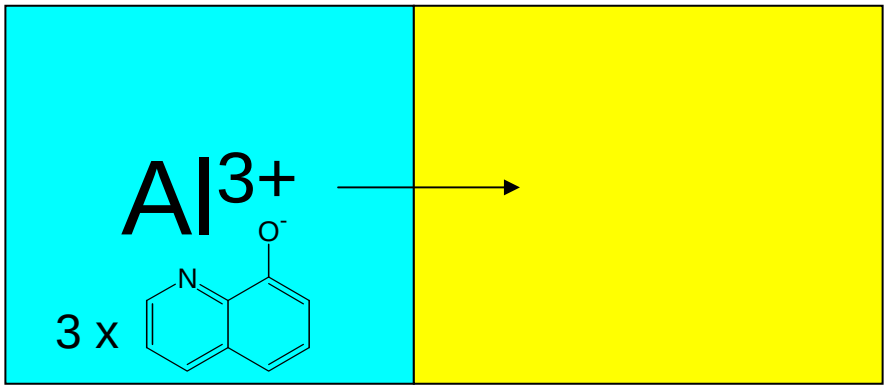
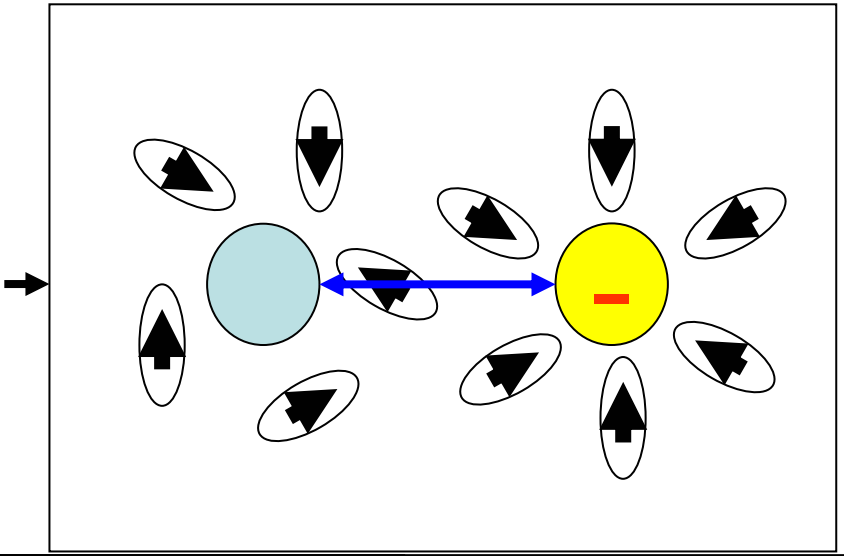
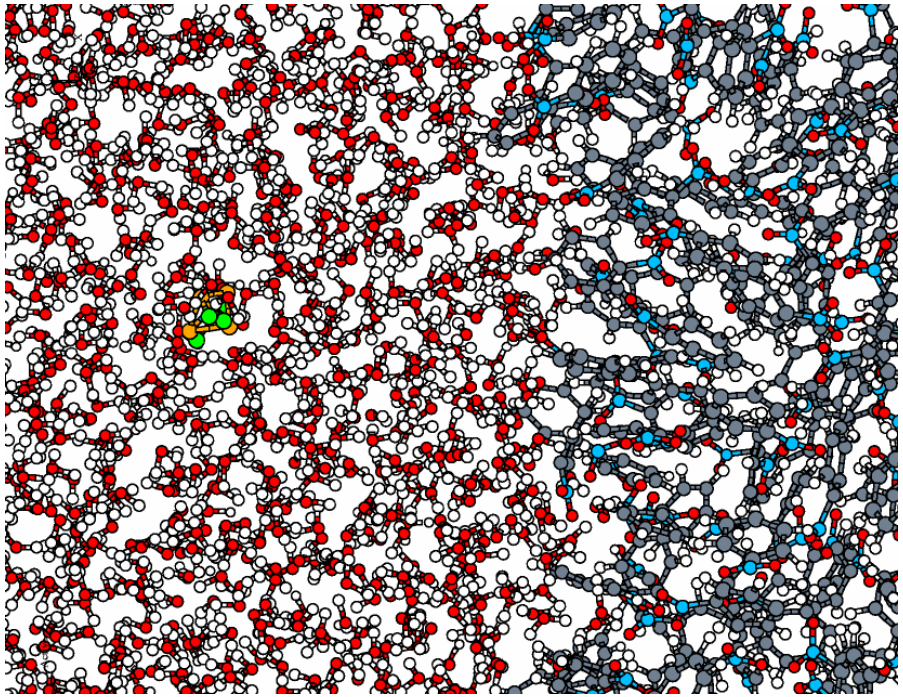
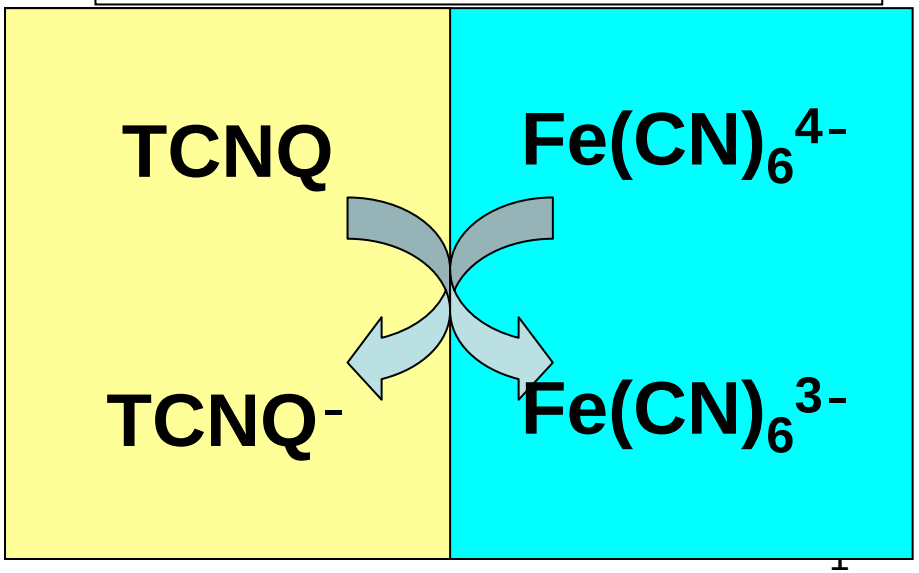
機能性溶液化学

