison of the CPU-times needed for the conventional vs PME calculation of the reciprocal sum. (a) CPU-time for the conventional calculation of the reciprocal sum as a function of system size at the three levels of accuracies described in the text; (b) CPU-time required for the same level of accuracies in the PME approach. For comparison the CPU-time for the calculation of the direct sum using a 9 Å cutoff is also shown.

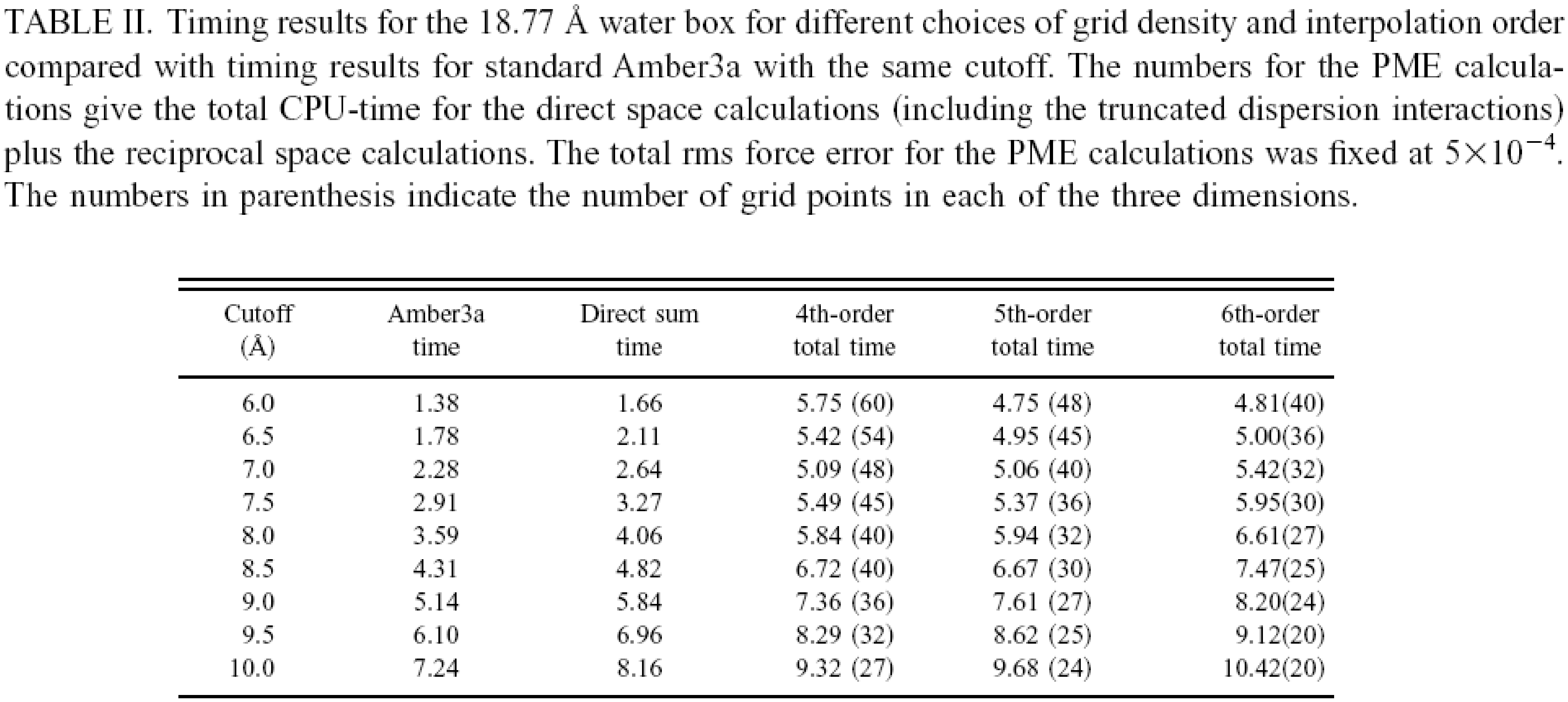


TABLE II. Timing results for the 18.77 Å water box for different choices of grid density and interpolation order compared with timing results for standard Amber3a with the same cutoff. The numbers for the PME calculations give the total CPU-time for the direct space calculations (including the truncated dispersion interactions) plus the reciprocal space calculations. The total rms force error for the PME calculations was fixed at 5×10^{-4}. The numbers in parenthesis indicate the number of grid points in each of the three dimensions.

