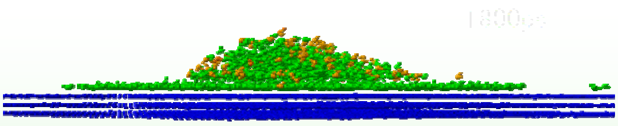
熱工学の新領域に関するクライミング･セミナー @ 仙台 2004.11.12

マイクロからナノへの熱工学
(1) 分子動力学の基礎と応用



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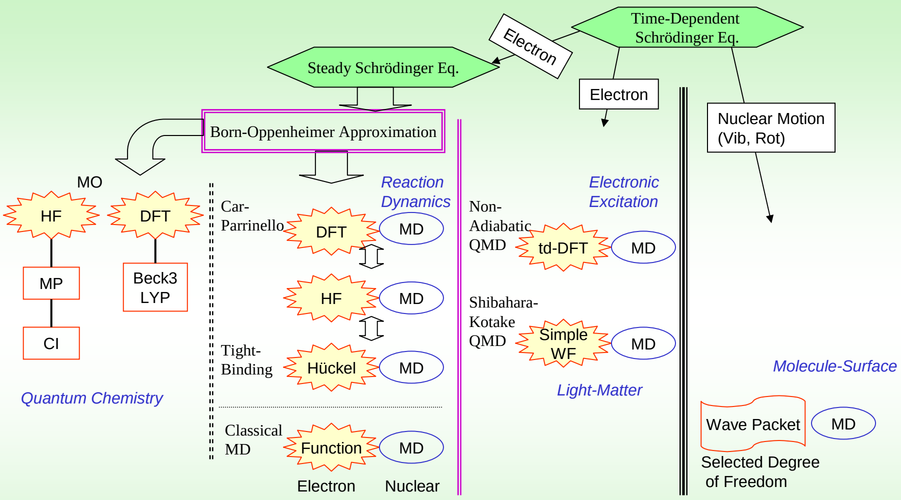


A Classification of Quantum Molecular Dynamics Methods

Schrödinger Equation

Time-Dependent Schrödinger Eq.

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \qquad H \approx H_0 + \left\{ -\sum_i e\mathbf{r}_i + \sum_k Z_k e \mathbf{R}_k \right\} \cdot \mathbf{E}$$

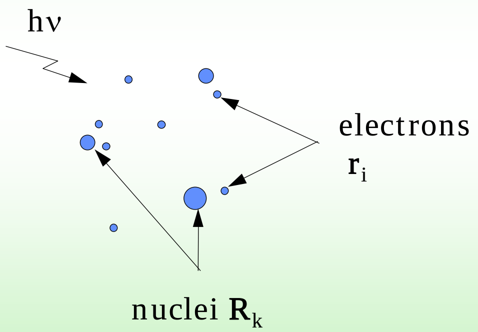
$$H_0 = -\sum_k \frac{\hbar^2}{2M_k} \nabla_k{}^2 - \sum_i \frac{\hbar^2}{2m} \nabla_i{}^2 + \sum_{k,l} \frac{Z_k Z_l e^2}{|\mathbf{R}_k - \mathbf{R}_l|} - \sum_{k,i} \frac{Z_k e^2}{|\mathbf{R}_k - \mathbf{r}_i|} + \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Electron

Steady Schrödinger Eq.

$$\psi(\vec{r}, t) = \psi_0(\vec{r}) e^{\frac{E}{i\hbar} t}$$

$$E\psi_0 = H\psi_0$$



The Born-Oppenheimer Approximation

Steady Schrödinger Eq.

Electron

Time-Dependent Schrödinger Eq.

$$H\Psi = E\Psi$$

$$\mathrm{H} = -\sum_k \frac{\hbar^2}{2M_k} \nabla_k{}^2 - \sum_i \frac{\hbar^2}{2m} \nabla_i{}^2 + \sum_{k,l} \frac{Z_k Z_l e^2}{|\mathbf{R}_k - \mathbf{R}_l|} - \sum_{k,i} \frac{Z_k e^2}{|\mathbf{R}_k - \mathbf{r}_l|} + \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Born-Oppenheimer Approximation

$$\Psi_{mol} = \psi_e(\mathbf{r};\mathbf{R}) \chi_N(\mathbf{R})$$

Electrons moves much slowly than nuclei

$$H_e \psi_e = \left\{ \sum_i \frac{\hbar^2}{2m} \nabla_i{}^2 - \sum_{k,i} \frac{Z_k e^2}{r_{ki}} + \sum_{i,j} \frac{e^2}{r_{ij}} \right\} \psi_e = E_e(R_{AB}) \psi_e$$

$$H_N \chi_N = \left\{ -\sum_{k=A,B} \frac{\hbar^2}{2M_k} \nabla_k{}^2 - E_e(R_{AB}) + \frac{Z_A Z_B e^2}{R_{AB}} \right\} \chi_N = \mathrm{E}_{\mathrm{Total}} \chi_N$$

Time-Dependent Schrödinger Eq.

Electron

Steady Schrödinger Eq.

Born-Oppenheimer Approximation

Molecular Orbital Method

LCMO(linear combination of atomic orbitals)

HF: Hartree-Fock Theory

Basis Sets

Polarized, Diffuse: 6-31G(d), 6-311+G(d,p), 6-311++G(3df, 3pd)

Electron Correlations

MP: Moller-Plesset Perturbation Theory, MP2, MP3, MP4

CI: Configuration Interaction

cf. Gaussian94

Molecular Orbital Calculations - Quantum Chemistry

Time-Dependent Schrödinger Eq.

Electron

Steady Schrödinger Eq.

Born-Oppenheimer Approximation

DFT: Density Functional Theory

$$\left[-\frac{1}{2}\nabla_i^{\,2} + V(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