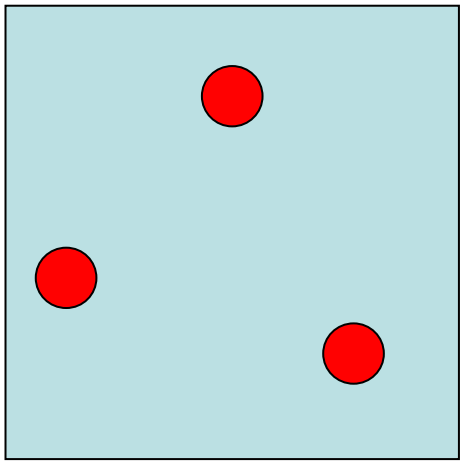




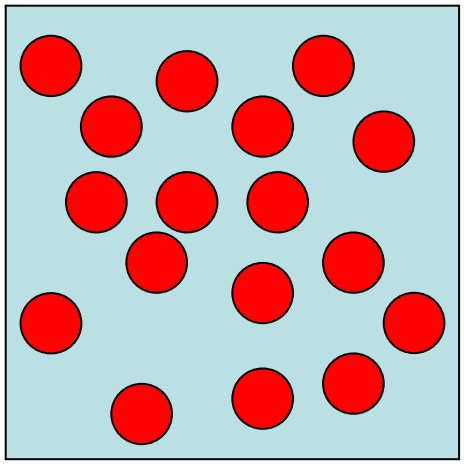




Phase diagram

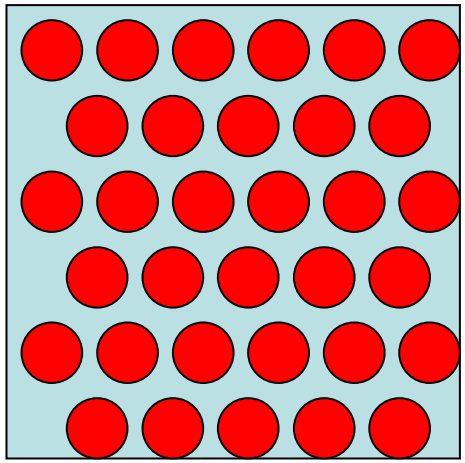


gas



liquid

solid



Static :radial distribution function

Dynamic: Self-diffusion constant

相律

$$F = C - P + 2$$

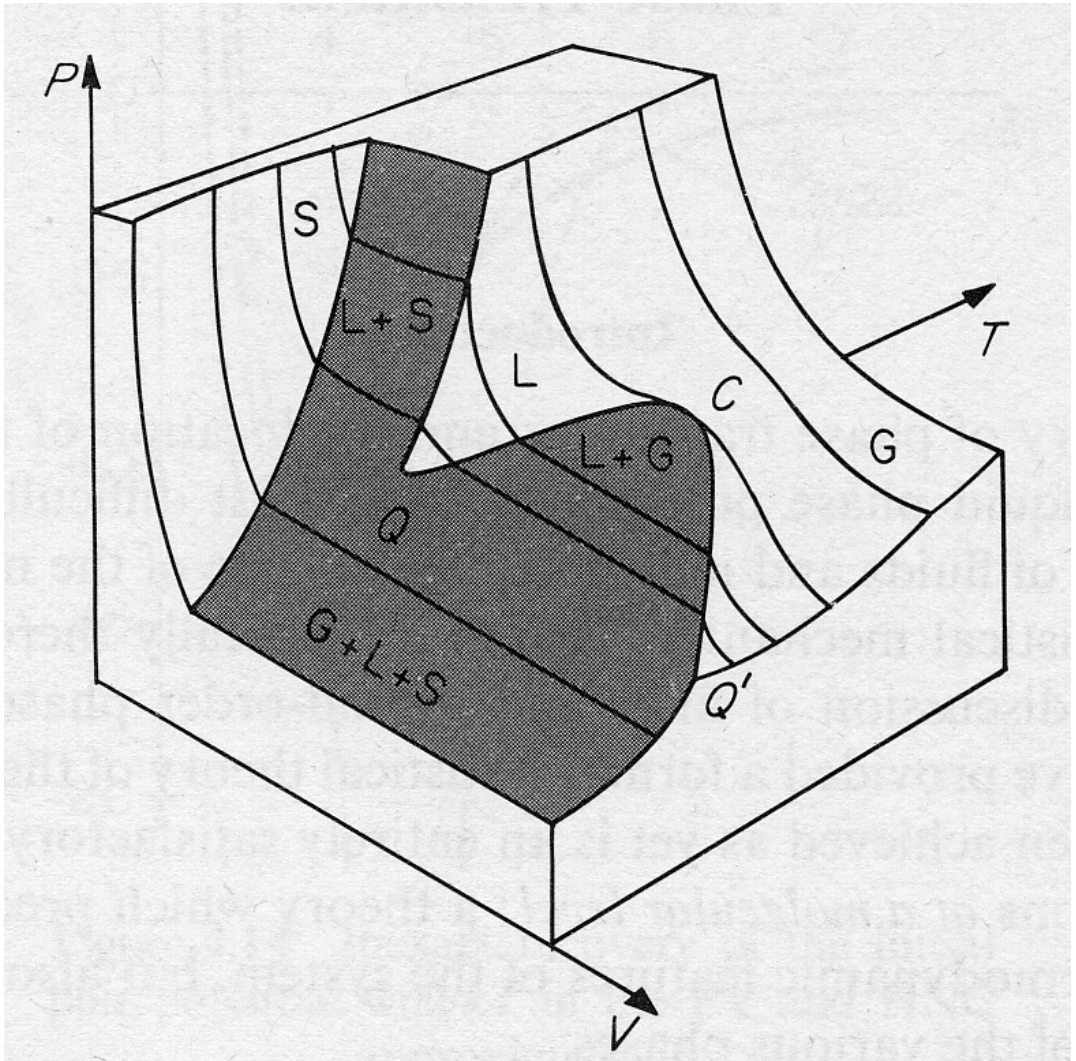
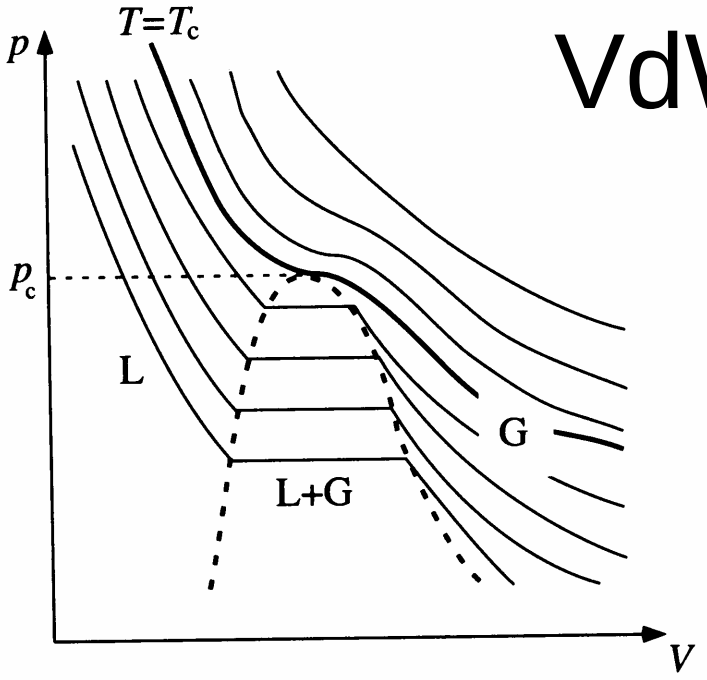


Figure 5.1 PVT surface of a realistic single-component system. The coexistence regions are shown shaded, where G, L and S refer to gas, liquid and solid phases respectively. *C* and *Q* are the critical and triple points



VdW Equation of State

$$p = \frac{NRT}{V - bN} - \frac{aN^2}{V^2}$$

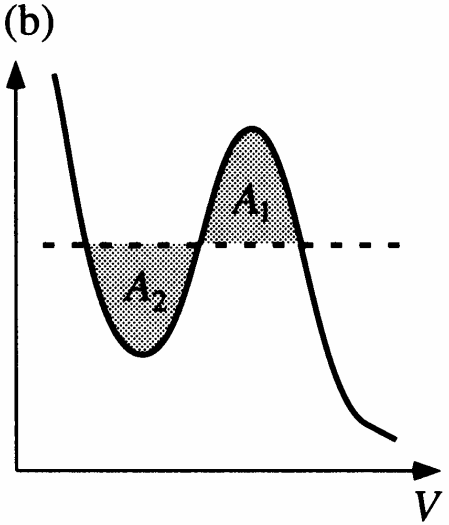
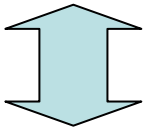
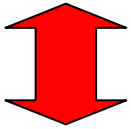


図 7.6　様々な温度における流体の圧力のふるまいの概形。横軸は体積 V，縦軸は圧力 p である。物質量 N は固定した。点線で囲った釣り鐘状の領域の中では，圧力が体積に依存しない。これが液体と気体が共存する領域である。これより左側が液体，右側が気体である。温度を上げて釣り鐘の上を経由すれば，液体から気体へと連続的に移行することができる。両者の間に本質的な区別はないことがわかる。

Thermodynamics



Statistical mechanics



Mechanics, Quantum Mechanics

Example:

- VdW Equation of State
- Statistical Mechanical Perturbation Theory
- Hard Sphere Model + Pair Potential

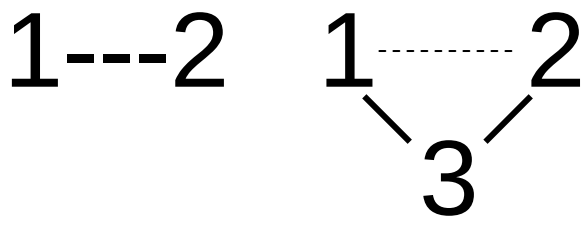
$$a = -2\pi \int_h^\infty dr r^2 v_{\text{pair}}(r)$$