Cutoff (Å)	Amber3a time	Direct sum time	4th-order total time	5th-order total time	6th-order total time
6.0	1.38	1.66	5.75 (60)	4.75 (48)	4.81(40)
6.5	1.78	2.11	5.42 (54)	4.95 (45)	5.00(36)
7.0	2.28	2.64	5.09 (48)	5.06 (40)	5.42(32)
7.5	2.91	3.27	5.49 (45)	5.37 (36)	5.95(30)
8.0	3.59	4.06	5.84 (40)	5.94 (32)	6.61(27)
8.5	4.31	4.82	6.72 (40)	6.67 (30)	7.47(25)
9.0	5.14	5.84	7.36 (36)	7.61 (27)	8.20(24)
9.5	6.10	6.96	8.29 (32)	8.62 (25)	9.12(20)
10.0	7.24	8.16	9.32 (27)	9.68 (24)	10.42(20)

Optimal CPU time is achieved at the smallest cutoff and 5th order interpolation

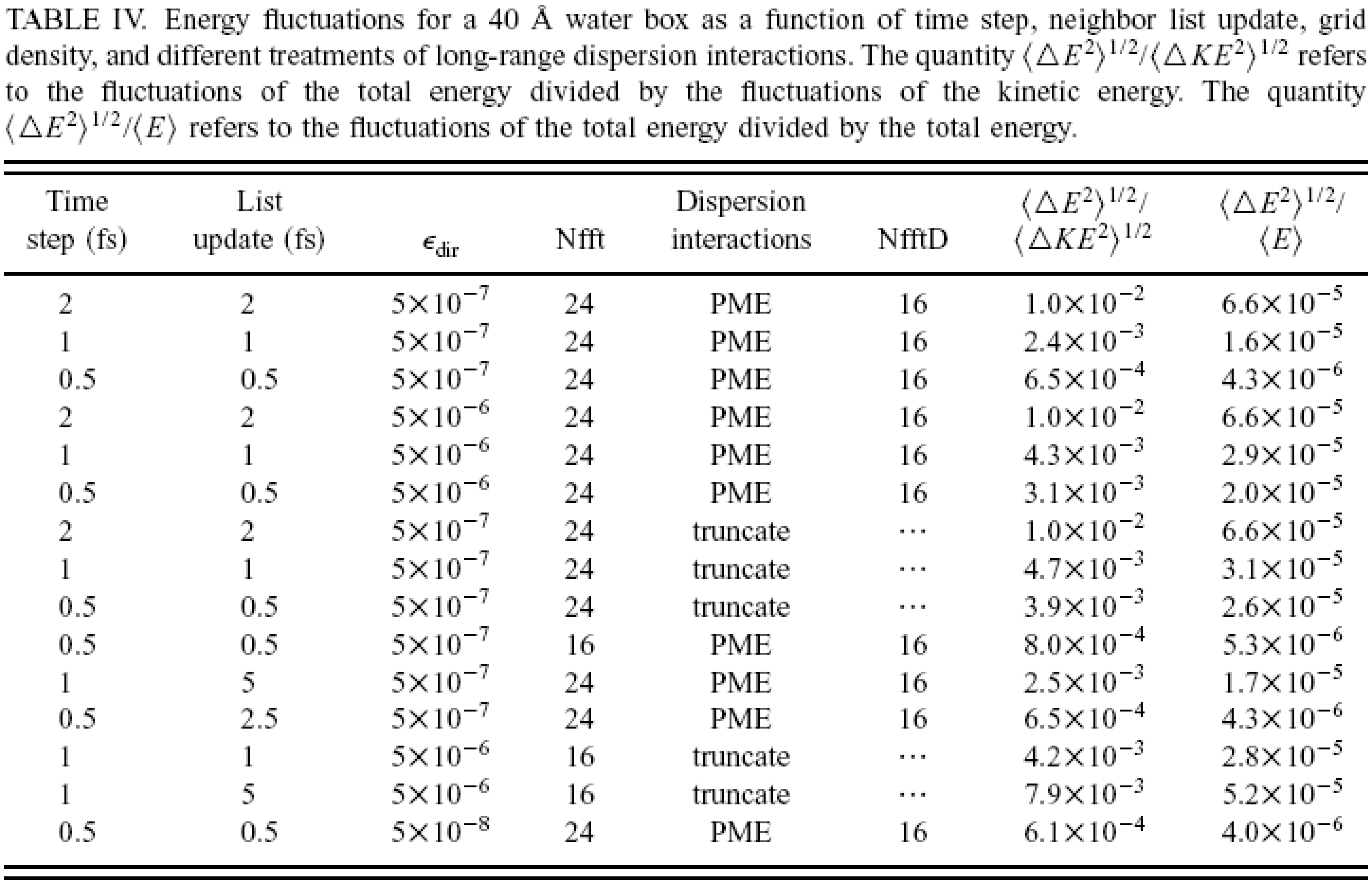


TABLE IV. Energy fluctuations for a 40 Å water box as a function of time step, neighbor list update, grid density, and different treatments of long-range dispersion interactions. The quantity $\langle \Delta E^2 \rangle^{1/2} / \langle \Delta KE^2 \rangle^{1/2}$ refers to the fluctuations of the total energy divided by the fluctuations of the kinetic energy. The quantity $\langle \Delta E^2 \rangle^{1/2} / \langle E \rangle$ refers to the fluctuations of the total energy divided by the total energy.

