2. Fundamentals of Molecular Dynamics Method

Newton's equation of motion

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i = -\nabla\Phi$$

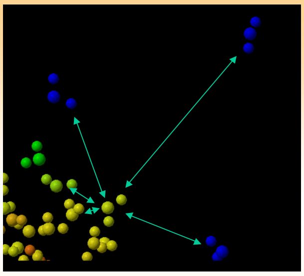
Approximation of Schrödinger Equation

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi$$

Pair Potential Approximation

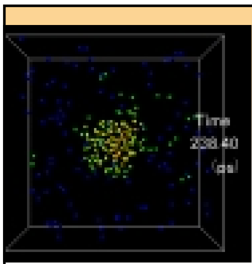
$$\Phi = \sum_i \sum_{j>i} \phi(r_{ij})$$

Equation of Motion and Potential

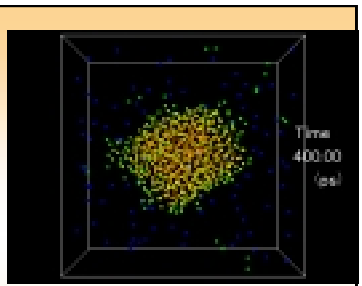


Newton's Equation $$\boldsymbol{F}_i = \sum_j \boldsymbol{F}_{ij} = m_i \frac{d^2\boldsymbol{r}_i}{dt^2}$$

Pair Potential Approximation

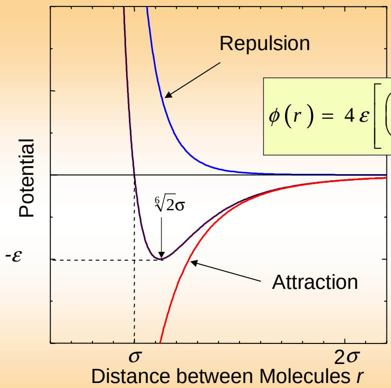


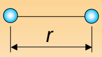
Only 256 molecules



864 molecules

Small Droplets





$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Lennard-Jones (12-6) Potential (1)

Parameters for inert molecules.

	σ [nm]	ε [J]	ε/k_B [K]
Ne	0.274	0.50×10^{-21}	36.2
Ar	0.340	1.67×10^{-21}	121
Kr	0.365	2.25×10^{-21}	163
Xe	0.398	3.20×10^{-21}	232

Cut-Off of potential: r_c = 2.5～5.5σ

$$\phi(r) = 4\varepsilon\left[\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} + \left(6r_C^{*-12} - 3r_C^{*-6}\right)\left(\frac{r}{r_C}\right)^2 - \left(7r_C^{*-12} - 4r_C^{*-6}\right)\right]$$

Lennard-Jones Potential (2)

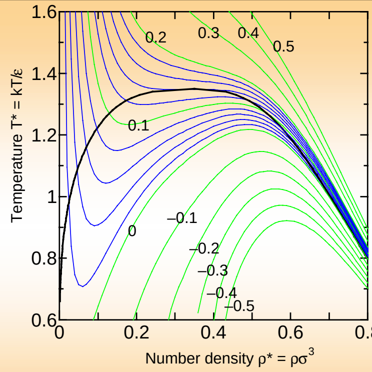
Non-dimensional Form for L-J System

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

$$\tau = \sigma\sqrt{m/\varepsilon}$$

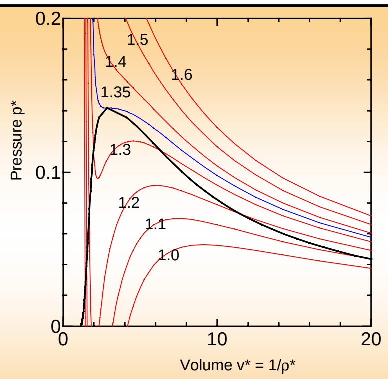
$$E = \frac{E}{N\varepsilon}$$

Lennard-Jones Potential (3)