$$b = 2\pi h^3/3$$

Liquid Theory

Integral Equation Theory

many-body interaction



J.P. Hansen and I. R. Macdonald
Theory of Simple Liquids 1986 Academic

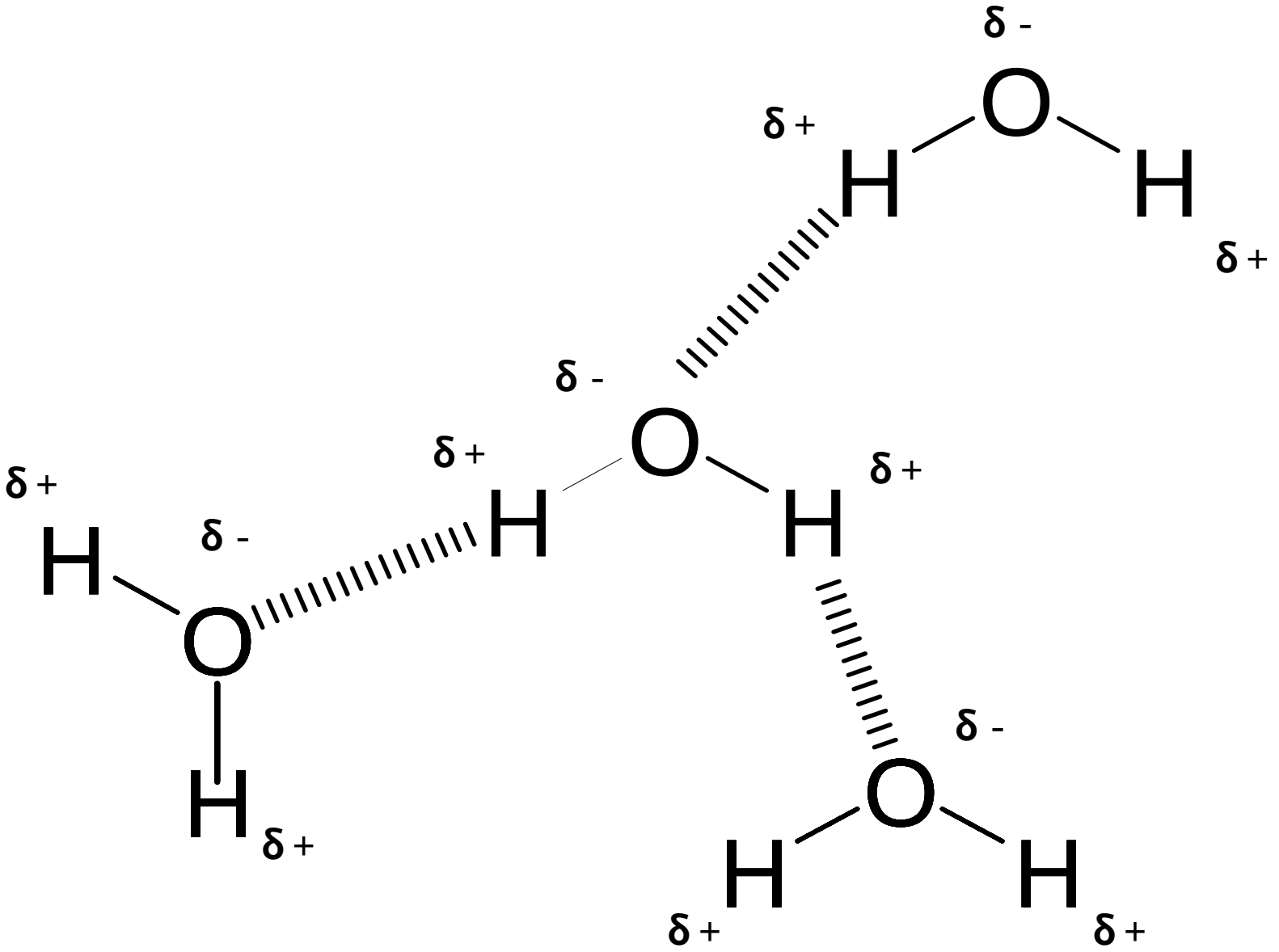
Molecular Simulation

Molecular Dynamics

Monte Carlo

1) M. P. Allen and D. J. Tildesley
Computer Simulation of Liquids 1987, Oxford

2) **岡崎進　*コンピュータシミュレーションの基礎*　2000化学同人**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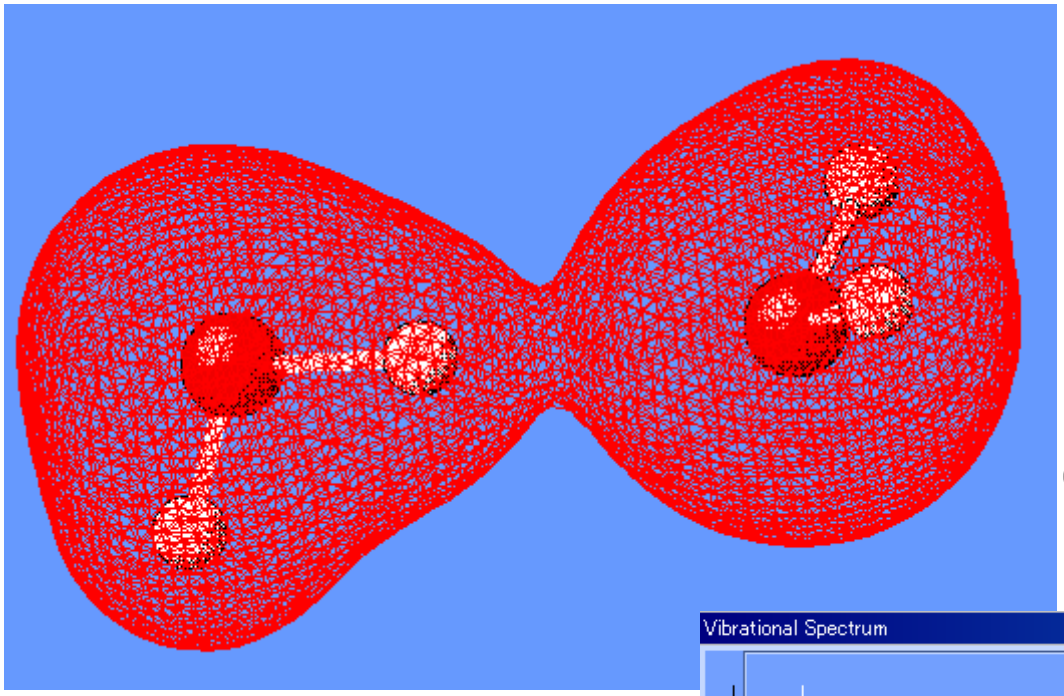
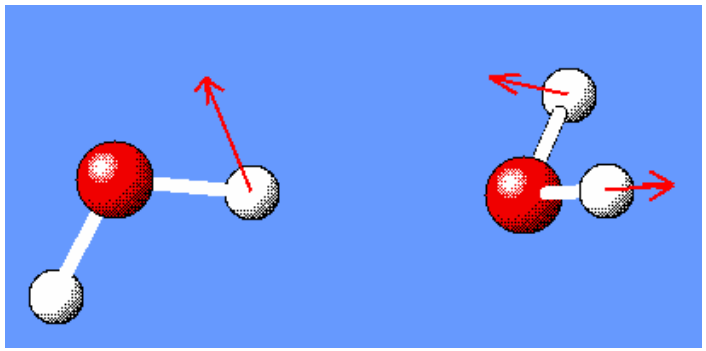
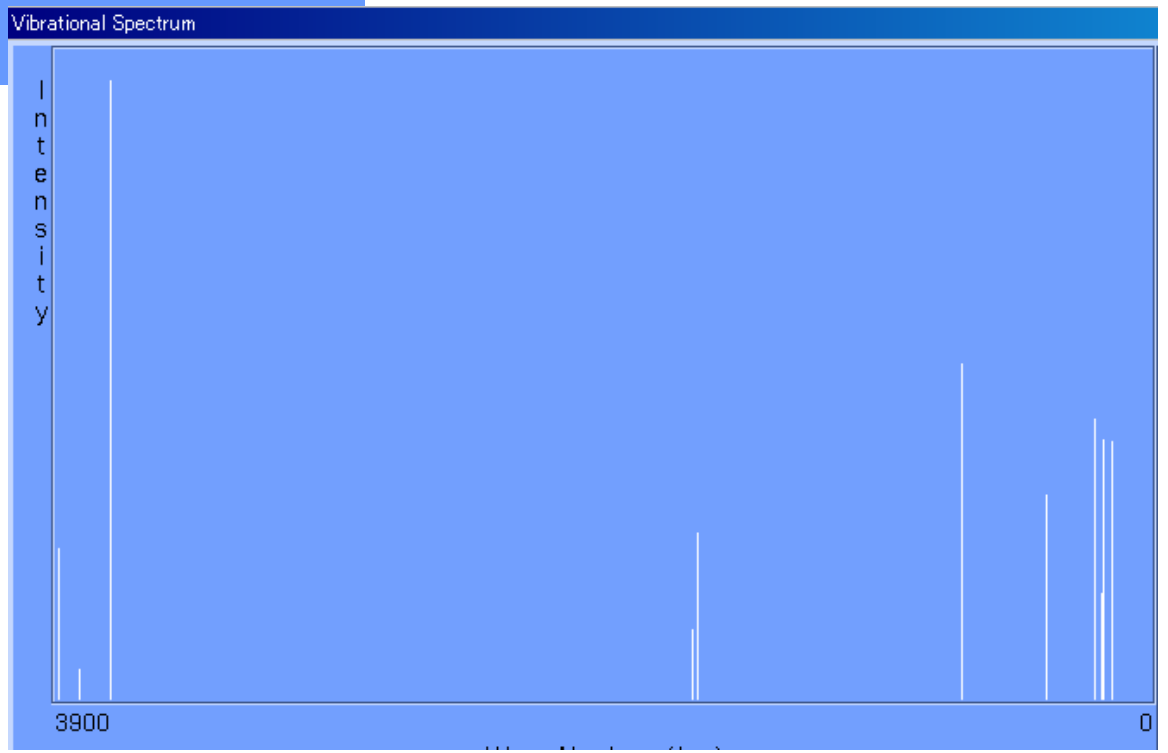


H_2O dimer
Ab-initio calculation

674 cm^{-1} liberational motion

⇨ **Hydrogen bond**





SPC model

(simple point charge/flexible) water model
[J. Lobaugh and G. A. Voth,

J. Chem. Phys. 106 (1997) 2400]

$$\mathcal{V}_{inter} = \frac{1}{2}\sum_{i}^{N_O}\sum_{j\neq i}^{N_O} 4\epsilon\left[\left(\frac{\sigma}{R_{O_iO_j}}\right)^{12} - \left(\frac{\sigma}{R_{O_iO_j}}\right)^{6}\right] + \sum_{m}\sum_{n}\frac{q_m q_n}{R_{ij}^{mn}}$$

Here $R_{O_iO_j}$ is the distance between the ith and jth oxygen and R_{ij}^{mn} is the distance between the mth charge on the ith water molecule and nth charge on the jth molecule.

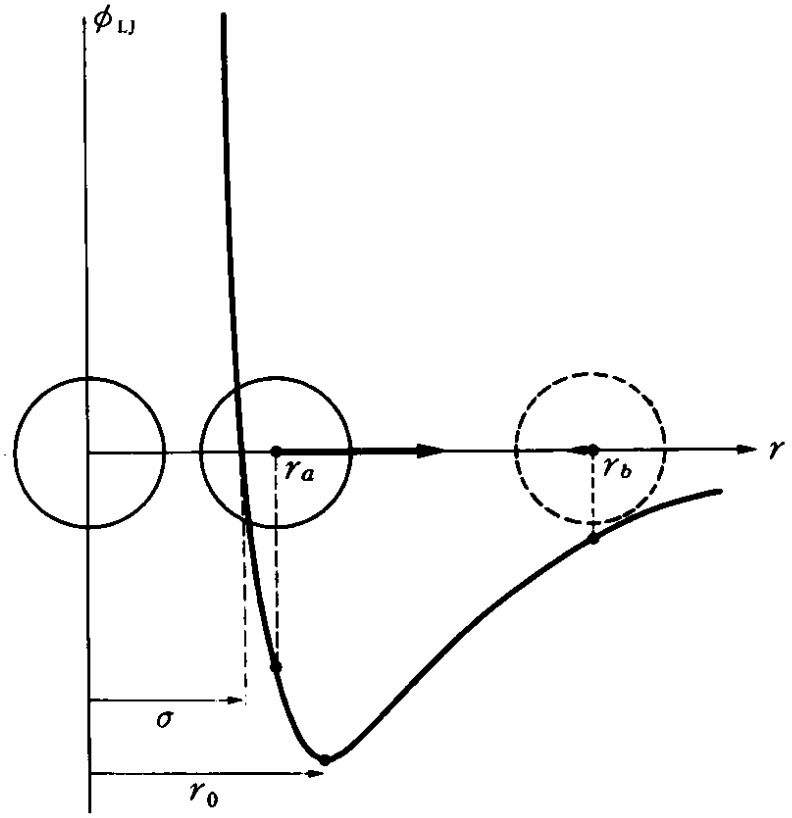


図 2.1 レナード-ジョンズポテンシャル

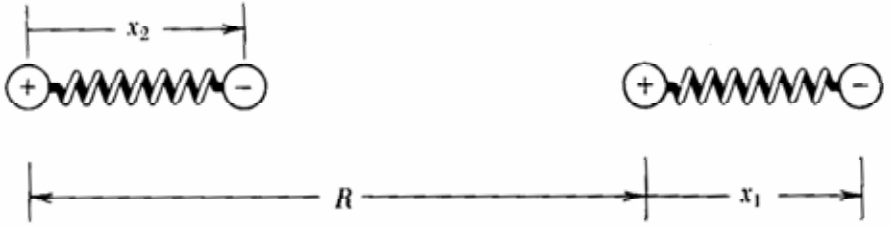


Figure 3 Coordinates of the two oscillators.

$$\Delta U = -\hbar\omega_0 \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2$$

Here ω_0 is the angular frequency of the oscillators and C is the force constant of the oscillators.

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$-\epsilon = v_{LJ}(r = 2^{1/6}\sigma)$$

The intramolecular potential of the water molecule is given by the harmonic parameterization of Kutchiso and Morino,

$$\begin{aligned}\mathcal{V}_{intra}^{H_2O} &= \sum_{i=1}^{2} \rho_W^2 D_W (b_{OH_i} - b_{OH_{eq}})^2 \\ &+ (1/2) b_{intra} (b_{HH} - b_{HH_{eq}})^2 \\ &+ c_{intra} (b_{OH_1} + b_{OH_2} - 2 b_{OH_{eq}}) (b_{HH} - b_{HH_{eq}})^2 \\ &+ d_{intra} (b_{OH_1} - b_{OH_{eq}}) (b_{OH_2} - b_{OH_{eq}}) \qquad (1)\end{aligned}$$

Here b_{ij} is the bond length between atoms i and j.