Time step (fs)	List update (fs)	ϵ_{dir}	Nfft	Dispersion interactions	NfftD	$\langle \Delta E^2 \rangle^{1/2} / \langle \Delta KE^2 \rangle^{1/2}$	$\langle \Delta E^2 \rangle^{1/2} / \langle E \rangle$
2	2	5×10^{-7}	24	PME	16	1.0×10^{-2}	6.6×10^{-5}
1	1	5×10^{-7}	24	PME	16	2.4×10^{-3}	1.6×10^{-5}
0.5	0.5	5×10^{-7}	24	PME	16	6.5×10^{-4}	4.3×10^{-6}
2	2	5×10^{-6}	24	PME	16	1.0×10^{-2}	6.6×10^{-5}
1	1	5×10^{-6}	24	PME	16	4.3×10^{-3}	2.9×10^{-5}
0.5	0.5	5×10^{-6}	24	PME	16	3.1×10^{-3}	2.0×10^{-5}
2	2	5×10^{-7}	24	truncate	⋯	1.0×10^{-2}	6.6×10^{-5}
1	1	5×10^{-7}	24	truncate	⋯	4.7×10^{-3}	3.1×10^{-5}
0.5	0.5	5×10^{-7}	24	truncate	⋯	3.9×10^{-3}	2.6×10^{-5}
0.5	0.5	5×10^{-7}	16	PME	16	8.0×10^{-4}	5.3×10^{-6}
1	5	5×10^{-7}	24	PME	16	2.5×10^{-3}	1.7×10^{-5}
0.5	2.5	5×10^{-7}	24	PME	16	6.5×10^{-4}	4.3×10^{-6}
1	1	5×10^{-6}	16	truncate	⋯	4.2×10^{-3}	2.8×10^{-5}
1	5	5×10^{-6}	16	truncate	⋯	7.9×10^{-3}	5.2×10^{-5}
0.5	0.5	5×10^{-8}	24	PME	16	6.1×10^{-4}	4.0×10^{-6}

RMS fluctuation in total energy is δt2, where δt is the time step. Direct sum cutoff is 8 Å and a cubic interpolation for the Coulombic reciprocal sum.