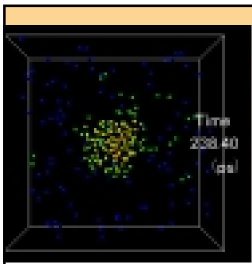
Phase Diagram
T-ρ

Lennard-Jones Potential (4)

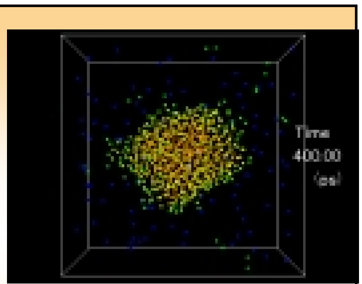


Phase Diagram
p-v

Lennard-Jones Potential (5)

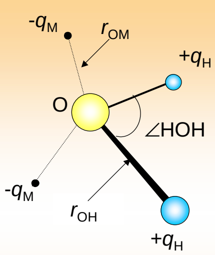


Only 256 molecules



864 molecules

Small Droplets



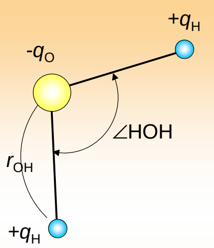
BNS potential
by Ben-Naim and Stillinger (1972)

ST2 potential
by Stillinger and Rahman (1974)

$$\angle HOH = 2\cos^{-1}\left(1/\sqrt{3}\right) = 109.47°$$

$$\phi_{12}(\boldsymbol{R}_1, \boldsymbol{R}_2) = 4\varepsilon_{OO}\left[\left(\frac{\sigma_{OO}}{R_{12}}\right)^{12} - \left(\frac{\sigma_{OO}}{R_{12}}\right)^{6}\right] + S(R_{12})\sum_i\sum_j \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

Potential for Water (BNS, ST2)

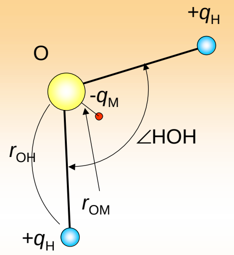


SPC potential
by Berendsen *et al*. (1981)
SPC/E potential
by Berendsen *et al*. (1987)

$$\angle HOH = 2\cos^{-1}\left(1/\sqrt{3}\right) = 109.47°$$

$$\phi_{12}(\boldsymbol{R}_1, \boldsymbol{R}_2) = 4\varepsilon_{OO}\left[\left(\frac{\sigma_{OO}}{R_{12}}\right)^{12} - \left(\frac{\sigma_{OO}}{R_{12}}\right)^{6}\right] + \sum_i\sum_j \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

Potential for Water (SPC, SPC/E)



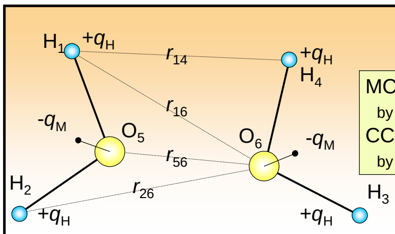
TIP4P potential
by Jorgensen *et al.* (1983)

$\angle HOH = 104.52°$

$$\phi_{12}(\boldsymbol{R}_1, \boldsymbol{R}_2) = 4\varepsilon_{OO}\left[\left(\frac{\sigma_{OO}}{R_{12}}\right)^{12} - \left(\frac{\sigma_{OO}}{R_{12}}\right)^{6}\right] + \sum_i \sum_j \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

Potential for Water (TIP4P)

Fitting to *ab initio*



MCY potential
by Matsuoka et al. (1976)
CC potential
by Carravetta & Clementi (1984)

$\angle HOH = 104.52°$

$$\begin{aligned}\phi_{12}(\boldsymbol{R}_1, \boldsymbol{R}_2) = \sum_i \sum_j \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} &+ a_1 \exp(-b_1 r_{56}) \\ &+ a_2[\exp(-b_2 r_{13}) + \exp(-b_2 r_{14}) + \exp(-b_2 r_{23}) + \exp(-b_2 r_{24})] \\ &+ a_3[\exp(-b_3 r_{16}) + \exp(-b_3 r_{26}) + \exp(-b_3 r_{35}) + \exp(-b_3 r_{45})] \\ &- a_4[\exp(-b_4 r_{16}) + \exp(-b_4 r_{26}) + \exp(-b_4 r_{35}) + \exp(-b_4 r_{45})]\end{aligned}$$