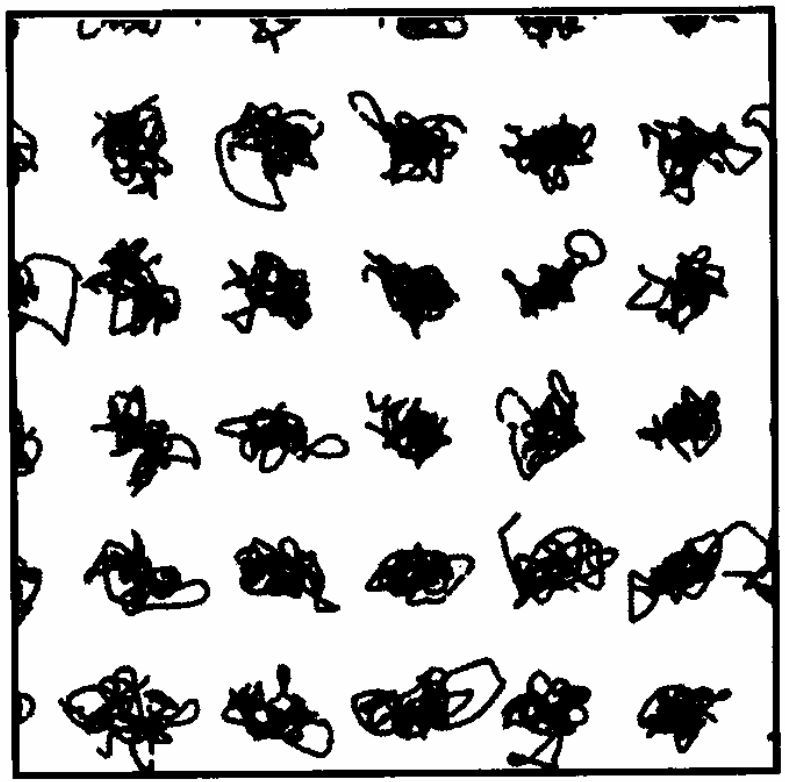
Intermolecular potential parameters for SPC water

O-O		H_2O	
ϵ/k_B (K)	σ (Å)	q_O (e)	q_H (e)
78.22	3.165	-0.82	0.41

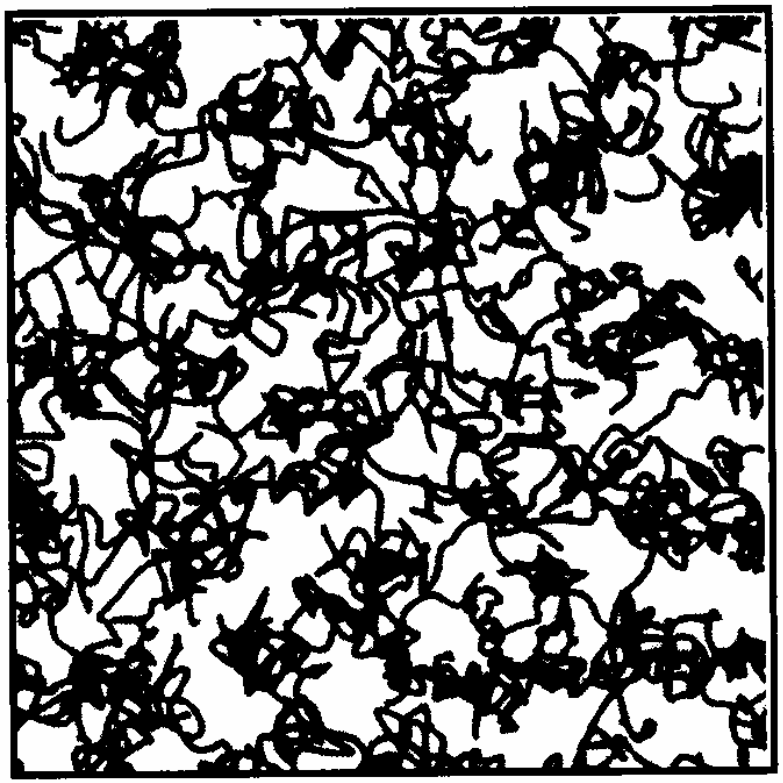
Intramolecular water potential parameters

Parameter	SPC/F
ρ_W	2.566 Å
D_W	0.708 mdyn Å
$b_{OH_{eq}}$	1.0 Å
HOH bond angle	109.47°
b_{intra}	2.283 mdyn $Å^{-1}$
c_{intra}	-1.469 mdyn $Å^{-1}$
d_{intra}	0.776 mdyn $Å^{-1}$

Xe固体　　Xe液体



(a)



(b)

Lennard-Jones Reduced Unit System

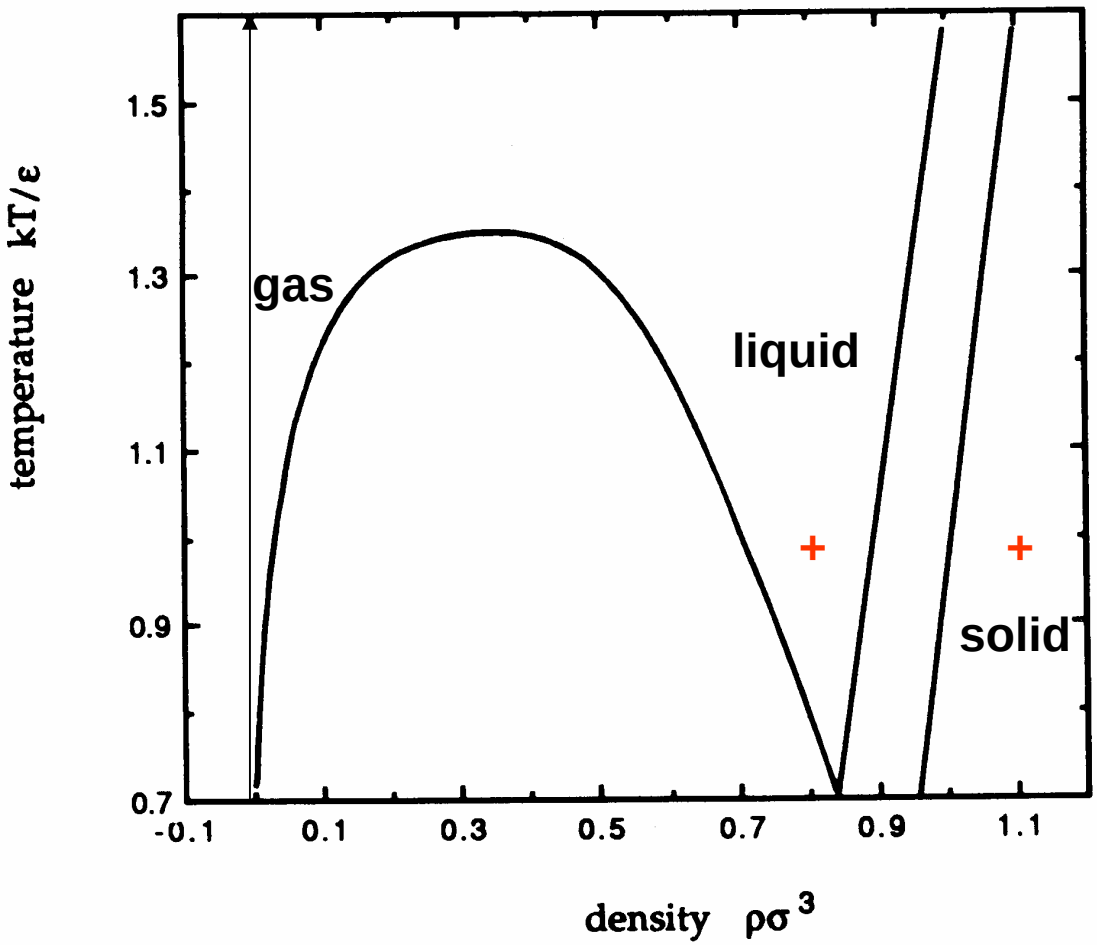


FIGURE 5.7 Temperature–density phase diagram for the pure Lennard-Jones (12,6) substance. The vapor–liquid saturation curve was computed using the Nicolas et al. [3] equation of state. The melting lines were taken from Hansen and McDonald [10].

XVI. REDUCED UNITS IN THE L-J POTENTIAL

Now the Lennard-Jones pair potential is described as

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^l\right] \tag{112}$$

We define the dimensionless $\tilde{r}$ and $\tilde{t}$ in the following way

$$r = \sigma\tilde{r}, \qquad \frac{d}{dr} = \frac{1}{\sigma}\frac{d}{d\tilde{r}} \tag{113}$$

$$t = \tau\tilde{t}, \qquad \frac{d^2}{dt^2} = \left(\frac{1}{\tau}\right)^2\frac{d^2}{d\tilde{t}^2} \tag{114}$$

$$\tilde{\phi}(\tilde{r}) \equiv \phi(\tilde{r})/\epsilon = 4(\tilde{r}^{-n} - \tilde{r}^{-l}) \tag{115}$$

$$\frac{d\tilde{\phi}(\tilde{r})}{d\tilde{r}} = -4n(\tilde{r}^{-n-1} - \frac{l}{n}\tilde{r}^{-l-1}) \tag{116}$$

The equation of motion in the reduced units become

$$\underbrace{\left(\frac{m_k\sigma^2}{\epsilon\tau^2}\right)}_{=1}\frac{d^2}{d\tilde{t}^2}\vec{\tilde{\mathbf{r}}}_k = \sum_i 4n(\tilde{r}_{ki}^{-n-1} - \frac{l}{n}\tilde{r}_{ki}^{-l-1}) \times (\frac{\tilde{x}_k - \tilde{x}_i}{\tilde{r}_{ki}}\mathbf{i} + \frac{\tilde{y}_k - \tilde{y}_i}{\tilde{r}_{ki}}\mathbf{j} + \frac{\tilde{z}_k - \tilde{z}_i}{\tilde{r}_{ki}}\mathbf{k}) \tag{117}$$

TABLE I: Translation of reduced units to real units for Lennard-Jones Argon. $m = 6.63 \times 10^{-26}$ kg, $\epsilon/k_B = 119.8$ K, and $\sigma = 3.405 \times 10^{-10}$ m.

