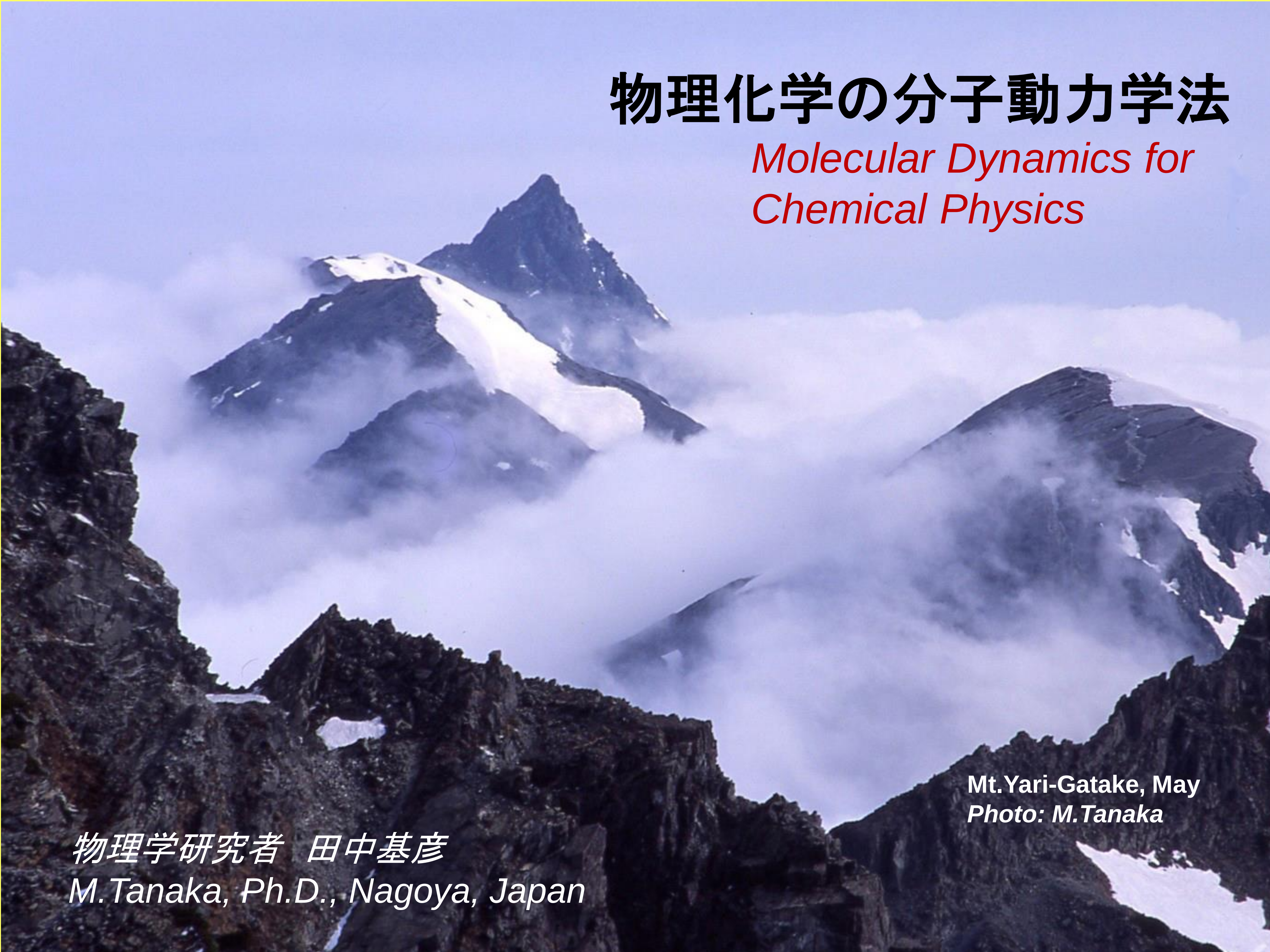
物理化学の分子動力学法

Molecular Dynamics for Chemical Physics



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M.Tanaka, Ph.D., Nagoya, Japan

分子系を扱う分子動力学
Molecular Dynamics of Small Molecules

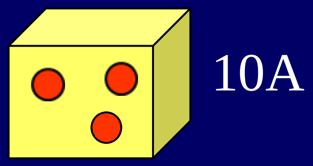
「氷（ice）は，マイクロ波オーブンでは融けない！」
“Ice state is frozen and not melted by microwaves”

Tanaka and Sato, JCP (2007)

In small molecules and matters
similar masses, Debye screening is weak
merely few or no charges in Debye radius

$$\lambda_D = \left(\varepsilon kT / 8\pi n e^2\right)^{1/2} \sim 2.4\,\text{Angstrom}, \quad n\lambda_D^3 \sim 0.014$$

charge *e*



$\varepsilon \approx 80$

⇓

Close interaction of atoms is quite frequent at a few Angstro
Coulombic interaction as two bodies is correctly calculated

References

1. *Classical Mechanics, H. Goldstein, C. Poole, J. Safko 3rd Edition, Pearson Education Inc., England, 2003.*
   「古典力学」, 吉岡書店, 2006。
2. *「分子シミュレーション」 上田顯, 裳華房。*
3. *「高温プラズマの物理学」 田中基彦, 西川恭治, 丸善, 1991,1996。*

Integrate Differential Equations

Translational part of Newton equation of motion

$$m_i \frac{d\mathbf{v}_\mathbf{i}}{dt} = F(\mathbf{r}^n) = -\nabla\left[\sum_j \frac{q_i q_j}{\varepsilon\,|\mathbf{r}_i - \mathbf{r}_\mathbf{j}|} + \Phi_{LJ}(\mathbf{r}_\mathbf{i})\right]$$

Point-to-point forces

Coulomb Lennard-Jones

Integration with

○ **Verlet algorithm**: 2-nd order O(Dt^2) scheme

○ **Leap frog algorithm**: similar to Verlet algorithm

$$\mathbf{v}^{n+1/2} - \mathbf{v}^{n-1/2} = \frac{\Delta t}{m} F(\mathbf{r}^\mathbf{n})$$

$$\mathbf{r}^{n+1} - \mathbf{r}^n = \Delta t\ \mathbf{v}^{n+1/2}$$

△ **Runge-Kutta algorithm** – accurate but computationally demanding; suitable for satellite (atomic) orbit tracking

Integrate Nonlinear Equations

- Nonlinear implicit equations

$$\frac{df}{dt} = \Phi(f)$$

Iterative procedures are required for solution

Euler equation of rigid-body rotation

Constrained dynamics of molecules

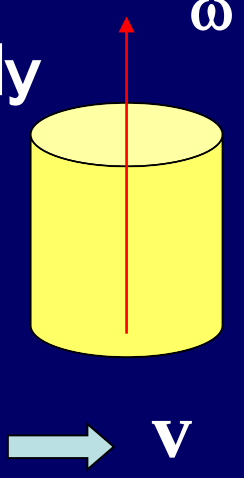
– SHAKE/RATTLE algorithm

Predictor-corrector algorithm

(1) - predictor step: Begin with an initial guess (usually the solution of a previous step), then (2) - corrector step.