Potential for Water (MCY, CC)

SPC/E, TIP4P, CC are currently used

		ST2	SPC/E	TIP4P	CC
r_{OH}	[nm]	0.100	0.100	0.095 72	0.095 72
∠HOH	[°]	109.47	109.47	104.52	104.52
σ_{OO}	[nm]	0.310	0.316 6	0.315 4	N/A
ε_{OO} $\times 10^{-21}$	[J]	0.526 05	1.079 7	1.077 2	N/A
r_{OM}	[nm]	0.08	0	0.015	0.024 994
q_H[a]	[C]	0.235 7 e	0.423 8 e	0.52 e	0.185 59 e
q_M	[C]	-0.235 7 e	-0.847 6 e	-1.04 e	-0.371 18 e

[a]Charge of electron $e = 1.60219\times10^{-19}$ C

Potential for Water (Comparison)

Rigid potentials are *Effective* Pair Potential

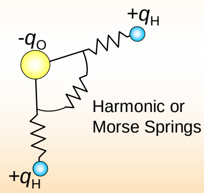
c/f Dipole moment:
Isolated water: 1.85 D
SPC/E: 2.351 D

Polarizable Potentials

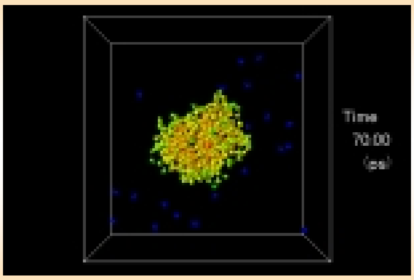
TIP4P: Dang & Chang (1997)
MCY: Niesar et al. (1990)
SPC: Bernardo et al. (1994)

Flexible Potentials

Dang & Pettitt (1987)
Anderson et al. (1987)



Potential for Water (Polarizable & Flexible)



Droplet of Water

Tersoff (1988, 1989), Brenner (1990)

$$\Phi = \sum_i \sum_{j(i<j)} f_C(r_{ij})\{V_R(r_{ij}) - b^*_{ij} V_A(r_{ij})\}$$

$$V_R(r) = f_C(r)\frac{D_e}{S-1}\exp\{-\beta\sqrt{2S}(r-R_e)\}$$

$$V_A(r) = f_C(r)\frac{D_e S}{S-1}\exp\{-\beta\sqrt{2/S}(r-R_e)\}$$

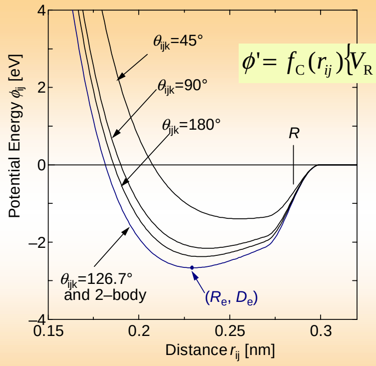
$$f_C(r) = \begin{cases} 1 & (r < R-D) \\ \frac{1}{2} - \frac{1}{2}\sin\left[\frac{\pi}{2}(r-R)/D\right] & (R-D < r < R+D) \\ 0 & (r > R+D) \end{cases}$$

$$b^*_{ij} = \frac{b_{ij} + b_{ji}}{2} \qquad b_{ij} = \left(1 + a^n \left\{\sum_{k(\neq i,j)} f_C(r_{ik}) g(\theta_{ijk})\right\}^n\right)^{-\delta}$$

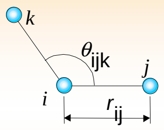
$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}$$

Potential for Covalent System (C, Si)