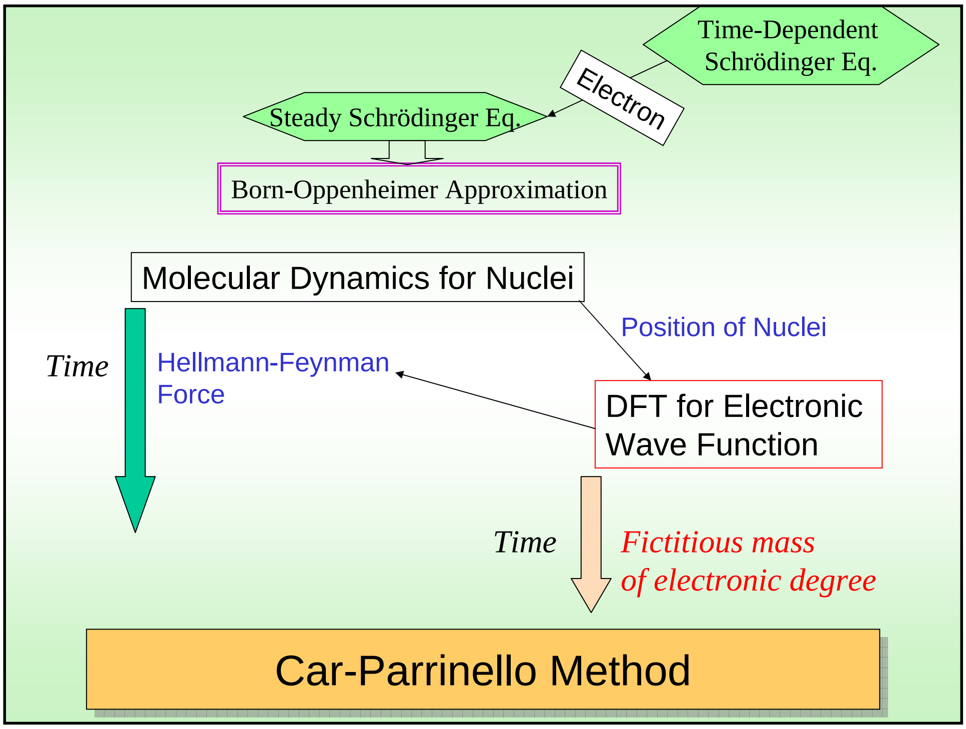
$$V(\mathbf{r}) = -\sum_{a=1}^{N}\frac{Z_a}{|\mathbf{r}-\mathbf{r}_a|} + \int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + V_{xc}(\mathbf{r})$$

Exchange-Correlation

B3LYP: Beck's 3 parameter Exchange Functional with
Lee-Yang-Parr Correlation

cf. Gaussian94

Density Functional Theory - Quantum Chemistry



Time-Dependent Schrödinger Eq.
Electron
Steady Schrödinger Eq.
Born-Oppenheimer Approximation
Molecular Dynamics for Nuclei
Position of Nuclei
Time
Hellmann-Feynman Force
DFT for Electronic Wave Function
Time
Fictitious mass of electronic degree
Car-Parrinello Method

分子動力学法の基礎

Approximation of Schrödinger Equation

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

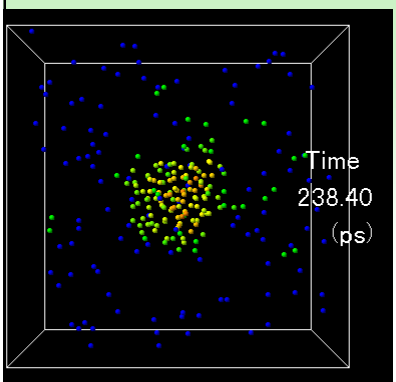
Newton's equation of motion

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

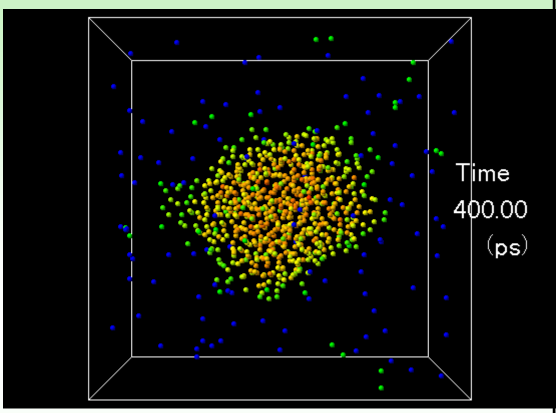
Pair Potential Approximation

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

運動方程式とポテンシャル

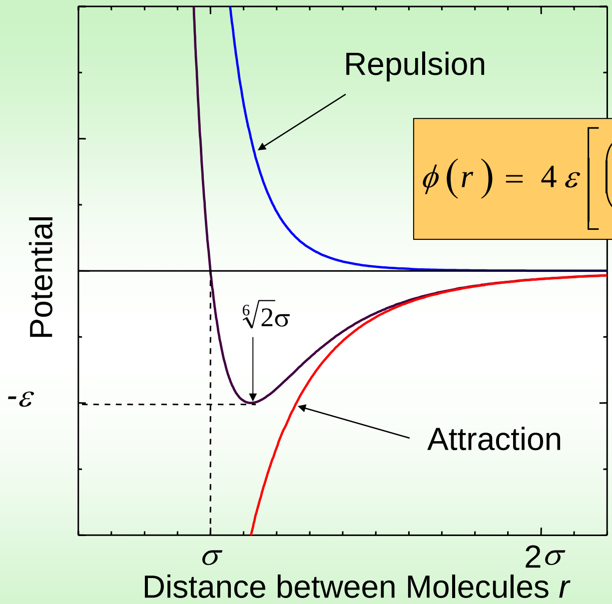


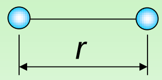
Only 256 molecules



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)

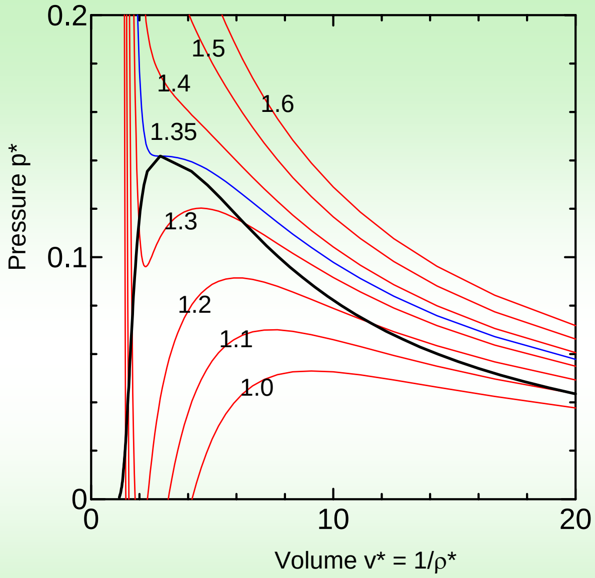
Lennard-Jones Potential (2)

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

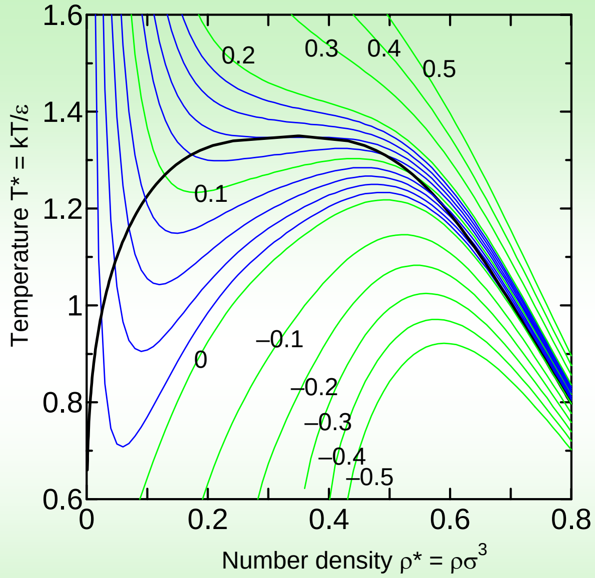
Non-dimensional Form for L-J System

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	$\gamma^* =$	$\gamma\sigma^2/\varepsilon$