Quantity	Reduced units		Real units
length	$\tilde{r} = 1$	$\leftrightarrow$	$r = \sigma = 3.405 \times 10^{-10}$ m
energy	$\tilde{E} = 1$	$\leftrightarrow$	$E = \epsilon = 1.654 \times 10^{-21}$ J
time	$\tilde{t} = 1$	$\leftrightarrow$	$t = \tau = 2.156 \times 10^{-12}$ s
velocity	$\tilde{v} = 1$	$\leftrightarrow$	$v = \sigma/\tau = 157.95$ m/s
temperature	$\tilde{T} = 1$	$\leftrightarrow$	$T = \epsilon/k_B$ =119.8 K
density	$\tilde{\rho} = 1$	$\leftrightarrow$	$\rho = \sigma^{-3} = 2.533 \times 10^{28}$ m^{-3}
pressure	$\tilde{P} = 1$	$\leftrightarrow$	$P = \epsilon/\sigma^3 = 41.9$ MPa
force	$\tilde{f} = 1$	$\leftrightarrow$	$f = \epsilon/\sigma = 4.858$ pN

$$\text{Then time} \quad \tau = \sqrt{\frac{m_k \sigma^2}{\epsilon}} \tag{118}$$

The velocity and temperature is also described in the reduced units.

$$\dot{\mathbf{r}} = \frac{d\mathbf{r}}{dt} = \frac{d(\sigma\tilde{\mathbf{r}})}{d(\tau\tilde{t})} = \underbrace{\left(\frac{\sigma}{\tau}\right)}_{=\sqrt{\frac{\epsilon}{m}}} \frac{d\tilde{\mathbf{r}}}{d\tilde{t}} \tag{119}$$

$$\text{temperature } \tilde{T} = \frac{k_B T}{\epsilon} \tag{120}$$

$$f(v_{ix})dv_{ix} = \sqrt{\frac{m_i}{2\pi k_B T}} e^{-\frac{1}{2}\frac{m v_{ix}^2}{k_B T}} dv_{ix}$$

$$= \sqrt{\frac{1}{2\pi\tilde{T}}} e^{-\frac{\tilde{v}_{ix}^2}{2\tilde{T}}} d\tilde{v}_{ix} = f(\tilde{v}_{ix})d\tilde{v}_{ix} \tag{121}$$

$$\text{density} \quad \tilde{\rho} = \rho\sigma^3 \tag{122}$$

$$\text{energy} \quad \tilde{E} = E/\epsilon \tag{123}$$

$$\text{kinetic energy} \quad \tilde{K} = K/\epsilon = \frac{mv^2}{2\epsilon} = \frac{m\tilde{v}^2}{2\epsilon}\frac{\epsilon}{m} = \frac{\tilde{v}^2}{2} \tag{124}$$

$$\text{pressure} \quad \tilde{P} = P\sigma^3/\epsilon \tag{125}$$

$$\text{force} \quad \tilde{\mathbf{f}} = -\tilde{\nabla}\tilde{V} = -\sigma\nabla(V/\epsilon) = (\sigma/\epsilon)\mathbf{f} \tag{126}$$

$$\mathcal{K} = \frac{1}{2}mv^2 = \frac{1}{2}m\frac{\epsilon}{m}\tilde{v}^2 \tag{127}$$

$$\tilde{\mathcal{K}} = \frac{\mathcal{K}}{\epsilon} = \frac{1}{2}\tilde{v}^2 \tag{128}$$

$$\mathcal{T} = \frac{2\mathcal{K}}{3Nk_B} \tag{129}$$

$$\tilde{\mathcal{T}} = \frac{k_BT}{\epsilon} = \frac{2}{3}\frac{\tilde{\mathcal{K}}}{N} \tag{130}$$

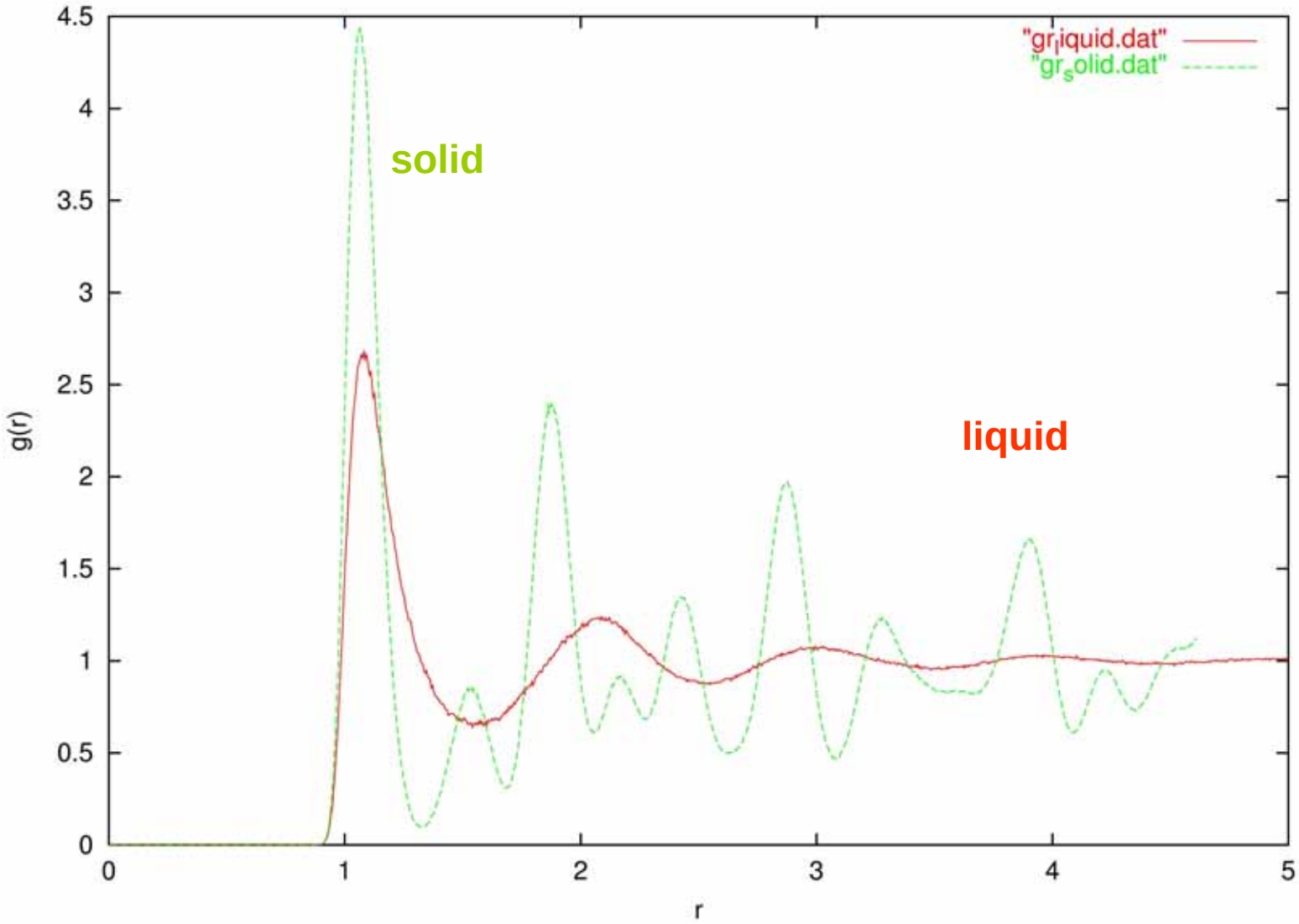
$$\tilde{\mathcal{P}} = (\frac{2}{3}\tilde{\mathcal{K}} + \tilde{\mathcal{W}})/\tilde{V} \tag{131}$$

$$\tilde{\mathcal{W}} = -\frac{1}{3}\sum_i\sum_{j>i}\tilde{w}(\tilde{r}_{ij}) \tag{132}$$

$$\tilde{w}(\tilde{r}) = \tilde{r}\frac{d\tilde{v}}{d\tilde{r}} \tag{133}$$

TABLE II: Translation of atomic unit to real units.