Tersoff's Silicon



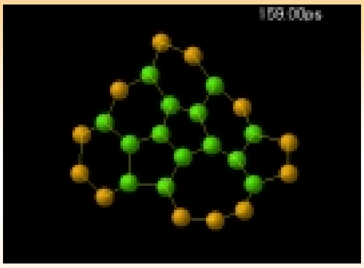
$$\phi' = f_C(r_{ij})\left\{V_R(r_{ij}) - b_{ij} V_A(r_{ij})\right\}$$



Potential for Covalent System (C, Si)

	Tersoff (Si)	Tersoff (C)	Brenner (C)
D_e [eV]	2.6660	5.1644	6.325
R_e [nm]	0.2295	0.1447	0.1315
S	1.4316	1.5769	1.29
β [nm^{-1}]	14.656	19.640	1.5
A	1.1000×10^{-6}	1.5724×10^{-7}	1.1304×10^{-2}
N	7.8734×10^{-1}	7.2751×10^{-1}	1
δ	$1/(2n)$	$1/(2n)$	0.80469
C	1.0039×10^{5}	3.8049×10^{4}	19
D	1.6217×10^{1}	4.384	2.5
H	-5.9825×10^{-1}	-5.7058×10^{-1}	-1
R [nm]	0.285	0.195	0.185
D [nm]	0.015	0.015	0.015

Potential for Covalent System (C, Si)



Example: Brenner Carbon (modified)

Potential for Covalent System (C, Si)

Verlet's Method

$$\boldsymbol{r}_i(t+\Delta t) = 2\boldsymbol{r}_i(t) - \boldsymbol{r}_i(t-\Delta t) + (\Delta t)^2\,\boldsymbol{F}_i(t)/m_i$$

$$\boldsymbol{v}_i(t) = \{\boldsymbol{r}_i(t+\Delta t) - \boldsymbol{r}_i(t-\Delta t)\}/2\Delta t$$

Leap Flog Method (Modified Verlet)

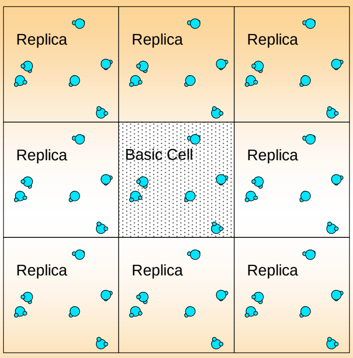
$$\boldsymbol{v}_i\left(t+\frac{\Delta t}{2}\right) = \boldsymbol{v}_i\left(t-\frac{\Delta t}{2}\right) + \Delta t\,\frac{\boldsymbol{F}_i(t)}{m_i}$$

$$\boldsymbol{r}_i(t+\Delta t) = \boldsymbol{r}_i(t) + \Delta t\,\boldsymbol{v}_i\left(t+\frac{\Delta t}{2}\right)$$

Gear's predictor-corrector method is also sometimes used

Order of Δt
0.005 τ or 10 fs with argon
0.5 fs for covalent Carbon

Integration of Newton's Equation



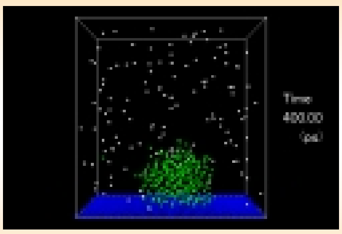
Potential must be Cut-Off at L/2

Ewald sum method for Coulomb Term

Boundary Condition (Periodic)

Example

Mirror Boundary
=Simple Reflection

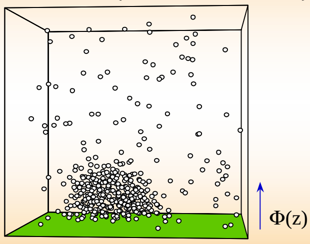


Periodic Boundary

Boundary Condition (Gas)