Phase Diagram
p-v

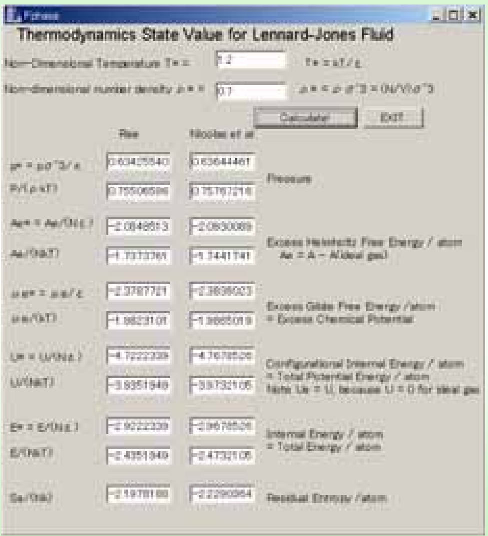
Lennard-Jones Potential (3)



Phase Diagram
T-ρ

Lennard-Jones Potential (4)

Empirical Relations

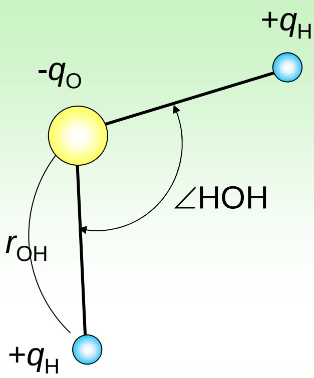


Temperature
Density

Pressure
Helmholtz Free Energy
Gibbs Free Energy
Potential Energy
Internal Energy
Entropy

Ree correlation
and Nicolas et al. correlation

http://www.photon.t.u-tokyo.ac.jp/~maruyama/ljphase/ljphase.html

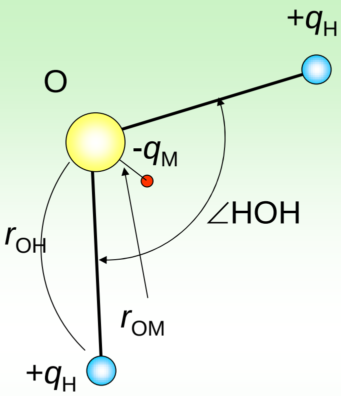


SPC potential
by Berendsen *et al*. (1981)
SPC/E potential
by Berendsen *et al*. (1987)

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

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

Potential for Water (SPC, SPC/E)



TIP4P potential

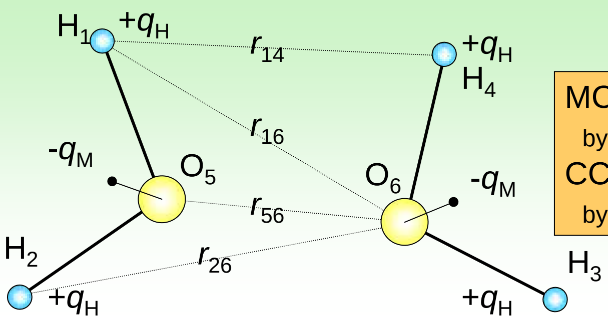
by Jorgensen *et al.* (1983)

$$\angle HOH = 104.52^\circ$$

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

Potential for Water (TIP4P)

Fitting to *ab initio*



MCY potential

by Matsuoka et al. (1976)

CC potential

by Carravetta & Clementi (1984)

$$\angle HOH = 104.52^\circ$$

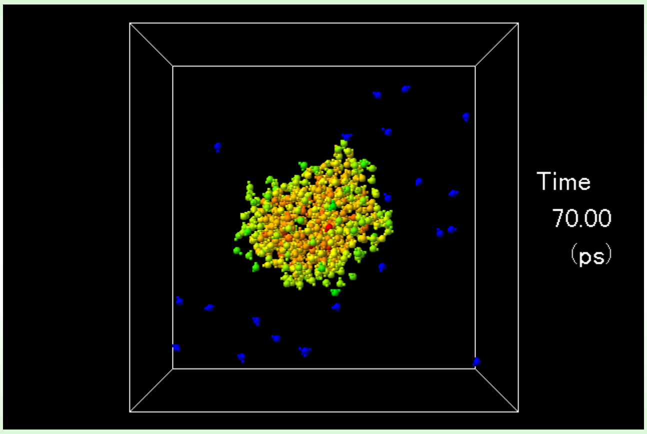
$$\begin{aligned}\phi_{12}(\boldsymbol{R}_1, \boldsymbol{R}_2) = {} & \sum_i \sum_j \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + a_1 \exp(-b_1 r_{56}) \\ & + a_2\left[\exp(-b_2 r_{13}) + \exp(-b_2 r_{14}) + \exp(-b_2 r_{23}) + \exp(-b_2 r_{24})\right] \\ & + a_3\left[\exp(-b_3 r_{16}) + \exp(-b_3 r_{26})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

Potential for Water (MCY, CC)

Potential for Water (Comparison)

			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 $e = 1.60219 \times 10^{-19}$ C



Droplet of Water

Tersoff (1988, 1989), Brenner (1990)

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

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

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

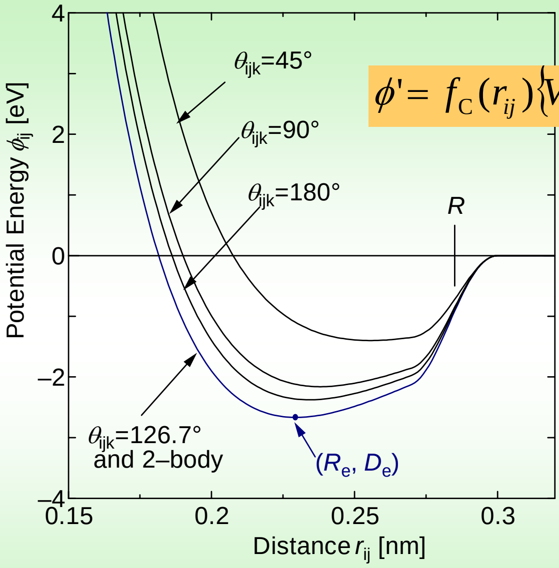
$$f_C(r) = \begin{cases} 1 & (r < R-D) \\ \frac{1}{2} - \frac{1}{2}\sin\left[\frac{\pi}{2}(r-R)/D\right] & (R-D < r < R+D) \\ 0 & (r > R+D) \end{cases}$$

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

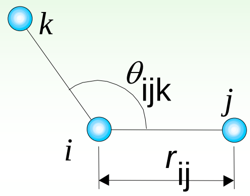
$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}$$

Potential for Covalent System (C, Si)