Motion of Rigid Molecules

1. Solve the rotation motion of a rigid body



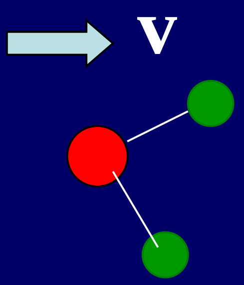
Suited for <u>a large (heavy) body, and water molecules</u>

- Translation + rotation motions
- Euler equations, quarternion representation

2. Set constraints among atoms

Good for <u>small (light) bodies</u>, like water molecules

A. Shake and rattle algorithm



$$\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = \ell_{ij}$$ for all atoms

$$\mathbf{r}_{ij} \bullet |\mathbf{v}_i - \mathbf{v}_j| = 0$$ for velocity

B. Translation + Rotation motions

-> next pages

水分子の5体・分子動力学法TIP5について

Nov.24,2020　田中基彦

水分子の分子動力学法である，5点法について解説する。最も進んでいる5つの質点を用いる原子5点法は，1個の酸素と2個の水素が質量を持ち，時間的に運動する。しかし離れた位置にある2個の水素L1, L2は，位置を決められるが運動には関与しないダミーサイトである。以下では5点法の分子動力学法を，英語で内容を述べる。

文献

1. Classical Mechanics, H. Goldstein, C. Poole, J. Safko, 3rd Edition, Pearson Education Inc., England, 2003. 「古典力学」, 吉岡書店, 2006。

2.「分子シミュレーション」 上田顕, 裳華房。

3.「高温プラズマの物理学」 田中基彦, 西川恭治, 丸善, 1991,1996。

Solving Rigid Molecules by Trans + Rotation Motions

Equation of motion

$$m_\alpha \ddot{\boldsymbol{r}}_\alpha = \boldsymbol{F}_\alpha + \sum_{\beta \neq \alpha}^{\ell} \boldsymbol{F}_{\alpha\beta}$$

α, β = 1, .. , l (atoms in the molecule)

Motion of translation

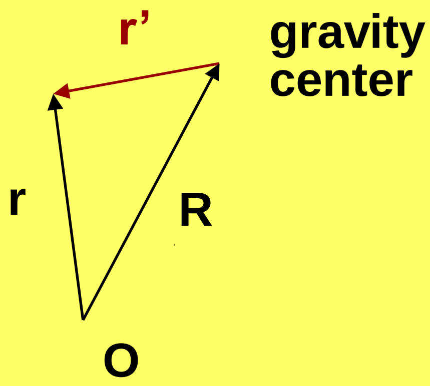
$$M_i \ddot{\boldsymbol{R}}_i = \sum_{\alpha=1}^{\ell} \boldsymbol{F}_\alpha$$

$$\boldsymbol{R}_i = \frac{\sum_{\alpha=1}^{\ell} m_\alpha \boldsymbol{r}_\alpha}{\sum_{\alpha=1}^{\ell} m_\alpha}$$

$$M_i = \sum_{\alpha=1}^{\ell} m_\alpha$$

Rigid body rotation

Make vector product with r' from the left side



$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{\alpha=1}^{\ell} \boldsymbol{r}'_\alpha \times m_\alpha \dot{\boldsymbol{r}}'_\alpha\right) = \sum_{\alpha=1}^{\ell} \boldsymbol{r}'_\alpha \times \boldsymbol{F}_\alpha$$

$$\frac{\mathrm{d}\boldsymbol{L}_i}{\mathrm{d}t} = \boldsymbol{N}_i$$

$$\boldsymbol{L}_i = \sum_{\alpha=1}^{\ell} \boldsymbol{r}'_\alpha \times \boldsymbol{p}'_\alpha$$ total angular momentum

$$\boldsymbol{N}_i = \sum_{\alpha=1}^{\ell} \boldsymbol{r}'_\alpha \times \boldsymbol{F}_\alpha$$ sum of torque

Solving Rigid Molecules (2)

Velocity of each atom on the rotating frame

$$\frac{\mathrm{d}\boldsymbol{r}'_\alpha}{\mathrm{d}t} = \boldsymbol{\omega} \times \boldsymbol{r}'_\alpha$$

$$\begin{aligned}
\boldsymbol{L}_i &= \sum_\alpha \boldsymbol{r}'_\alpha \times m_\alpha \dot{\boldsymbol{r}}'_\alpha \\
&= \sum_\alpha m_\alpha \boldsymbol{r}'_\alpha \times (\boldsymbol{\omega} \times \boldsymbol{r}'_\alpha) \\
&= \sum_\alpha m_\alpha \{ \boldsymbol{r}'^2_\alpha \boldsymbol{\omega} - (\boldsymbol{\omega} \cdot \boldsymbol{r}'_\alpha) \boldsymbol{r}'_\alpha \}
\end{aligned}$$

Total angular momentum of the rigid body is written

$$\boldsymbol{L} = \boldsymbol{I} \boldsymbol{\omega}$$

inertial moment

$$\boldsymbol{I} = \begin{pmatrix}
\sum_\alpha m_\alpha (y'^2_\alpha + z'^2_\alpha) & -\sum_\alpha m_\alpha x'_\alpha y'_\alpha & -\sum_\alpha m_\alpha x'_\alpha z'_\alpha \\
-\sum_\alpha m_\alpha y'_\alpha x'_\alpha & \sum_\alpha m_\alpha (z'^2_\alpha + x'^2_\alpha) & -\sum_\alpha m_\alpha y'_\alpha z'_\alpha \\
-\sum_\alpha m_\alpha z'_\alpha x'_\alpha & -\sum_\alpha m_\alpha z'_\alpha y'_\alpha & \sum_\alpha m_\alpha (x'^2_\alpha + y'^2_\alpha)
\end{pmatrix}$$