One-Dimensional Function by Bulk Integration

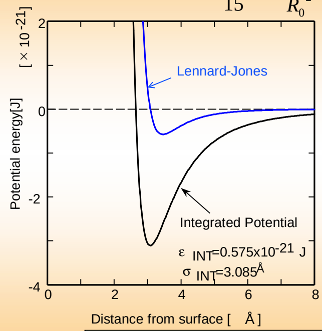
$$\Phi(z) = \frac{2\pi}{45}\frac{\rho_S}{m_S}\varepsilon_{INT}\sigma_{INT}^{\ 3}\left\{2\left(\frac{\sigma_{INT}}{z}\right)^9 - 15\left(\frac{\sigma_{INT}}{z}\right)^3\right\}$$



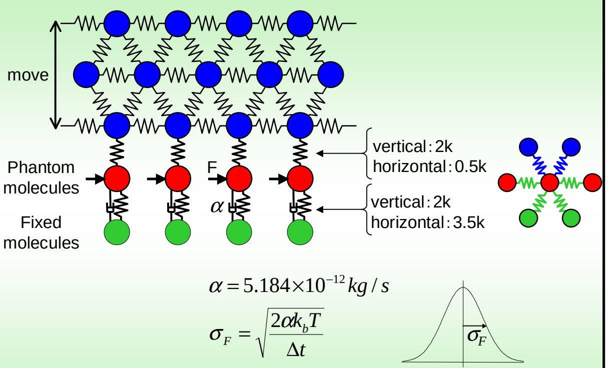
Boundary Condition (Solid Wall)

One-Dimensional Function by Surface Integration

$$\Phi(z) = \frac{4\sqrt{3}\pi}{15}\frac{\varepsilon_{INT}\sigma_{INT}^{\ 2}}{R_0^{\ 2}}\left\{2\left(\frac{\sigma_{INT}}{z}\right)^{10} - 5\left(\frac{\sigma_{INT}}{z}\right)^4\right\}$$



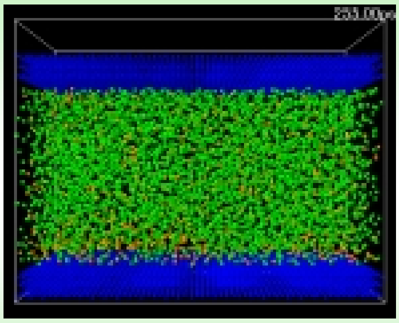
Boundary Condition (Solid Wall)



$$\alpha = 5.184 \times 10^{-12}\, kg/s$$

$$\sigma_F = \sqrt{\frac{2\alpha k_b T}{\Delta t}}$$

Boundary Condition (Phantom Method)

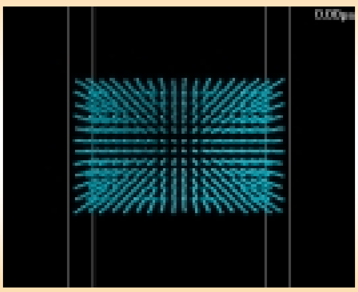


Phantom (Not Shown)

Phantom (Not Shown)

Boundary Condition (Phantom Method)

Constant velocity for random direction or Maxwell-Boltzmann distribution



$$v = \sqrt{3k_B T_C / m}$$

Make Sure Potential is not Too Large

Initial Condition

Velocity Scaling

$$v_i' = v_i\sqrt{T/T_C}$$

Anderson method [Anderson (1980)]

Replace Velocity of Randomly Selected Molecule to Maxwell-Boltzmann Distribution

Nosé-Hoover Thermostat [Nosé(1984), Hoover(1985)]

$$m_i\frac{d^2\boldsymbol{r}_i}{dt^2} = \boldsymbol{F}_i - \zeta m_i\frac{d\boldsymbol{r}_i}{dt}$$

$$\frac{d\zeta}{dt} = \frac{2\left(E_k - E_k^{\ 0}\right)}{Q}$$

Temperature Control

Andersen (1980)

Change Box Size as if Piston is Connected

Parrinello and Rahman (1980, 1981)

Extension of Anderson: Change Shape of Box

Berendsen et al. (1984)

$dP/dt = (P_C - P)/t_P$

$\mathbf{r}' = \chi^{1/3}\mathbf{r}$

$\chi = 1 - \beta_T \frac{\Delta t}{t_p}(P_C - P)$

Pressure & Stress Control