Tersoff's Silicon



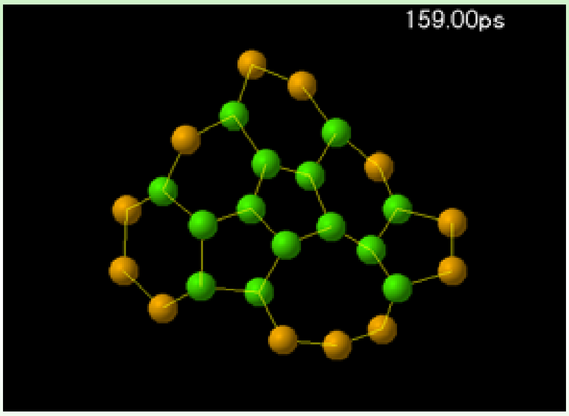
$$\phi' = f_C(r_{ij})\{V_R(r_{ij}) - b_{ij} V_A(r_{ij})\}$$



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)

Integration of Newton's Equation

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)

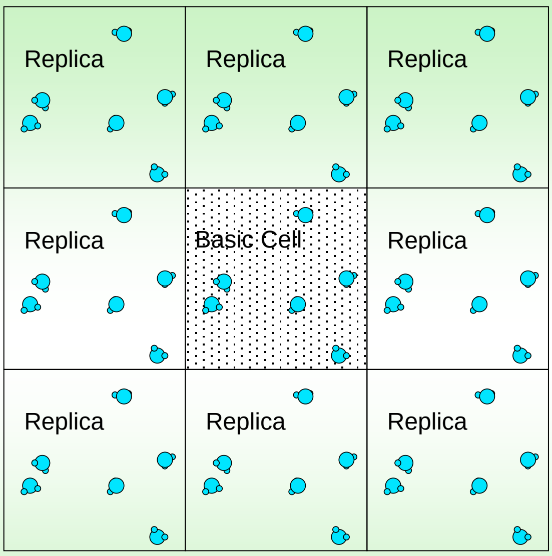
$$\boldsymbol{v}_i\left(t+\frac{\Delta t}{2}\right) = \boldsymbol{v}_i\left(t-\frac{\Delta t}{2}\right) + \Delta t\,\frac{\boldsymbol{F}_i(t)}{m_i}$$

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

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

Gear's predictor-corrector method is also sometimes used

Boundary Condition (Periodic)

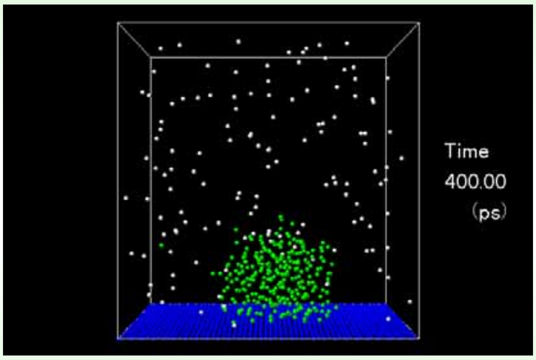


Potential must be Cut-Off at L/2

Ewald sum method for Coulomb Term

Example

Mirror Boundary
=Simple Reflection

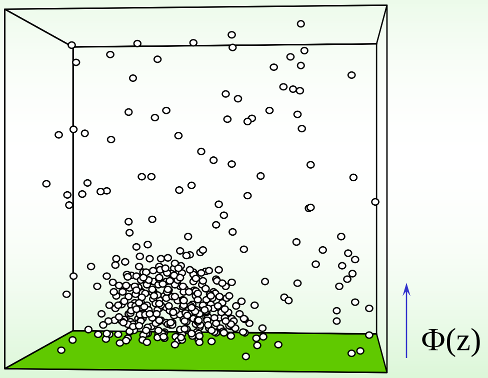


Periodic Boundary

Boundary Condition (Gas)

One-Dimensional Function by Bulk Integration

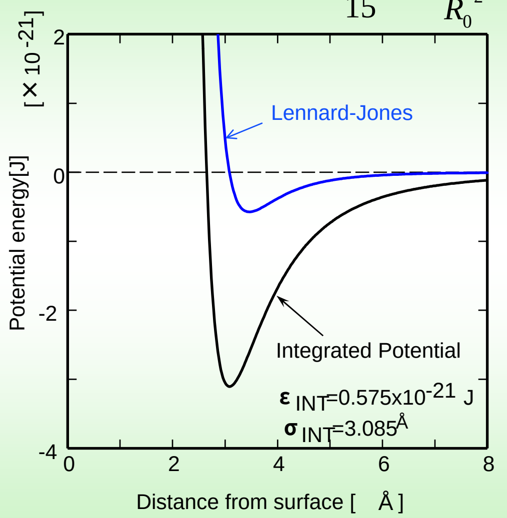
$$\Phi(z)=\frac{2\pi}{45}\frac{\rho_S}{m_S}\varepsilon_{INT}\sigma_{INT}{}^3\left\{2\left(\frac{\sigma_{INT}}{z}\right)^9-15\left(\frac{\sigma_{INT}}{z}\right)^3\right\}$$



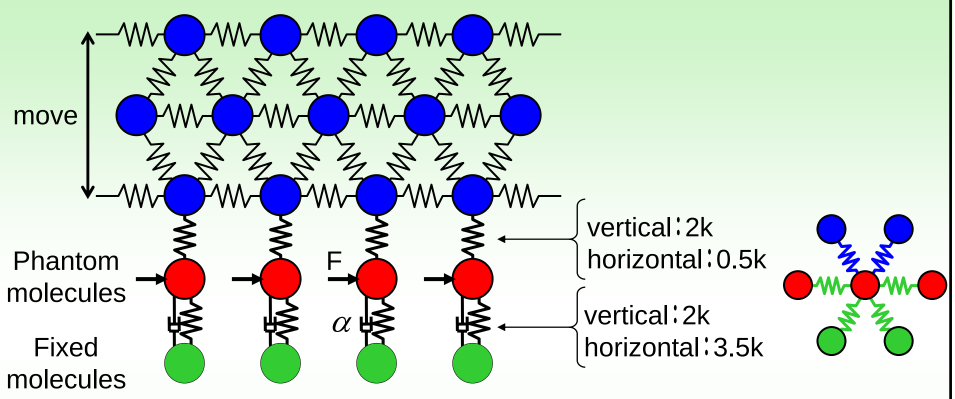
Boundary Condition (Solid Wall)

One-Dimensional Function by Surface Integration

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

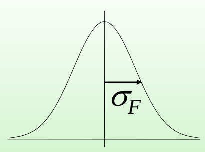


Boundary Condition (Solid Wall)



$$\alpha = 5.184\times10^{-12}\,kg/s$$

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



Boundary Condition (Phantom Method)

Temperature Control

Velocity Scaling

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

Anderson method [Anderson (1980)]

Replace Velocity of Randomly Selected Molecule to Maxwell-Boltzmann Distribution

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

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

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

Pressure & Stress 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)