Euler Equation for Rigid-Body Rotation

Derivative d'/dt viewed on the rotating frame

$$\frac{d\boldsymbol{L}_i}{dt} = \frac{d'\boldsymbol{L}_i}{dt} + \boldsymbol{\omega}_i \times \boldsymbol{L}_i = N_i$$ Euler equation

$$\frac{d'L_x}{dt} + (\omega_y L_z - \omega_z L_y) = N_x$$

$$\frac{d'L_y}{dt} + (\omega_z L_x - \omega_x L_z) = N_y$$

$$\frac{d'L_z}{dt} + (\omega_x L_y - \omega_y L_x) = N_z$$

By choosing a proper molecule frame (principal coordinate), the matrix becomes a constant of motion

$$L_x = I_x \omega_x$$

$$L_y = I_y \omega_y$$

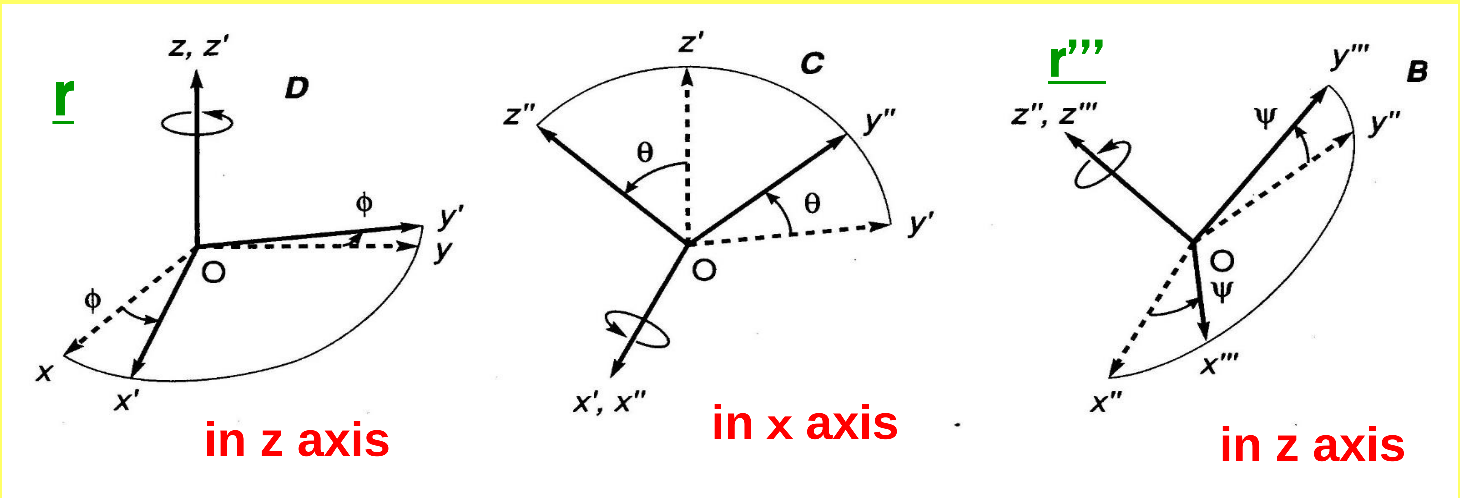
$$L_z = I_z \omega_z$$

$$I_x \dot{\omega}_x - (I_y - I_z)\omega_y \omega_z = N_x$$

$$I_y \dot{\omega}_y - (I_z - I_x)\omega_z \omega_x = N_y$$

$$I_z \dot{\omega}_z - (I_x - I_y)\omega_x \omega_y = N_z$$

Euler Angle Representation



Molecular frame '''

$$r''' = BCDr = Ar$$

Hereafter, r' is simply written r

Rotation matrix is unitary

$$A^t = A^{-1}$$

Rotation matrix

$$A = BCD \qquad A(\phi,\psi,\theta) \text{ representation}$$

$$= \begin{pmatrix} \cos\psi\cos\phi - \cos\theta\sin\phi\sin\psi & \cos\psi\sin\phi + \cos\theta\cos\phi\sin\psi & \sin\psi\sin\theta \\ -\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi & -\sin\psi\sin\phi + \cos\theta\cos\phi\cos\psi & \cos\psi\sin\theta \\ \sin\theta\sin\phi & -\sin\theta\cos\phi & \cos\theta \end{pmatrix}$$

Euler Angle Representation

$$r = R + A^t r'''$$

$$\omega_\phi = \dot{\phi}, \quad \omega_\theta = \dot{\theta}, \quad \omega_\psi = \dot{\psi}$$

Time derivatives of Euler angles

$$\omega = BC\begin{pmatrix} 0 \\ 0 \\ \dot{\phi} \end{pmatrix} + B\begin{pmatrix} \dot{\theta} \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \dot{\psi} \end{pmatrix}$$

Molecular frame

$$\dot{\phi} = \frac{\omega_x \sin\psi + \omega_y \cos\psi}{\sin\theta}$$

$$\dot{\theta} = \omega_x \cos\psi - \omega_y \sin\psi$$

$$\dot{\psi} = \omega_z - \frac{(\omega_x \sin\psi + \omega_y \cos\psi)\cos\theta}{\sin\theta}$$

Singular at $\theta = 0$, or π !!

To be safe from singularity, the quarternion method is used to connect with the molecular frame.

Molecular Dynamics of Water

Procedures of water molecules in molecular dynamics simulation are shown for the 5-points molecule.
This approach is done with five-water molecules with two hydrogens and two L1, L2 hydrogens of dummy sites.
A oxygen site is used with Lennard-Jones potential eps_A/r^12 +eps_B /r^6.

The ice state of freezing due to microwaves, our theory discovery in J.Chem.Phys. 2007, remains the same, due to the structure of six-membered ice !