Cell Multipole Method

$$\Phi(x) = \frac{1}{2}\sum_{i \neq j} \frac{q_i q_j}{r_{ij}} = \frac{1}{2}\sum_{j} q_j \Phi(x_j)$$

$$\Phi(x_j) = \sum_{i \neq j} q_j / r_{ij}$$

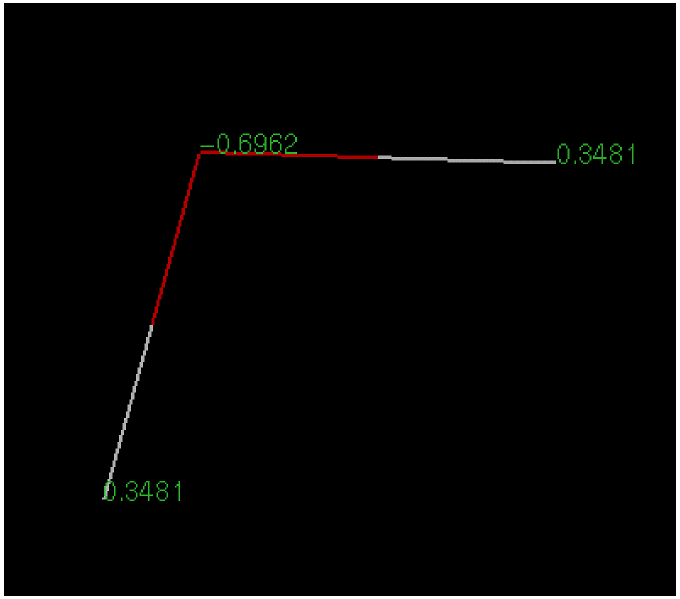
$$\Phi(x_j) = \sum_{i=1}^{N} \frac{q_i}{\left[(x_{i1} - x_{j1})^2 + (x_{i2} - x_{j2})^2 + (x_{i3} - x_{j3})^2\right]^{1/2}}$$

$$= \Phi(0) + \sum_{i=1}^{N}\sum_{k=1}^{3} \frac{\partial \Phi}{\partial x_{ik}} x_{ik} + \frac{1}{2}\sum_{i=1}^{N}\sum_{l=1}^{3}\sum_{k=1}^{3} \frac{\partial^2 \Phi}{\partial x_{ik}\partial x_{il}} x_{ik} x_{il} + higher\ order$$

$$= \Phi(0) + \nabla\Phi^T x + \frac{1}{2} x^T H x + O(x^3)$$

Structure of water

For TIP3P water
H=0.417
O=-0.834



LMP2 charges

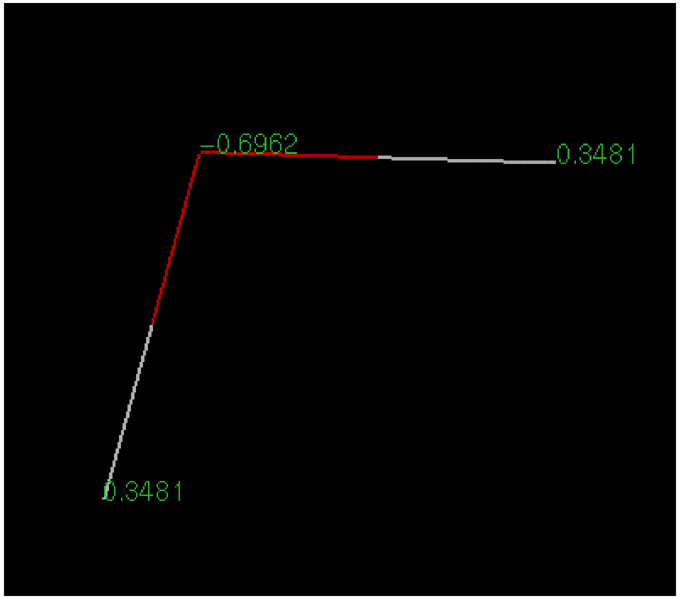
For SPC/E water
H=0.4238
O=-0.8476

Quantum Mulliken charges averaged from cluster solvation in water dielectric, single point 6-311g** DFT=Becke_3_Parameter/HF+Slater+Becke88+PW91+PW-GGAIIC (B3GGA-II)