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

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

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

Temperature

$$T = \frac{1}{3Nk_B}\left\langle \sum_{i=1}^{N} m_i v_i^2 \right\rangle$$ For Monatomic Molecule

Remember Thermodynamics

$$\frac{E_k}{n_f N} = \frac{1}{2}k_B T$$ Kinetic energy for each freedom

$$n_f = \begin{cases} 3 & \text{for monoatomic molecules} \\ 5 & \text{for diatomic molecules} \end{cases}$$

Thermodynamics Properties

Internal Energy or Total Energy

$$U = E_k + E_p = \frac{3}{2}Nk_B T + \left\langle \sum_i \sum_{j>i} \phi(\mathbf{r}_{ij}) \right\rangle$$

Remember Thermodynamics for Ideal Gas

$$U = E_k = \frac{n_f}{2} N_A k_B T = \frac{n_f}{2} R_0 T$$ per mol

$$u = \frac{U}{m'} = \frac{n_f}{2}\frac{R_0}{m'}T = \frac{n_f}{2} RT$$ per mass

k_B : Boltzmann Constant, 1.38066×10^{-23} J/K
N_A : Avogadro Number, 6.02205×10^{23} 1/mol
R_0 : Universal Gas Constant, 8.31433 J/(mol K)
m': Molecular Weight (kg/mol)

Pressure by virial theorem

$$P = \frac{N}{V} k_B T - \frac{1}{3V} \left\langle \sum_i \sum_{j>i} \frac{\partial \phi}{\partial \mathbf{r}_{ij}} \cdot \mathbf{r}_{ij} \right\rangle$$

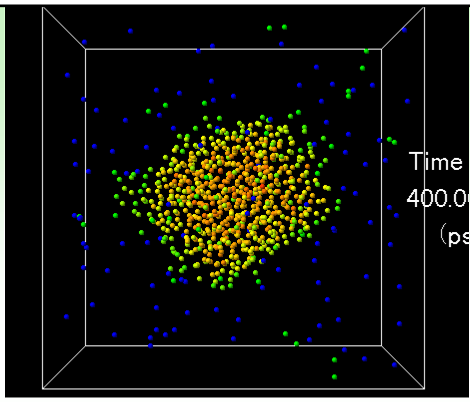
Thermodynamics for Ideal Gas

$$P = \frac{N}{V} k_B T$$

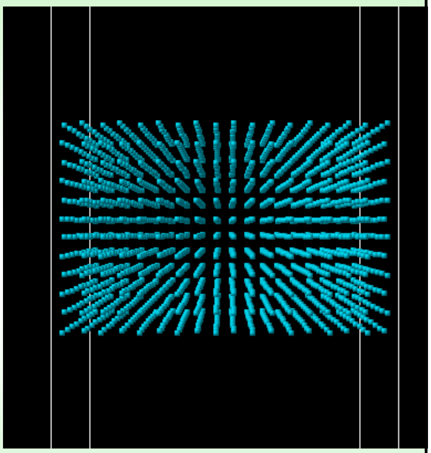
$$PV = nN_A k_B T = nR_0 T$$ For n mol

$$P = \frac{nN_A}{V} k_B T = \rho k_B T$$ ρ: Number density

相界面･濡れ･核生成



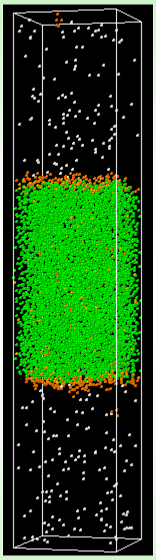
Liquid Droplet

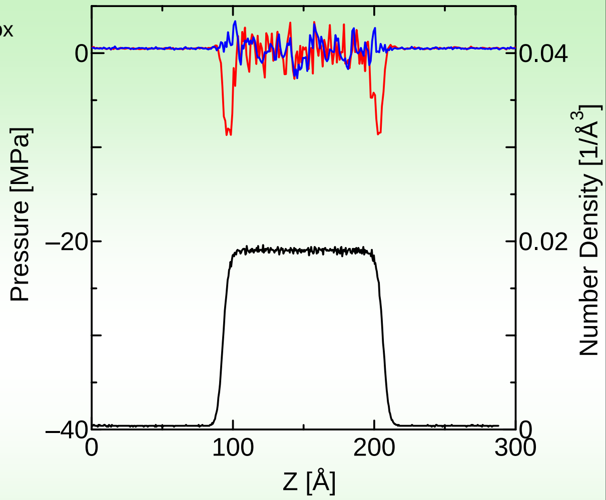


Flat Interface

Liquid-Vapor Interface

8000 molecules in 60×60×300 box

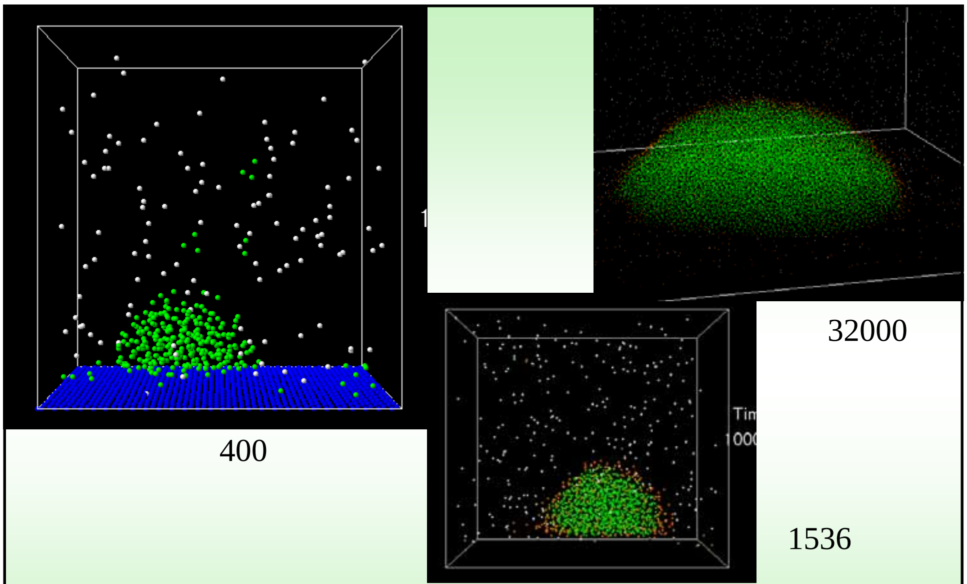




$$P_{ij}V = \sum_{m \in V} m^m \overline{v_i^m v_j^m} + \sum_{m \in V} \overline{x_i^m F_j^m}$$

Surface Tension

$$\gamma_{\mathrm{LG}} = \int_{z_{\mathrm{L}}}^{z_{\mathrm{G}}} \left[P_{\mathrm{N}}(z) - P_{\mathrm{T}}(z) \right] dz$$