$*$ *Procedures of water molecules by the 5 – points method*

Dr. Motohiko Tanaka, Professor, Chubu University

a. *Five sites are oxygen (O), hydrogen 1 and 2 (H), and hydrogen virtual L sites. They have, 0, +0.241e, and –0.241e charges, respectively. The L1 and L2 are the dummy sites.*

b. *Separate* $\mathbf{R}_i$, $\mathbf{V}_i$ *and* $\mathbf{r}_k$ *for water with* $i = 1 - N$ *molecules, and* $\mathbf{s}_{i,k} = (x_{i,k}, y_{i,k}, z_{i,k})$ *means for the five sites* $k = 1 - 5$.
The separation is done at the starting step only; once determined at $t = 0$, *they are constant in time.*

c. *The half time step is first executed for a predictor step, and the full time step is made for advance of time.*

d. *Before the end of one step, the forces are calculated at* $\mathbf{r}_{i,k} = \mathbf{R}_i + A^{-1}\mathbf{s}_k$ *with the three sites of* $k = 1 - 3$, *and the L sites are also calculated by algebraic operation.*

e. *After correction of quarternions, go to the beginning of the cycle.*
The leap – frog method is used for the plasmas and waters.

The Lennard-Jones potential

With the Coulombic interactions, the Lennard–Jones 12–6 potential is adopted for the TIP4P and TIP5P cases:

$$\Phi(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}}$$

$$for\ TIP4$$

$$A = 4.17 \times 10^{-8}\, erg \bullet Ang^{12},\ B = 4.24 \times 10^{-11}\, erg \bullet Ang^{6}$$

$$for\ TIP5 - Ewald\ \ sum$$

$$A = 3.85 \times 10^{-8}\, erg \bullet Ang^{12},\ B = 4.36 \times 10^{-11}\, erg \bullet Ang^{6}$$

Some parameters are,

$$r(OH) = 0.9572\,\mathrm{Ang},\ \Delta HOH\ = 104.52^{\circ}$$

$$r(OM) = 0.15\,\mathrm{Ang}\ \ for\ TIP4P\ only$$

The equipartition line of the virtual M site is on the plain that equally separates the HOH angle. The TIP5P cases are also available.

** Each step is translation(1), rotation(2-4), and adding the fields(5-8).*

0. *Read the quarternions from the file, read*(30)*e*0,*e*1,*e*2,*e*3 (*by Dr.M.Matsumoto, Okayama University*).

1. *Sum up the five sites and advance* $\frac{d\mathbf{V}_i}{dt} = \frac{1}{m_i}\sum_{k=1}^{5}\mathbf{F}_{i,k}, \quad \frac{d\mathbf{R}_i}{dt} = \mathbf{V}_i$ *for each of the translation motion.*

2. $\frac{d\mathbf{L}_i}{dt} = \sum_k \left(y_{i,k}F_{i,k}^z - z_{i,k}F_{i,k}^y, \quad z_{i,k}F_{i,k}^x - x_{i,k}F_{i,k}^z, \quad x_{i,k}F_{i,k}^y - y_{i,k}F_{i,k}^x \right)$ *for the rotation motion: the sums are made over the five sites.*

3. $\omega_{i,\alpha} = (A_{\alpha 1}L_x + A_{\alpha 2}L_y + A_{\alpha 3}L_z) / Im_{i,\alpha}$ *, the angular frequency for speices* $A_{\alpha\beta}$ *and inertia moments* $Im_{i,\alpha}$ *at* $\alpha = x, y, z$.

4. $\frac{d\mathbf{q}_i}{dt} = \frac{1}{2}Q(e_{i,0}, e_{i,1}, e_{i,2}, e_{i,3})\left(\omega_{i,x}, \quad \omega_{i,y}, \quad \omega_{i,z}, \quad 0\right)$

$\dot{\mathbf{q}}_i$ *of Q and* $\boldsymbol{\omega}$ *has four components found in the Goldstein's book.*

Use Quaternion in Place of Angles

$$e_0 = \cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$
$$e_1 = \sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$
$$e_2 = \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$
$$e_3 = \cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

Classical Mechanics (3rd Edition)
H. Goldstein , C.P. Poole, J.Safko,
Pearson Education Inc., England 2003.

Only three of them are independent
to avoid a gimbal lock

Quaternion representation **(4.47')**

Rotation matrix

$$\boldsymbol{r} = \boldsymbol{R} + \mathbf{A}^t \boldsymbol{r}'''$$

$$A = \begin{pmatrix} e_0^2+e_1^2-e_2^2-e_3^2 & 2(e_1e_2+e_0e_3) & 2(e_1e_3-e_0e_2) \\ 2(e_1e_2-e_0e_3) & e_0^2-e_1^2+e_2^2-e_3^2 & 2(e_2e_3+e_0e_1) \\ 2(e_1e_3+e_0e_2) & 2(e_2e_3-e_0e_1) & e_0^2-e_1^2-e_2^2+e_3^2 \end{pmatrix}$$

Time derivative of quaternions e0,e1,e2,e3

$$\begin{pmatrix} \dot{e}_0 \\ \dot{e}_1 \\ \dot{e}_2 \\ \dot{e}_3 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} -e_1 & -e_2 & -e_3 & e_0 \\ e_0 & -e_3 & e_2 & e_1 \\ e_3 & e_0 & -e_1 & e_2 \\ -e_2 & +e_1 & e_0 & e_3 \end{pmatrix}\begin{pmatrix} \omega_{x'} \\ \omega_{y'} \\ \omega_{z'} \\ 0 \end{pmatrix}$$

(*continued*)

5. *Get a new rotation matrix* $A_{ij}(e_0, e_1, e_2, e_3)$ *written in the book p.*205 *for the next time step.*

6. $\mathbf{r}_{i,k} = \mathbf{R}_i + \begin{pmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{pmatrix} \begin{pmatrix} x_{i,k} \\ y_{i,k} \\ z_{i,k} \end{pmatrix}$ *at the three sites* $\mathbf{r}_{i,k}$ *and the position* $\mathbf{R}_i$. *The dummy sites are determined by algebraic operation.*

7. *Forces at Coulomb + LJ potentials are calculated using five sites.*

8. *Normalization* (*correction*) *of quarternions is made at every* 10 *steps, and go to the next time step of Step* (1).