Charges: H = 0.36433 O = -0.72866

Structure of water

For TIP3P water
H=0.417
O=-0.834



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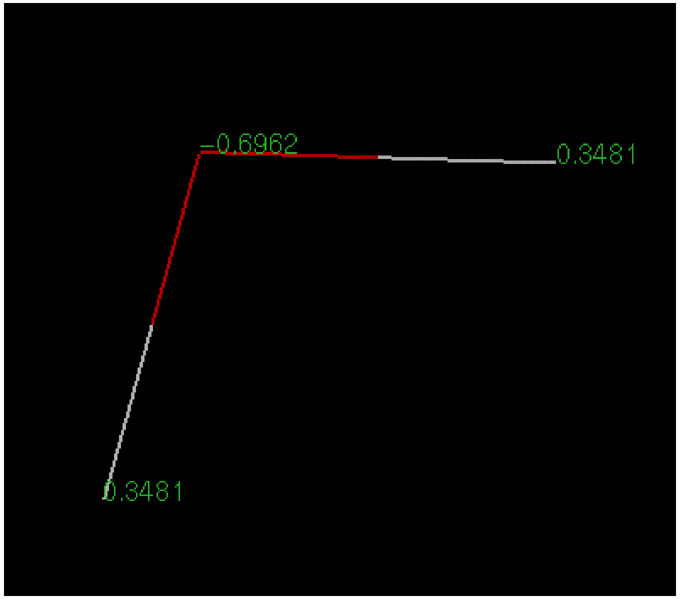
Structure of water

For TIP3P water
H=0.417
O=-0.834



LMP2 charges

For SPC/E water
H=0.4238
O=-0.8476

Quantum Mulliken charges averaged from cluster solvation in water dielectric, single point 6-311g** DFT=Becke_3_Parameter/HF+Slater+Becke88+PW91+PW-GGAIIC (B3GGA-II)