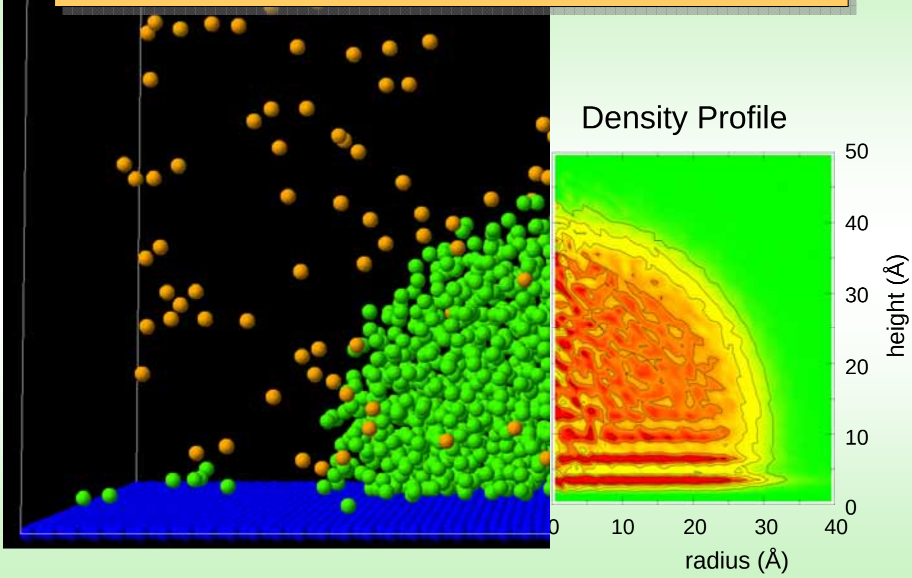
400

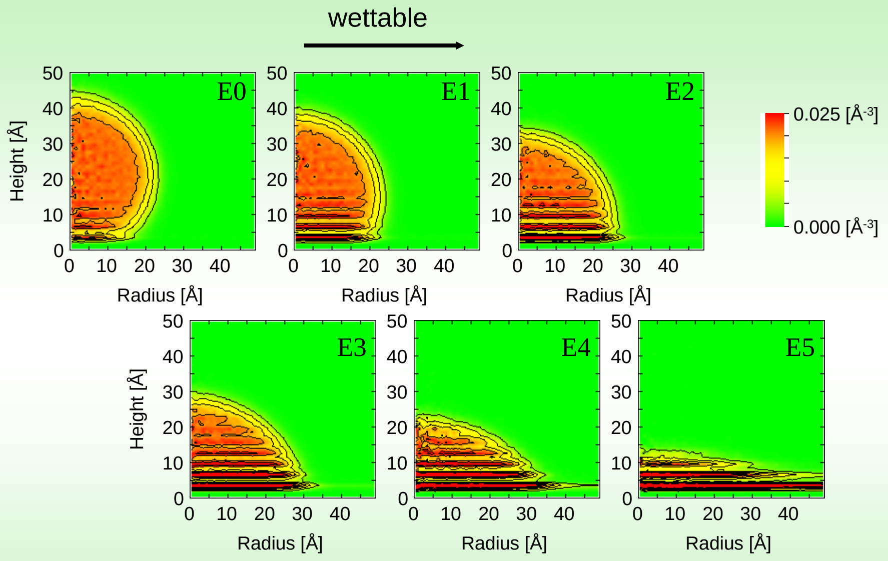
32000

1536

Liquid Droplet on Solid Surface

Liquid Droplet in Contact with a Surface



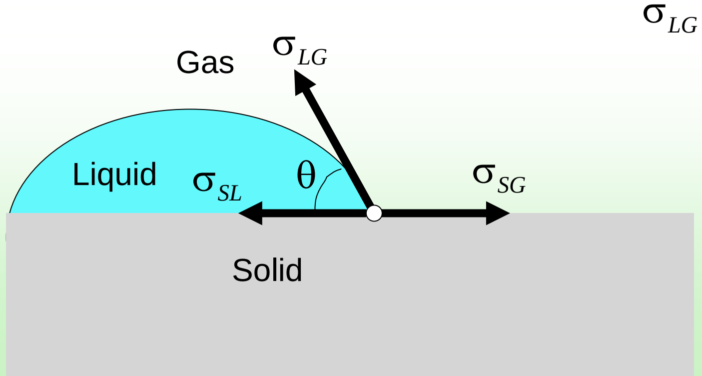


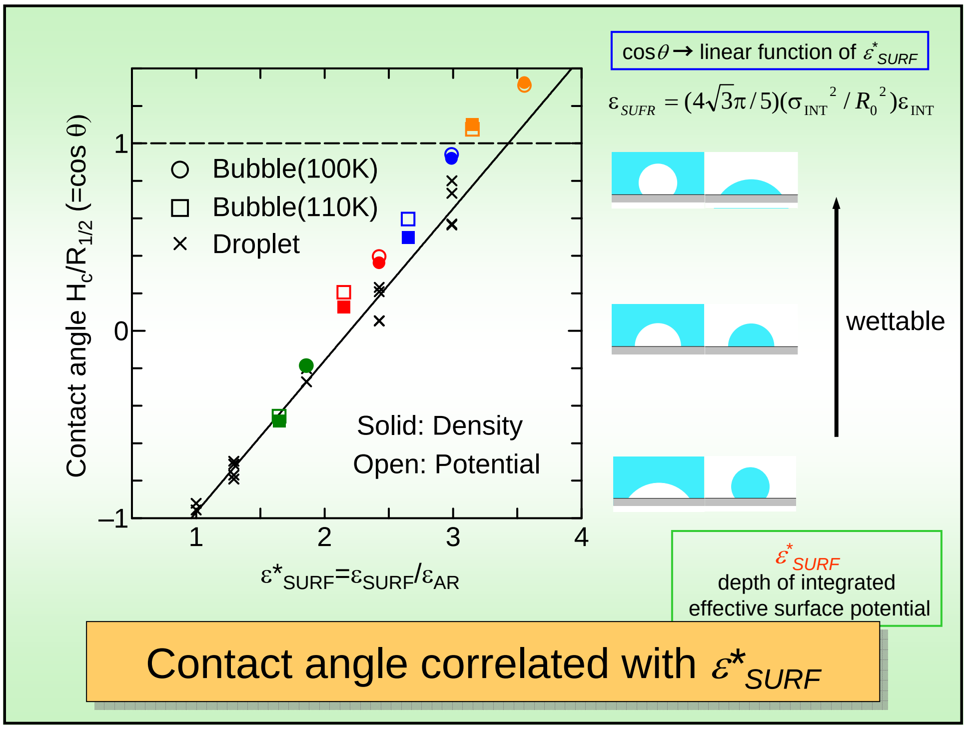
2-D Density Distributions for L-J Droplet