Note that a time step is important. It will be $\Delta t = 0.025. - 0.05$, *else the code is inaccurate or overflow.*

Goldstein，松本の方法

さきの方法との違いは，
第１項　同じ　thetaだけ関与
第２項　（phi-psi）が逆になる

$$2\dot{\xi} = 2\left(\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} \right)'$$

$$= \dot{\theta}\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + (\dot{\phi}-\dot{\psi})\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$

$$= (\omega_x\cos\psi - \omega_y\sin\psi)\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + [(\omega_x\sin\psi + \omega_y\cos\psi)/\sin\theta$$
$$-\{\omega_z - (\omega_x\sin\psi + \omega_y\cos\psi)\frac{\cos\theta}{\sin\theta}\}]\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$

$$= \begin{cases} \omega_x : \cos\psi\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + \sin\psi(1+\cos\theta)/\sin\theta\times\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} \\ \omega_y : -\sin\psi\cos\frac{\theta}{2}\sin\frac{\phi-\psi}{2} + \cos\psi(1+\cos\theta)/\sin\theta\times\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} \\ \omega_z : -\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2} = -\eta \quad \leftarrow \text{minus } -\eta \end{cases}$$

第１項　同じ　thetaが関与
第２項　（phi-psi）が逆になる

$$2\dot{\eta} = 2\left(\sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}\right)'$$

$$= \dot{\theta}\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} - (\dot{\phi}-\dot{\psi})\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$

$$= (\omega_x\cos\psi - \omega_y\sin\psi)\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} \quad +[-(\omega_x\sin\psi + \omega_y\cos\psi)/\sin\theta$$

$$+[\omega_z - (\omega_x\sin\psi + \omega_y\cos\psi)\cos\theta)/\sin\theta]\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$

$$= \begin{cases} \omega_x : \cos\psi\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} - \sin\psi(1-\cos\theta)/\sin\theta\times\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} \\ \omega_y : -\sin\psi\cos\frac{\theta}{2}\cos\frac{\phi-\psi}{2} - \cos\psi(1-\cos\theta)/\sin\theta\times\sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} \\ \omega_z : \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2} = \xi \quad \leftarrow \ \text{minus} - \xi \end{cases}$$

こちらはすべて同じに

$$2\dot{\varsigma} = 2\left(\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}\right)'$$

$$= -\dot{\theta}\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + (\dot{\phi}+\dot{\psi})\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$

$$= -(\omega_x\cos\psi - \omega_y\sin\psi)\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + [(\omega_x\sin\psi + \omega_y\cos\psi)/\sin\theta$$

$$+\omega_z - (\omega_x\sin\psi + \omega_y\cos\psi)\cos\theta/\sin\theta]\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$

$$= \begin{cases} \omega_{x:} : -\cos\psi\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + \sin\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} \\ \omega_{y:} : \sin\psi\sin\frac{\theta}{2}\sin\frac{\phi+\psi}{2} + \cos\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} \\ \omega_{z:} : \cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2} = \chi \end{cases}$$

すべて同じになる

$$2\dot{\chi} = 2\left(\cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}\right)' = -\dot{\theta}\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} - (\dot{\phi}+\dot{\psi})\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

$$= -(\omega_x\cos\psi - \omega_y\sin\psi)\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} + [-(\omega_x\cos\psi + \omega_y\sin\psi)]/\sin\theta$$

$$-(\omega_z - (\omega_x\cos\psi + \omega_y\sin\psi)\frac{\cos\theta}{\sin\theta})]\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

$$= \begin{cases} \omega_x : -\cos\psi\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} - \cos\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} \\ \omega_y : \sin\psi\sin\frac{\theta}{2}\cos\frac{\phi+\psi}{2} - \sin\psi(1+\cos\theta)/\sin\theta\times\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} \\ \omega_z : -\cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2} \end{cases}$$