Quantity	Reduced units		Real units
length	Bohr radius	$\leftrightarrow$	$0.5291772083(19) \times 10^{-10}$ m
energy	Hartree	$\leftrightarrow$	27.2113834 eV $= 4.35974381(34) \times 10^{-18}$ J
mass	$m_e = 1$	$\leftrightarrow$	$9.10938188(72) \times 10^{-31}$ kg, 1822.88848119684 au for C/12
time	from $\hbar(= 1.05457159682 \times 10^{-34}$ J s$) = 1$	$\leftrightarrow$	1 fs = 41.3413733742361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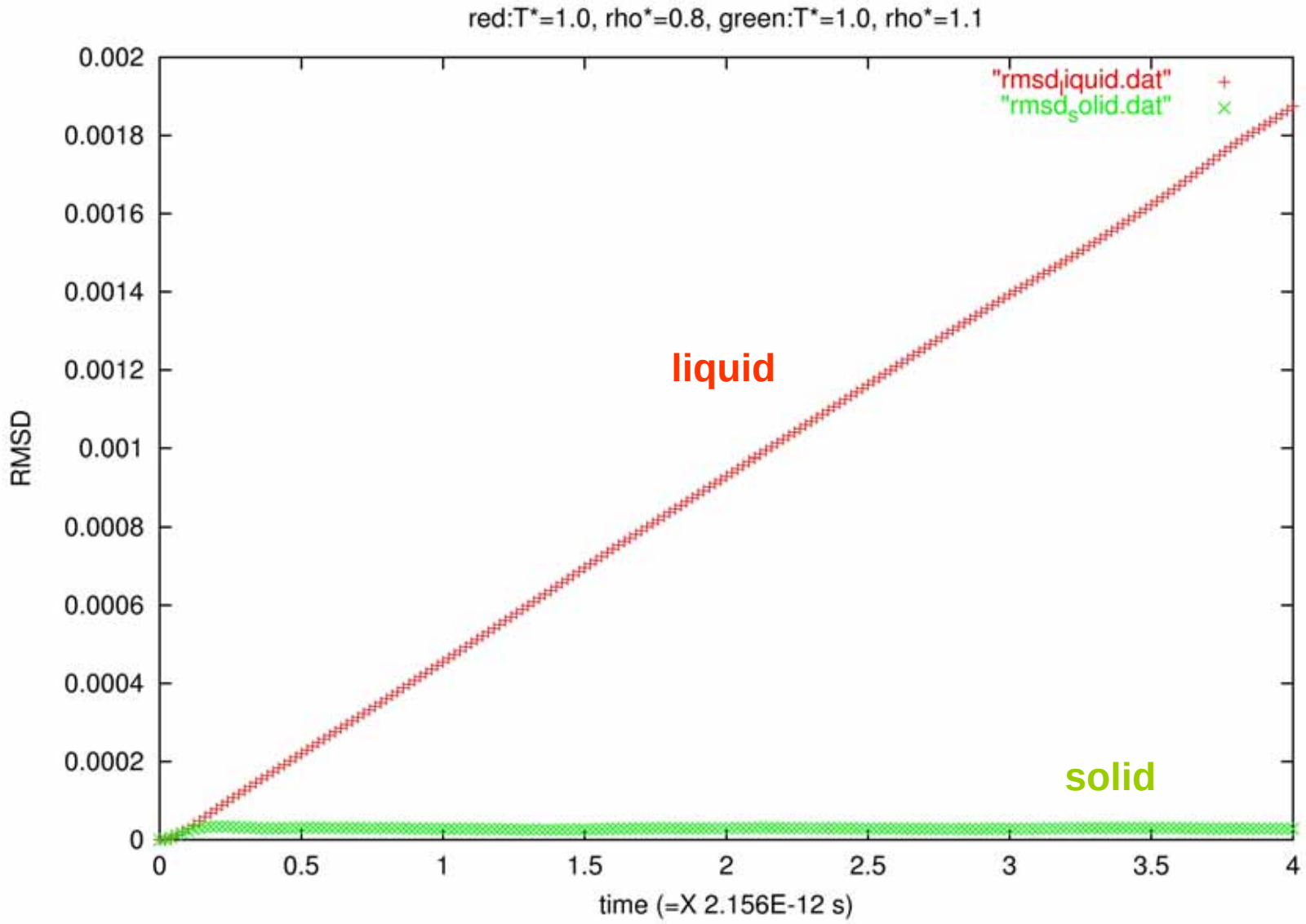
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0.0014
0.0012
0.001
0.0008
0.0006
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3
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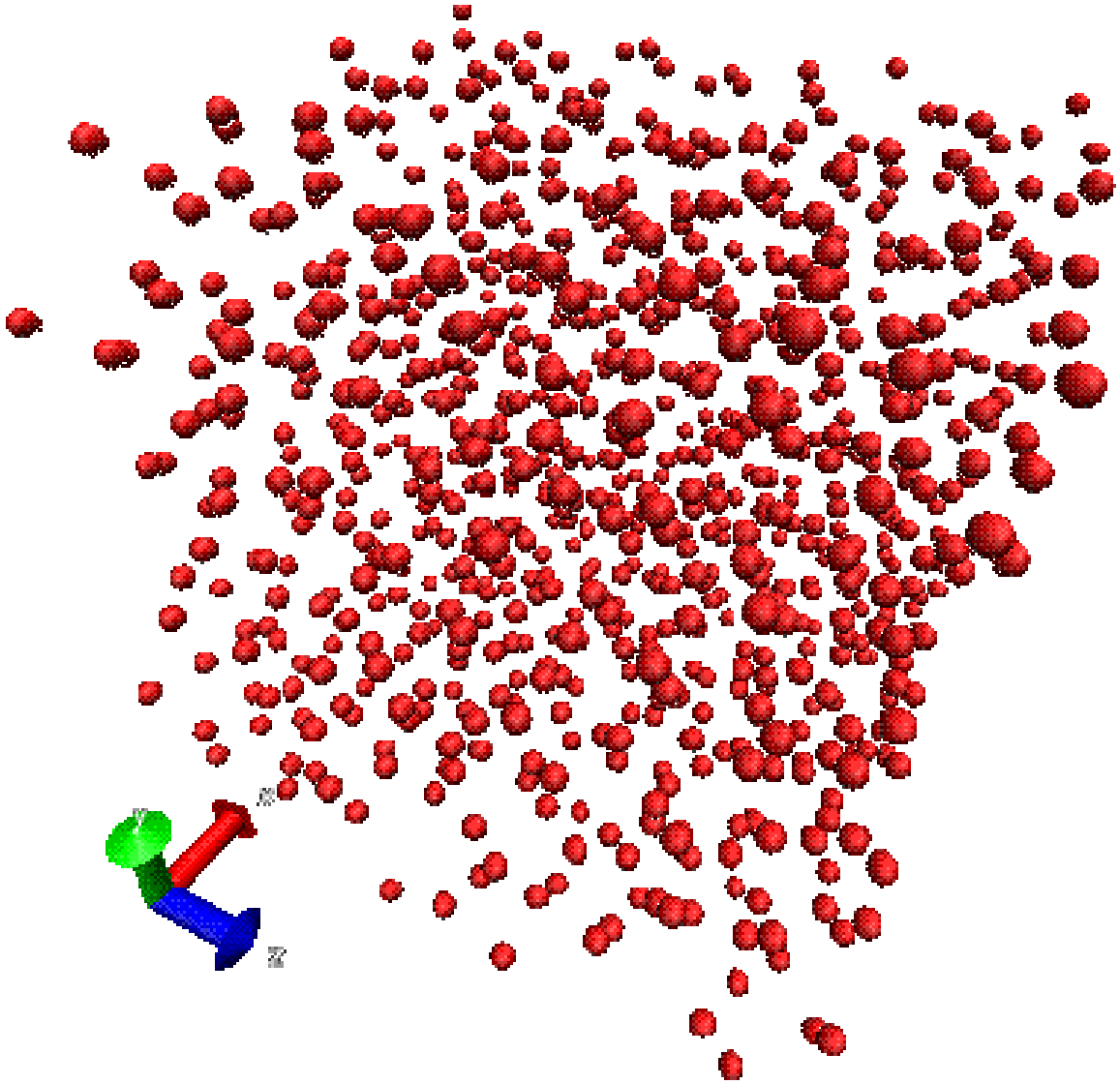
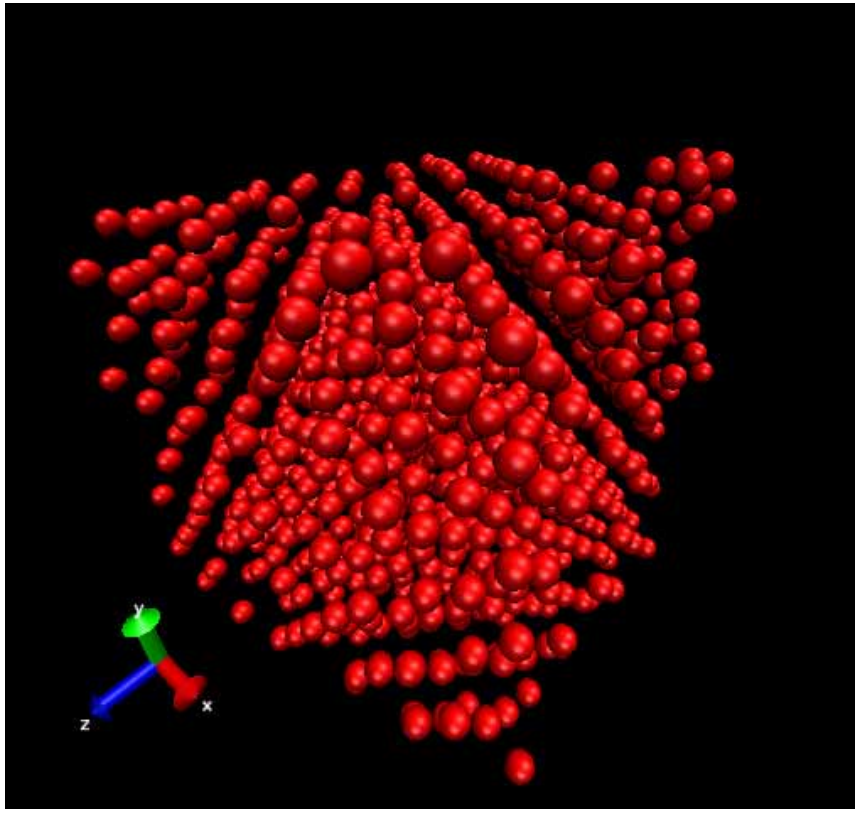
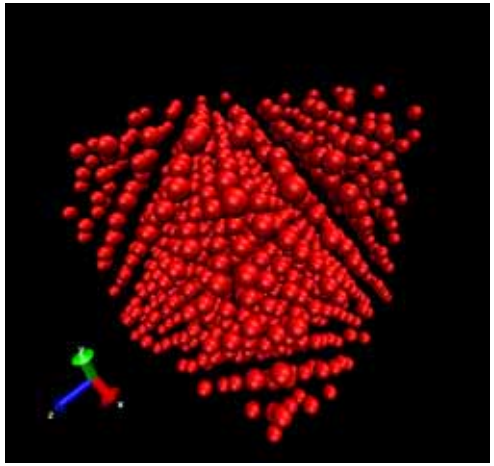
4