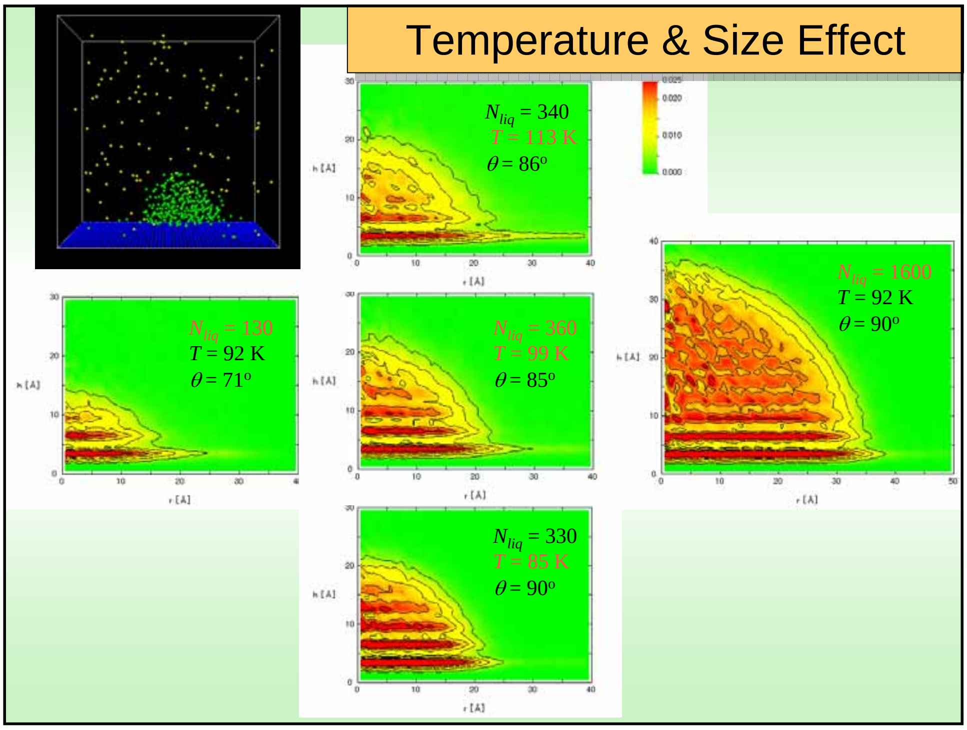
Young's Equation (Macroscopic)

$$\sigma_{LG}\cos\theta + \sigma_{SL} = \sigma_{SG}$$

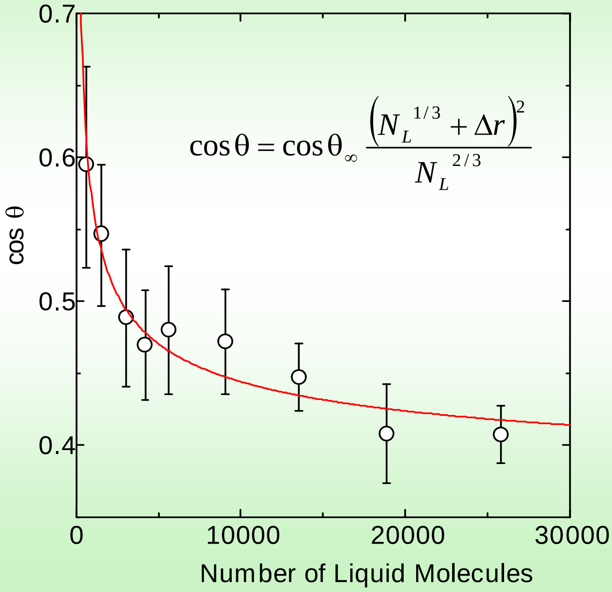
$$\cos\theta = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}$$




cosθ → linear function of ε*SURF
ε_SUFR = (4√3π/5)(σ_INT² / R_0²)ε_INT
Contact angle H_c/R_1/2 (=cos θ)
Bubble(100K)
Bubble(110K)
Droplet
Solid: Density
Open: Potential
ε*SURF=εSURF/εAR
wettable
ε*SURF
depth of integrated
effective surface potential
Contact angle correlated with ε*SURF


Temperature & Size Effect
N_liq = 340
T = 113 K
θ = 86°
N_liq = 130
T = 92 K
θ = 71°
N_liq = 360
T = 99 K
θ = 85°
N_liq = 1600
T = 92 K
θ = 90°
N_liq = 330
T = 85 K
θ = 90°

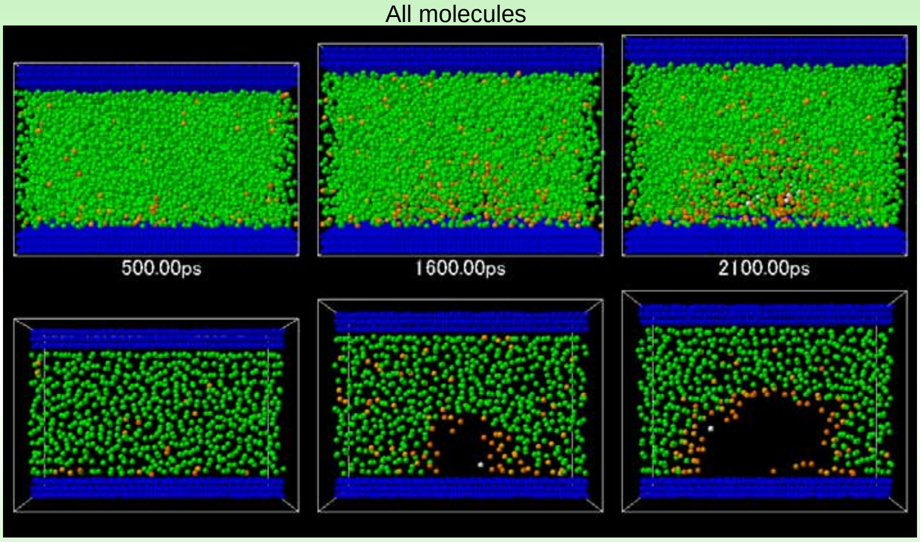
Asymptotic Macro-System



$$\cos\theta = \cos\theta_\infty \frac{\left(N_L^{1/3} + \Delta r\right)^2}{N_L^{2/3}}$$