Charges: H = 0.36433 O = -0.72866

Structure of Liquid water

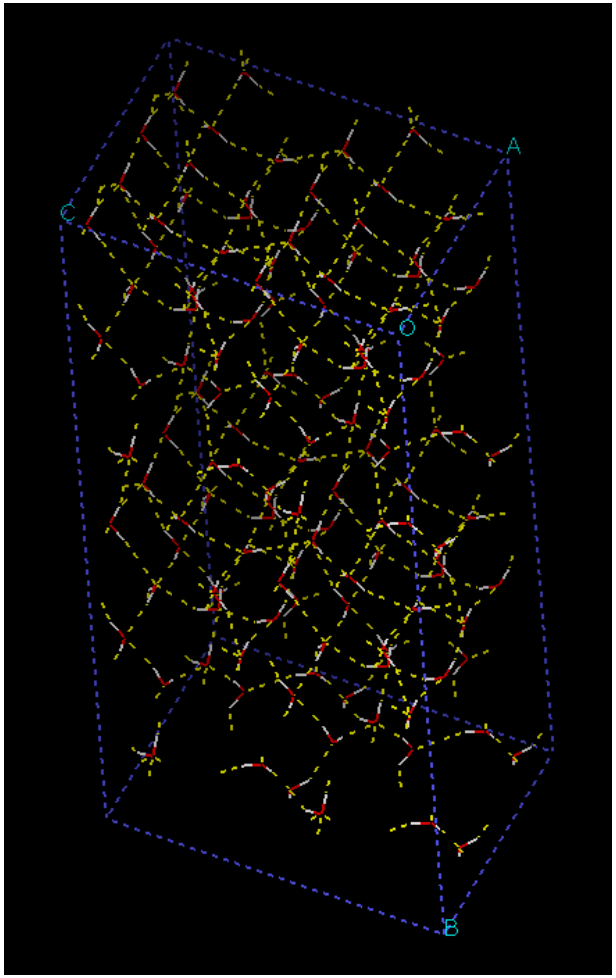
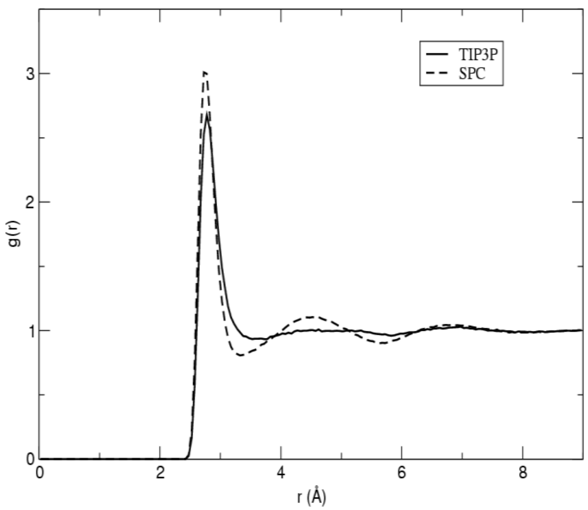
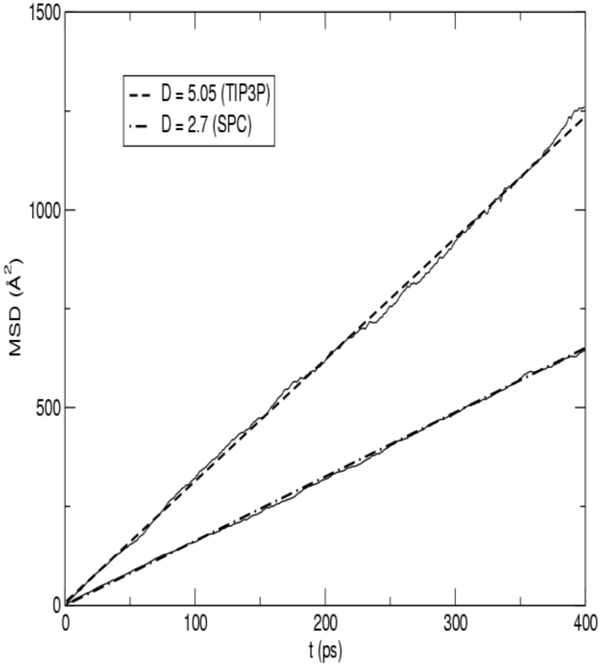


TABLE VI. Physical characteristics of different water simulations.

Water model	Num waters	Cutoff (Å)	Coulomb interactions	Dispersion interactions	E_{pot} (kcal/mol)	Density (g/cm^3)	Diff. const. (10^{-5}cm^2/s)
TIP3P	216	8.5	truncate	truncate	−9.7	0.99	5.3
TIP3P	216	8.0	Ewald	truncate	−9.5	0.97	5.1
TIP3P	216	9.0	PME	truncate	−9.5	0.97	5.1
TIP3P	216	8.0	PME	truncate	−9.5	0.97	5.1
TIP3P	2038	8.0	PME	PME	−9.6	0.98	5.8
SPC/E	216	8.5	truncate	truncate	−11.3	1.00	2.5
SPC/E	216	8.0	Ewald	truncate	−11.1	0.98	2.4
SPC/E	216	8.0	PME	truncate	−11.1	0.98	2.3
SPC/E	216	9.0	PME	truncate	−11.1	0.99	2.7
SPC/E	216	8.0	PME	PME	−11.2	1.00	2.3
SPC/E	216	9.0	PME	PME	−11.2	1.00	2.5
SPC/E	2038	9.0	PME	truncate	−11.1	0.99	2.6
SPC/E	2038	8.0	PME	PME	−11.2	1.00	2.6


TIP3P
SPC
g(r)
0
1
2
3
0
2
4
6
8
r (Å)


D = 5.05 (TIP3P)
D = 2.7 (SPC)
MSD (Å^2)
0
500
1000
1500
0
100
200
300
400
t (ps)