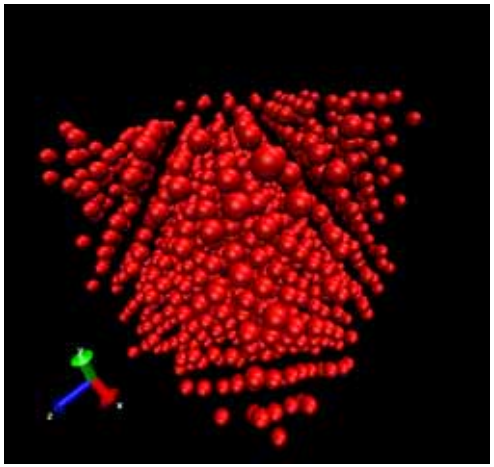
LJ-Liquid movie



LJ-Solid Snapshot





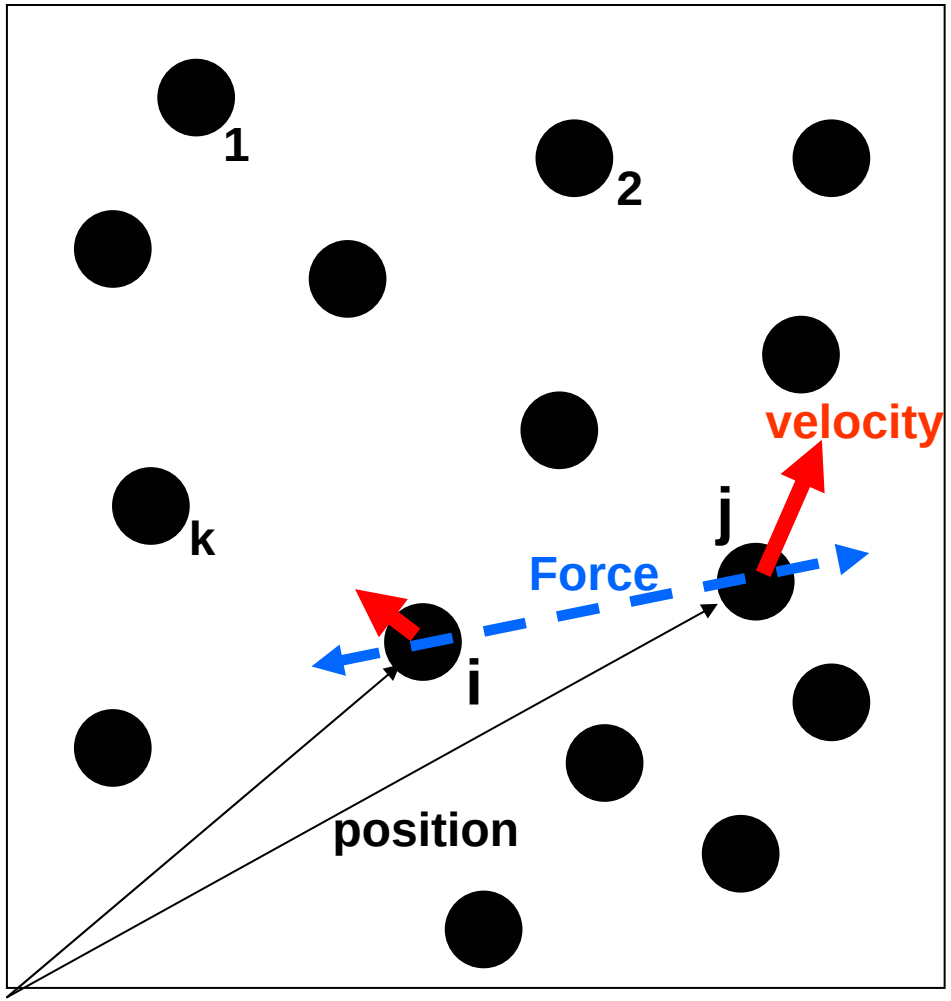


$$\Phi_{ij}(\mathbf{r}_i,\mathbf{r}_j) = \Phi_{ij}(|\mathbf{r}_i-\mathbf{r}_j|)$$

$\{\mathbf{r}_i\}$:position
$\{\mathbf{v}_i\}$:velocity
$\{\mathbf{F}_i\}$:Force

Molecular Dynamics

Monte Carlo (Energy only)



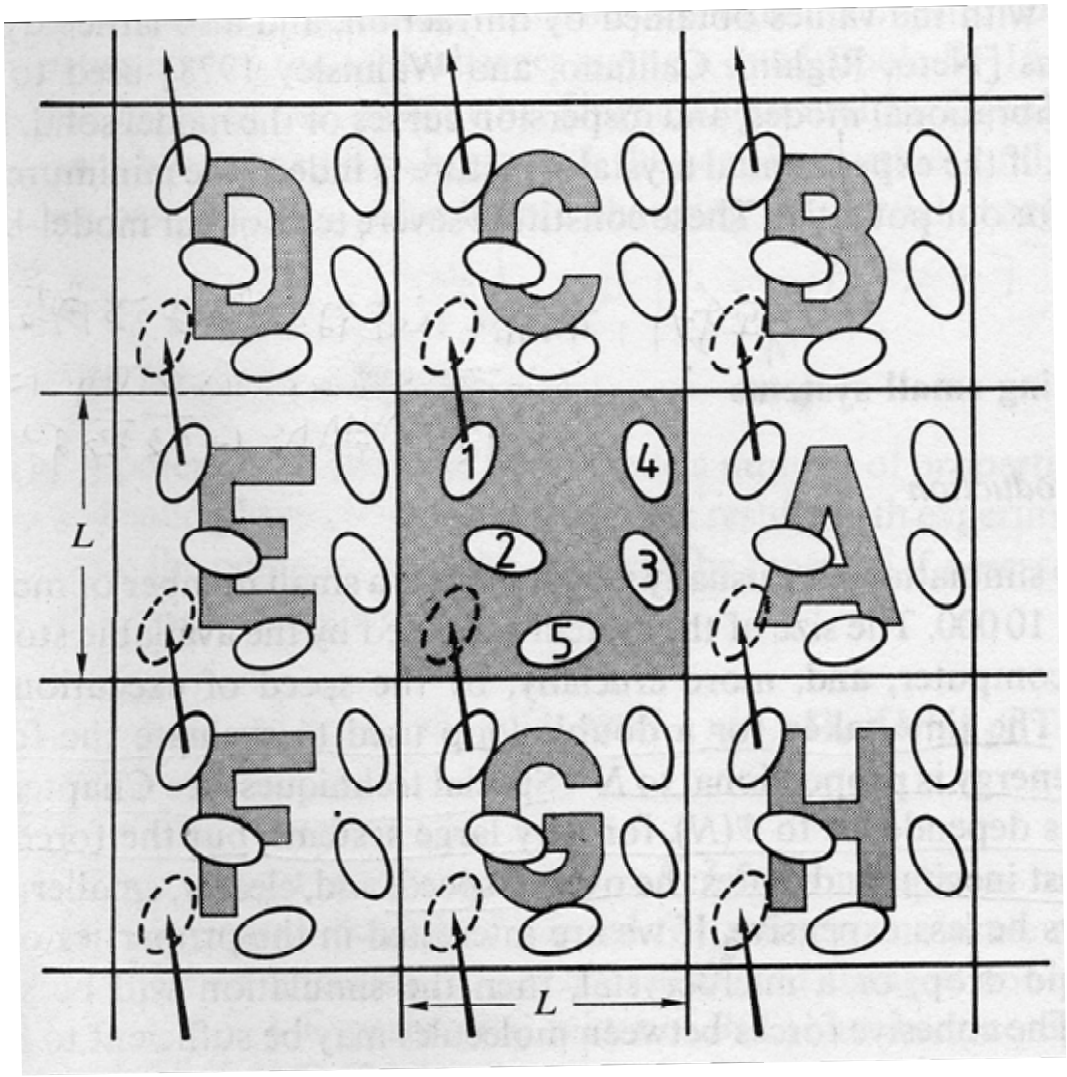
Pair potential If the interaction between i and j is pairwise, the potential energy is given by

$$\mathcal{V} = \frac{1}{2}\sum_{i,j}\phi(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i<j}\phi(|\mathbf{r}_i - \mathbf{r}_j|) \qquad (1)$$

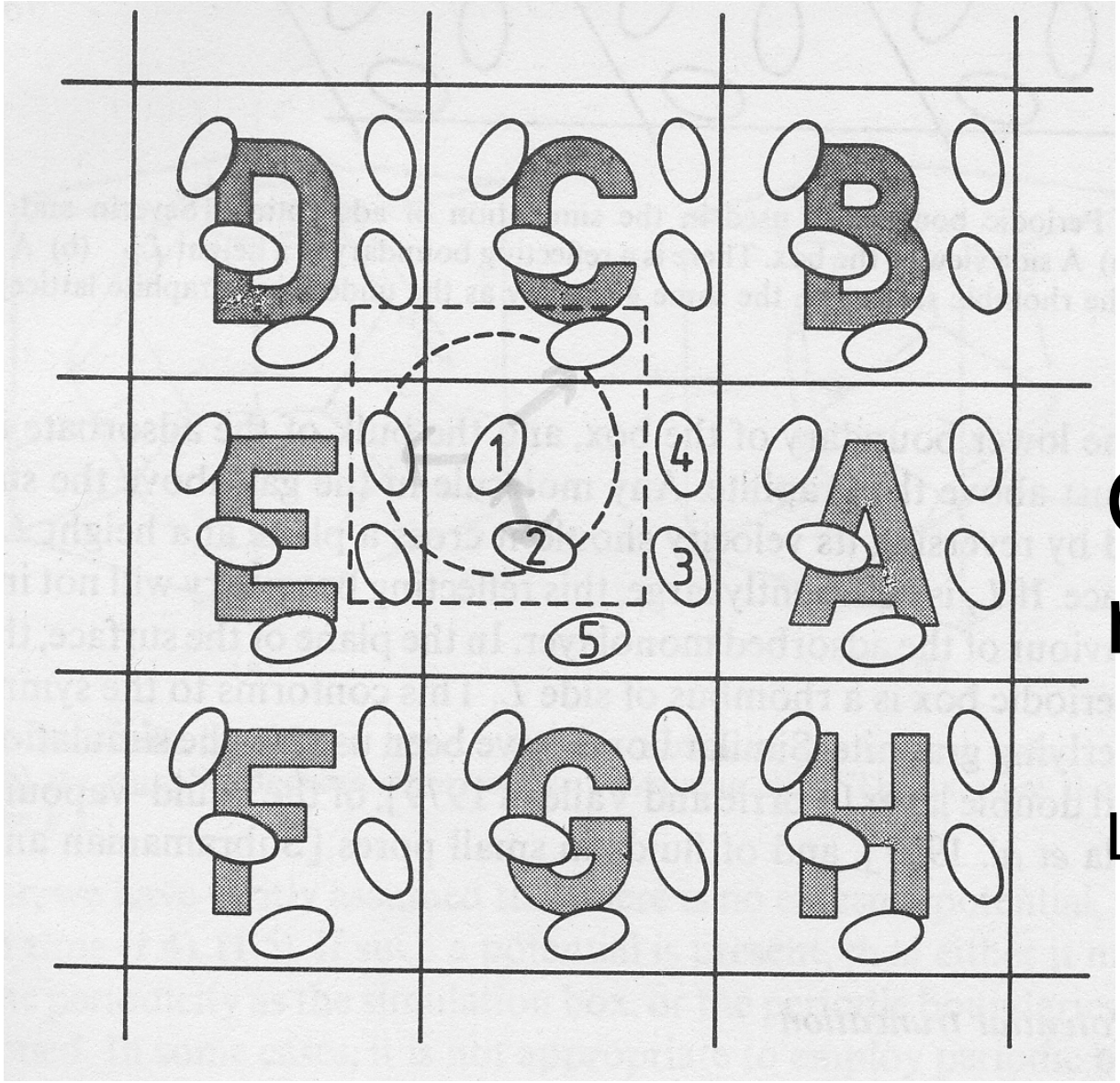
The force acting on the atom k can be written as