Inter-Molecule Potentials

Flexible Model

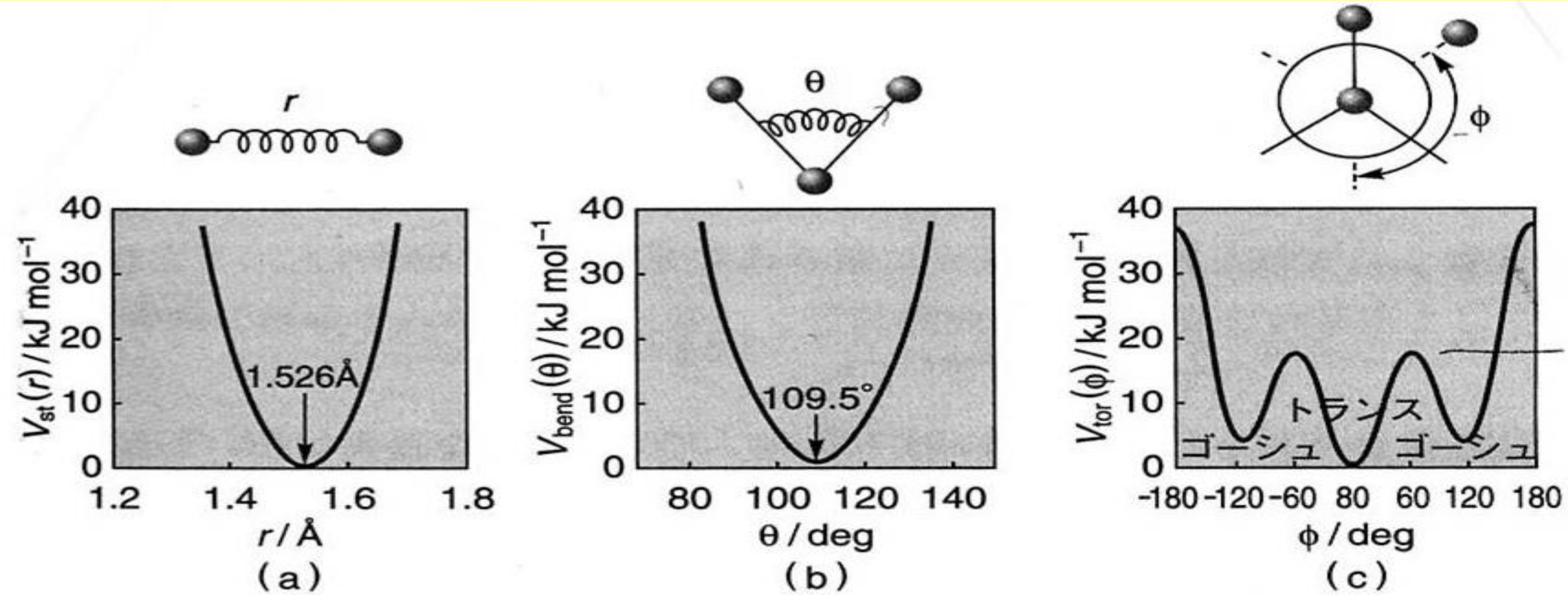


図4.5　炭化水素鎖の分子内自由度に対するポテンシャル関数
r = 結合距離，θ = 結合角，ϕ = ねじれ角．

General-Purpose Atomic Potentials

For amino acids, proteins, and DNA models

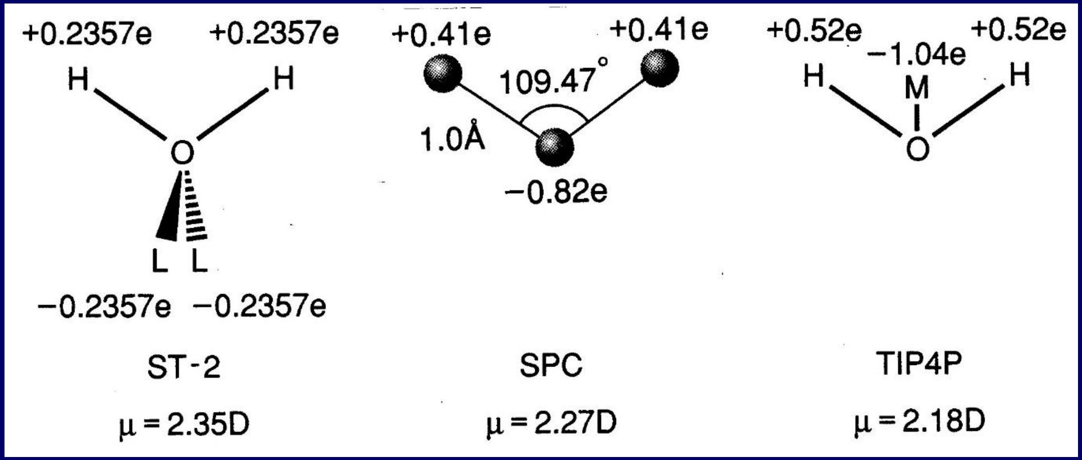
量子力学：（中性の）原子間にも、力がはたらく
（古典）分子動力学では、原子種ごとに力を与える必要がある

各原子について、結合形態（アミノ基、カルボニル基、アルキル基）ごとに、また部分電荷、LJ パラメタ (e_i, A_i, B_i)により与える

C−link： アルキル基の１重結合、２重結合、ベンゼン環で値が異なる

プログラム名	ポテンシャル名	開 発 者
AMBER	AMBER	Kollman
CHARMm	○ CHARMm	Karprus
DISCOVER	DISCOVER ほか	Molecular Simulation Inc.
DLPOLY	DLPOLY	Smith (free ware)
GEMS	GEMS	CRC
GROMOS	○ GROMOS	Berendsen
IMPACT	IMPACT	Levy
MASPHYC	DREIDING ほか	Fujitsu
	ECEPP	Scheraga
	○ OPLS	Jorgensen

水分子のモデル（右のTIP4Pが普通）

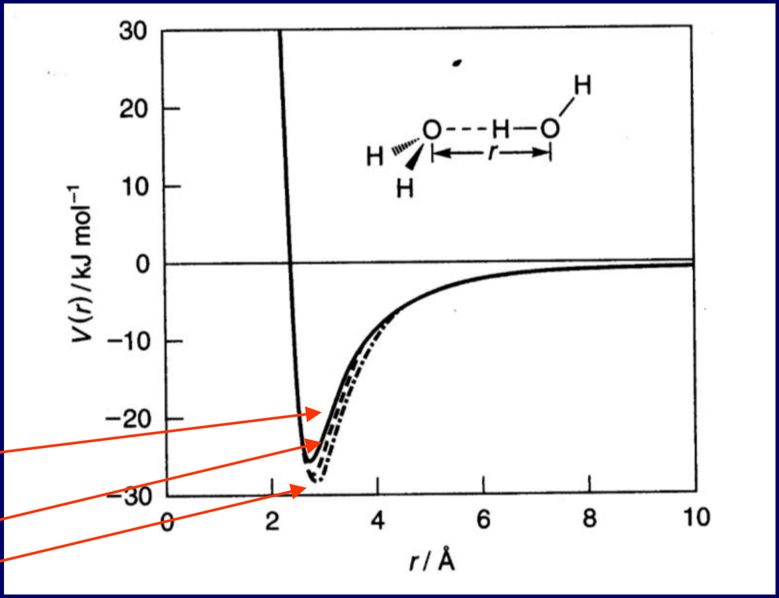


対応する水の
ポテンシャル関数

点電荷モデル

コア斥力と分散力は、酸素原子間に
はたらくLJポテンシャルで表す

気体相での物性値を再現するように、
部分電荷、原子間距離などを決めた
（量子力学的な平均的電子分布の中心
ではない）



水の点電荷モデルの比較

表4.3　三つのポテンシャルモデルを用いたコンピュータ・シミュレーションから求めた熱力学量〔参考文献(4.6)〕

モデル	密度/g cm^{-3}	蒸発熱/kJ mol^{-1}	定圧比熱/J mol^{-1} K^{-1}	熱膨張率	g_{00} 第一ピークの位置/Å	高さ	最大相互作用/kJ mol^{-1}
ST-2	0.925 ✕	45.8	92.8 ✕	-6.9×10^{-4}	2.85 ~~2.11~~ ○	3.22	28.6
SPC	0.971	45.0	97.8 ✕	5.8×10^{-4}	2.76 ~~2.01~~	2.91	27.5
TIP4P	0.999 ○	44.6 ○	80.7	9.4×10^{-4}	2.75 ~~2.02~~	2.99	26.1
実験値	0.997	43.9	75.2	2.6×10^{-4}	~~2.14~~	2.34	—

Coulombic Force in Periodic Boundary Condition

To gain the forces, the base cell L^3 and neighbor cells must be collected to infinity r= ∞.

interaction energy $V = \int nV(\mathbf{r})d\mathbf{r} = 4\pi\int_0^\infty r^2 nV(r)\,dr$

Coulombic energy $V_C = 4\pi\int_0^\infty r^2 \frac{ne^2}{r} dr \to \infty \qquad n(r) = n_0 \sin(kr)$

Physically, it is converged in three dimensions

Ex.) Crystal of *NaCl (salt)*

● ***How do we treat it ?*** **Ewald method**

“Introduction to Solid State Physics”, Kittel, chap.3, and B

Short-range interaction: direct sum

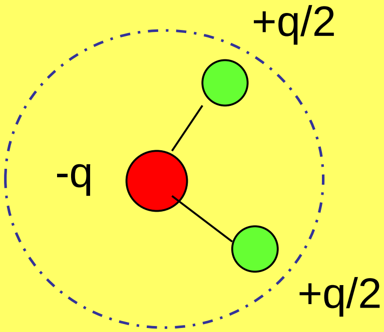
Long-range interaction: take in Fourier space

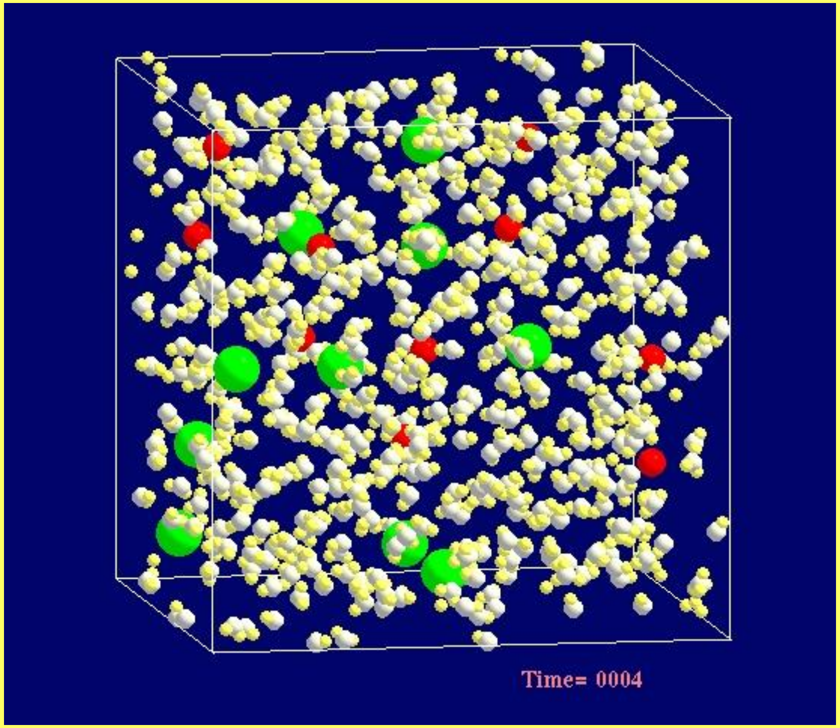
$$V(r) = \frac{1}{r} = \frac{1}{r} f(r) + \frac{1}{r}[1 - f(r)], \quad f(r) = \exp(-\alpha r^2)$$

Molecular Dynamics with Water Model

Express water molecules with simple point charges
- quite a few models:

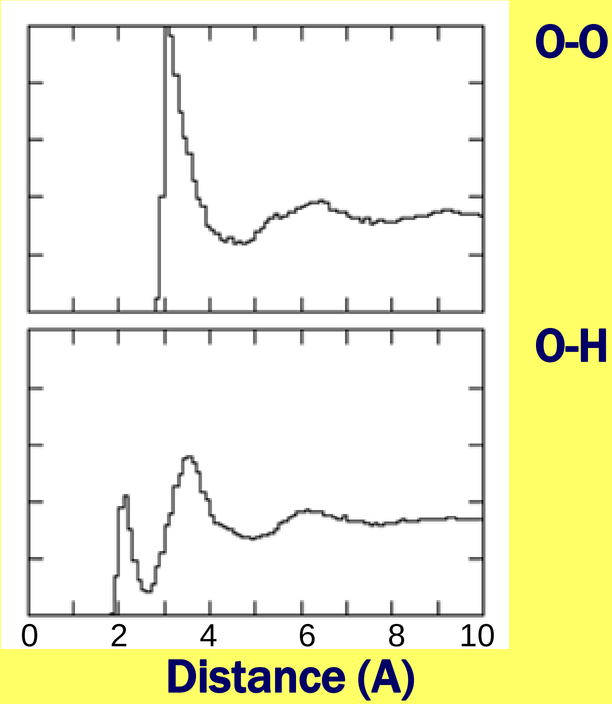
Coulomb + Lennard-Jones forces
SPC/E – 3 charges (good dielectric properties)





SPC/E model, 4096 water molecules
(only 1024 are drawn)