$$\begin{aligned}
\vec{\mathbf{f}}_k &= -\nabla_k \mathcal{V} = -\left(\mathbf{i}\frac{\partial}{\partial x_k} + \mathbf{j}\frac{\partial}{\partial y_k} + \mathbf{k}\frac{\partial}{\partial z_k}\right)\mathcal{V} \qquad (2)\\
r_{ij} &= |\mathbf{r}_i - \mathbf{r}_j|\\
&= [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2} \qquad (3)\\
\frac{\partial|\mathbf{r}_i - \mathbf{r}_j|}{\partial x_k} &= \frac{1}{2}|\mathbf{r}_i - \mathbf{r}_j|^{-1} 2(x_i - x_j)(\delta_{ki} - \delta_{kj}) \qquad (4)\\
\vec{\mathbf{f}}_k &= -\frac{1}{2}\sum_{i,j}[\mathbf{i}\phi'(r_{ij})\frac{x_i - x_j}{r_{ij}} + \mathbf{j}\phi'(r_{ij})\frac{y_i - y_j}{r_{ij}}\\
&\quad +\mathbf{k}\phi'(r_{ij})\frac{z_i - z_j}{r_{ij}}](\delta_{ki} - \delta_{kj}) \qquad (5)\\
&= -\sum_{i}[\phi'(r_{ki})\frac{x_k - x_i}{r_{ki}}\mathbf{i} + \phi'(r_{ki})\frac{y_k - y_i}{r_{ki}}\mathbf{j}\\
&\quad +\phi'(r_{ki})\frac{z_k - z_i}{r_{ki}}\mathbf{k}] \qquad (6)
\end{aligned}$$

Periodic Boundary Condition



Minimum image convention



Cutoff

$r_{cutoff} < L / 2$

L:PBC box length

Verlet

If the classical trajectory is continuous, the estimate of the positions at $t + \delta t$ may be given by

$$\vec{\mathbf{r}}(t+\delta t) = 2\vec{\mathbf{r}}(t) - \vec{\mathbf{r}}(t-\delta t) + (\delta t)^2 \vec{\mathbf{a}}(t) + O[(\delta t)^4] \quad (1)$$

The velocities do not appear in the above formula. They have been eliminated by addition of the equations obtained by Taylor expansion about $\vec{\mathbf{r}}(t)$:

$$\begin{aligned} \vec{\mathbf{r}}(t+\delta t) &= \vec{\mathbf{r}}(t) + \delta t \vec{\mathbf{v}}(t) + \frac{(\delta t)^2}{2}\vec{\mathbf{a}}(t) + \frac{(\delta t)^3}{6}\vec{\mathbf{b}}(t)... \\ \vec{\mathbf{r}}(t-\delta t) &= \vec{\mathbf{r}}(t) - \delta t \vec{\mathbf{v}}(t) + \frac{(\delta t)^2}{2}\vec{\mathbf{a}}(t) - \frac{(\delta t)^3}{6}\vec{\mathbf{b}}(t)... \end{aligned}$$

The velocities are not needed to compute the trajectories, but they are useful for estimating kinetic energy. They may be obtained by

$$\vec{\mathbf{v}}(t) = \frac{\vec{\mathbf{r}}(t+\delta t) - \vec{\mathbf{r}}(t-\delta t)}{2\delta t} + O[(\delta t)^2] \quad (2)$$

Velocity Verlet

Firstly, the new velocities at mid-step time $t + (\delta t/2)$ are calculated in the following way.

$$\vec{\mathbf{v}}(t + \frac{\delta t}{2}) = \vec{\mathbf{v}}(t) + \frac{\delta t}{2}\vec{\mathbf{a}}(t) = \vec{\mathbf{v}}(t) + \frac{\delta t}{2}\frac{\vec{\mathbf{f}}(t)}{m} \quad (1)$$

The new positions are calculated using these velocities at the mid-time-step.

$$\begin{aligned}
\vec{\mathbf{r}}(t + \delta t) &= \vec{\mathbf{r}}(t) + \delta t\vec{\mathbf{v}}(t) + \frac{(\delta t)^2}{2}\vec{\mathbf{a}}(t) \\
&= \vec{\mathbf{r}}(t) + \delta t\vec{\mathbf{v}}(t + \frac{\delta t}{2}) \\
&= \vec{\mathbf{r}}(t) + \delta t\left[\vec{\mathbf{v}}(t) + \frac{\delta t}{2}\frac{\vec{\mathbf{f}}(t)}{m}\right] + O[(\delta t)^4]
\end{aligned}$$

The forces and accelerations ($\vec{\mathbf{f}} = m\vec{\mathbf{a}}$) at time $t + \delta t$ are then computed from $\vec{\mathbf{r}}(t + \delta t)$, and the velocity at time $t + \delta t$ is estimated by

$$\begin{aligned}
\vec{\mathbf{v}}(t + \delta t) &= \vec{\mathbf{v}}(t + \frac{\delta t}{2}) + \frac{\delta t}{2}\vec{\mathbf{a}}(t + \delta t) \\
&= \vec{\mathbf{v}}(t + \frac{\delta t}{2}) + \frac{\delta t}{2}\frac{\vec{\mathbf{f}}(t + \delta t)}{m}
\end{aligned}$$

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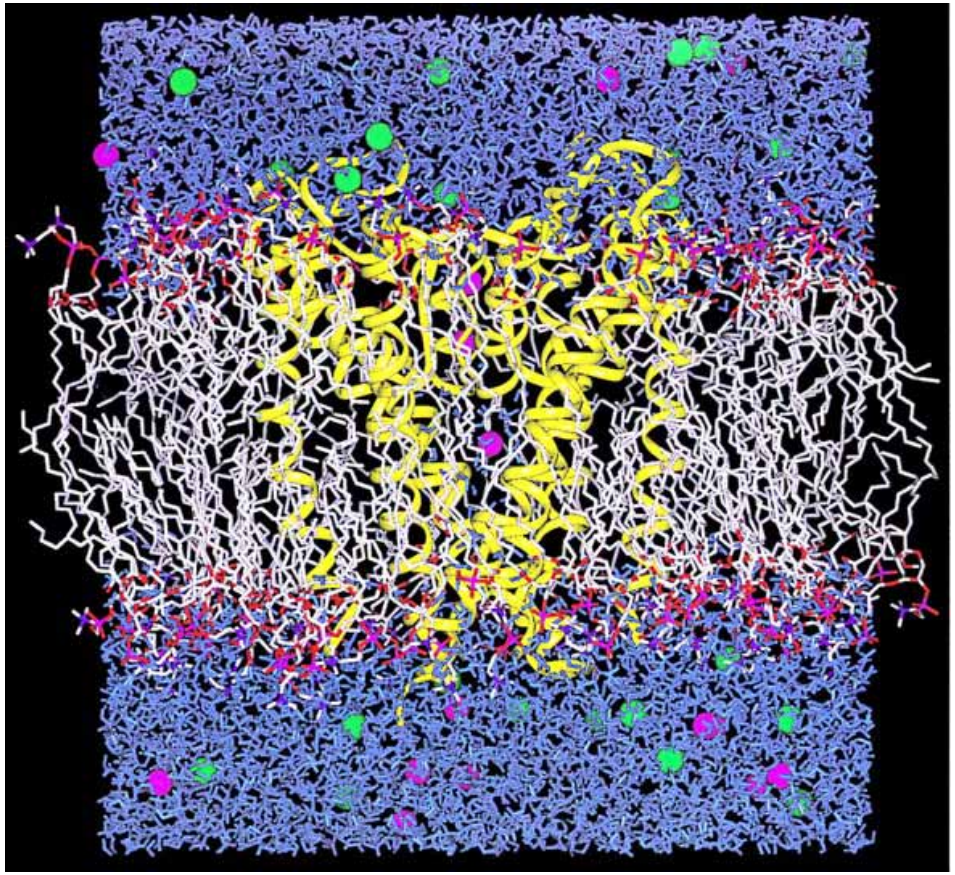
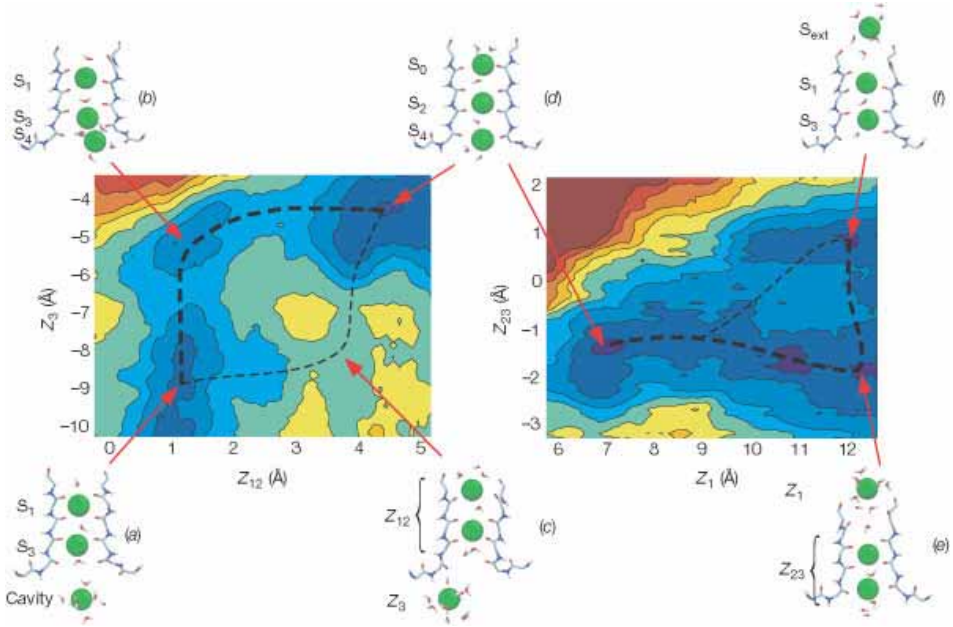
Energetics of ion conduction through the K+ channel





Simulations and parameters All simulations were carried out using the program CHARMM23. The total number of atoms in the simulation system is slightly above 40,000 (KcsA, 112 dipalmitoyl phosphatidylcholine (DPPC), 6,532 water molecules, 3 K+ in the pore, and 12 K+ and 23 Cl- in the bulk solution).