Radial distribution



統計的熱平衡の達成法

● **ミクロカノニカル・アンサンブル**　　何もしない場合

NVE：　粒子数、体積、全エネルギーが一定

● **カノニカル・アンサンブル**　　熱浴をつけて温度制御する

NVT：　粒子数、体積、温度が一定

● **等温等圧・アンサンブル**

NPT：　粒子数、圧力、温度が一定　－　大気圧下での実験環境

どのようなテクニックを採用するか？

圧力制御（NPT）：可変体積とし、運動方程式を修飾　Andersen method

温度制御（NVT）：システムに熱浴を付加する　Nose thermostat

ハミルトニアン H(r,p) にシステムの運動自由度s を付け加える。
一般化座標で作用最小原理により、sの運動方程式を求め、解く。

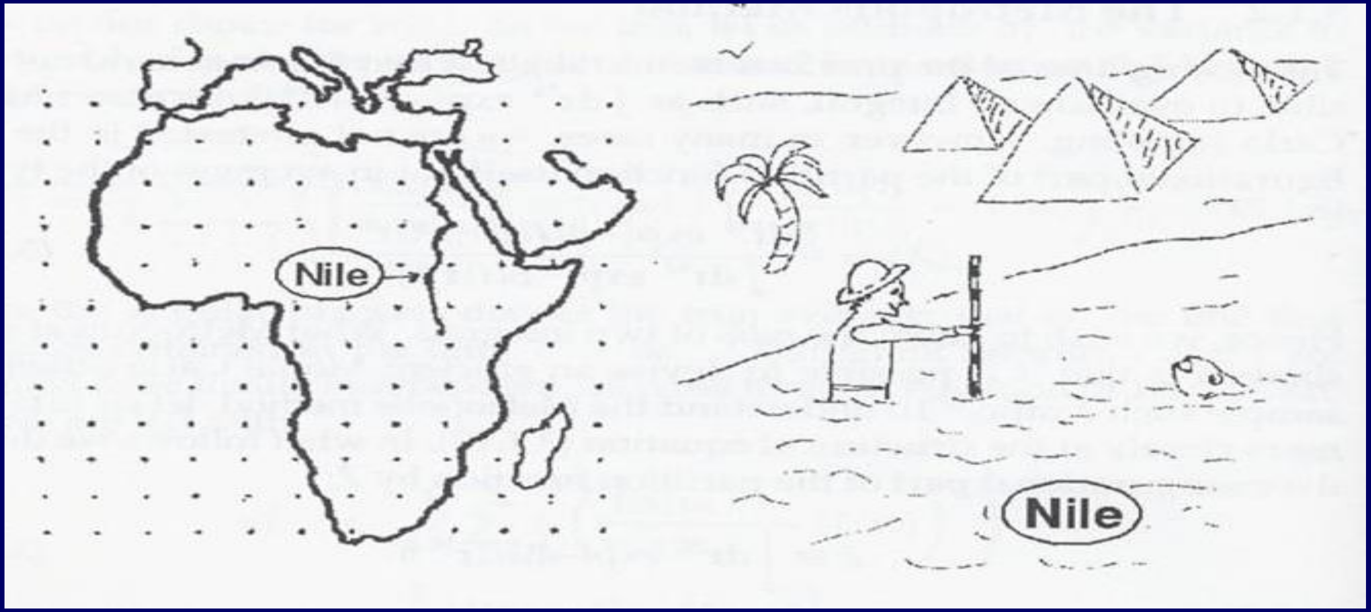
Monte Carlo Simulation

ポテンシャルエネルギーに基づく系の最適化を行い（軌道運動は考慮しない）
出現頻度の小さい状態も正しく考慮して、物理量の統計的アンサンブル平均を求める.

$$< A > = \int A(\mathbf{r}) \exp(-V_N(\mathbf{r})/kT)\, d\mathbf{r}^{3N} / Z_N(V,T)$$

進化の遅い系、障壁を越えて起きる状態も，サンプリングできる

"importance sampling"



Measuring the depth of the Nile, a comparison of conventional quadrature and the Metropolis scheme, Understanding Molecular Simulation (Frenkel and Smit, Academic Press, 1996)

How to make Monte Carlo simulation

- 1ステップで1粒子だけ動かす試行を行う
- その試行状態でポテンシャルエネルギーを求め、前ステップと比較。Metropolis criterionに従い、その試行の採択/棄却を決める

一様乱数（サイコロを振る）

$$p = \Pi_{trial} / \Pi_{\nu} = \exp(-\Delta V_N / kT) > \varepsilon$$

ΔV<0 のとき必ず採択、ΔV>0 ならば確率的に採択する

Vが減少して、系は安定な方向に進化する

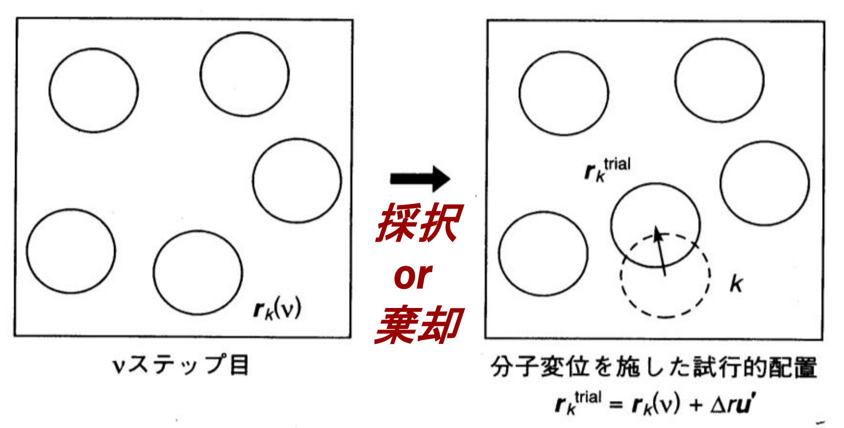
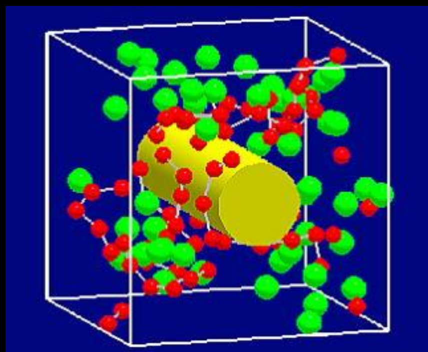


図12.1 NVT アンサンブルにおける分子変位の試行

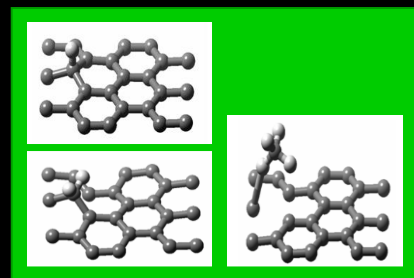
こうして実現される平衡状態について、測定した物理量Aの単純平均が、統計平均 ⟨A⟩ を与える

Plasma and Ionic Condensed Matters by Molecular Dynamics Simulations

http://physique.isc.chubu.ac.jp/



Charge inversion



Graphen destruction

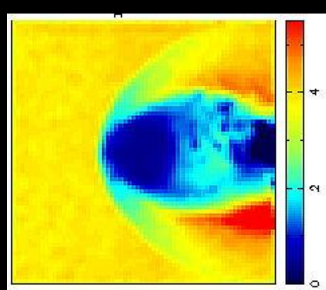
Boewulf PC cluster

Publications
Cover Pictures

Ionic Soft Condensed Matters

First Principle (ab initio) Molecular Dynamics

Method and Tools of Molecular Dynamics



Planetary shock

High Temperature Plasmas

- **First proof of Collisionless Magnetic Reconnection**
- **Development of Mesoscale Particle Code**
- **Planetary Shocks**

Scalapack on PGI & Red Hat Linux 7.3
Pentium 4 and its performance

1. Ionic soft condensed matters (Polymers, Charge inversion), 2. First principle molecular dynamics (Quantum mechanics), 3. High-temperature plasmas (Magnetic reconnection, Mesoscale particle code, Planetary shocks), 4. Method of molecular dynamics and Boewulf PC cluster, 5. Published papers and books (Cover pictures)

＊Video movies of molecular dynamics simulations