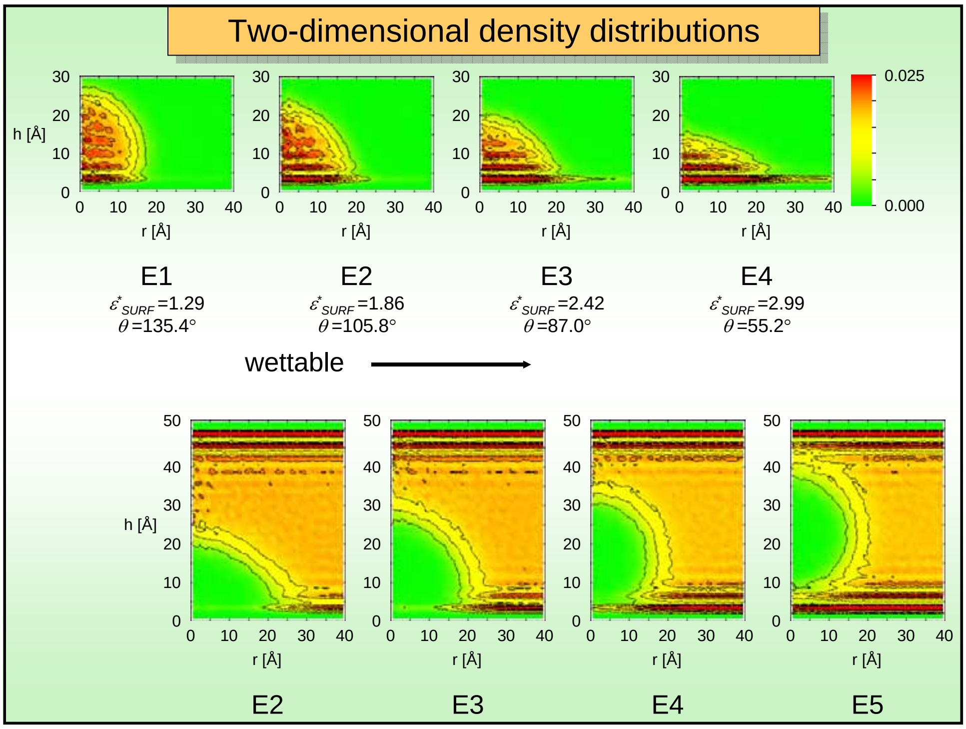
$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

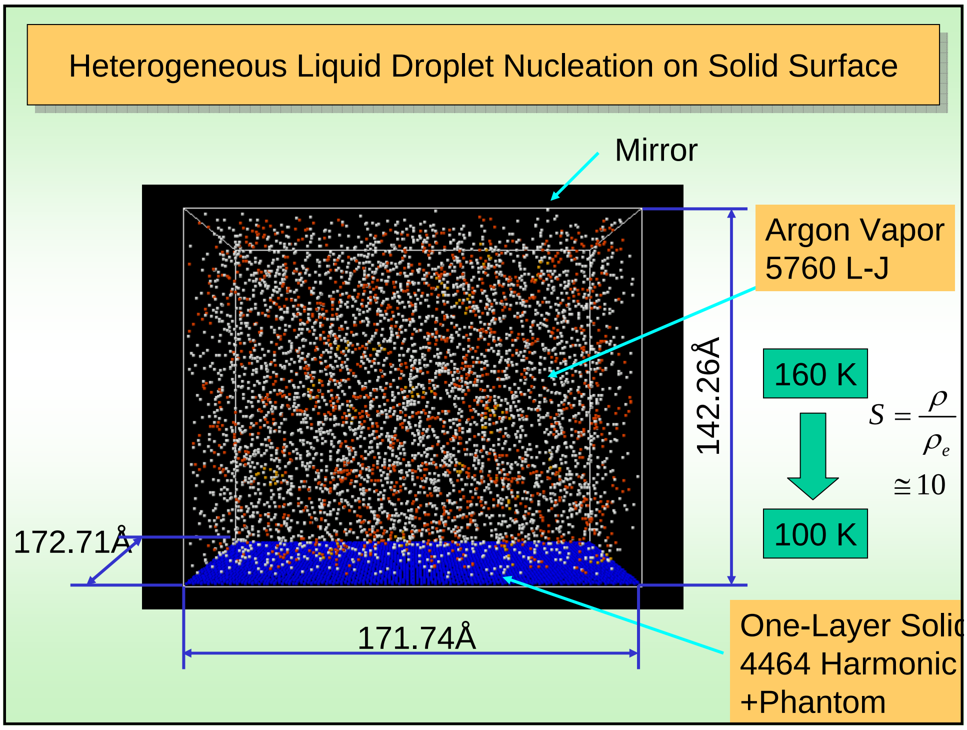
All molecules



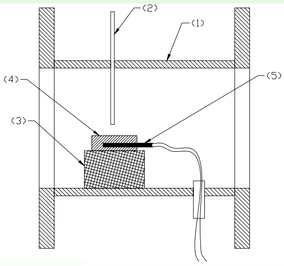
Sliced view (central 10Å)

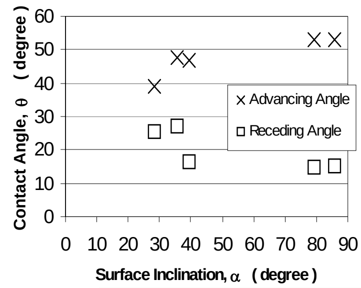
Snapshots of bubble formation for E3


Two-dimensional density distributions
h [Å]
r [Å]
0.025
0.000
E1
ε^*_{SURF}=1.29
θ=135.4°
E2
ε^*_{SURF}=1.86
θ=105.8°
E3
ε^*_{SURF}=2.42
θ=87.0°
E4
ε^*_{SURF}=2.99
θ=55.2°
wettable
E2
E3
E4
E5


Heterogeneous Liquid Droplet Nucleation on Solid Surface
Mirror
Argon Vapor
5760 L-J
142.26Å
160 K
100 K
$S = \frac{\rho}{\rho_e}$
$\cong 10$
172.71Å
171.74Å
One-Layer Solid
4464 Harmonic
+Phantom

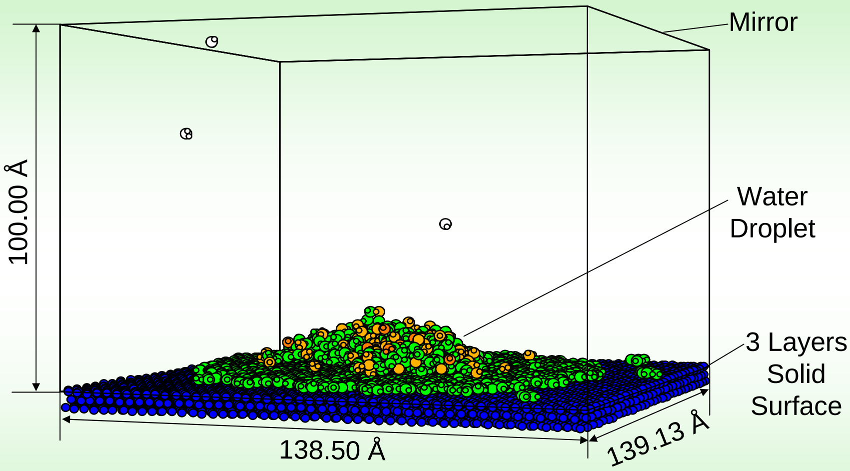
Experiments by Satish G. KANDLIKAR
Rochester Institute of Technology





$m = 1.15 \times 10^{-6}$ kg, $\alpha = 0^{\circ}$, T = 22°C, and $\theta = 22.05^{\circ}$.

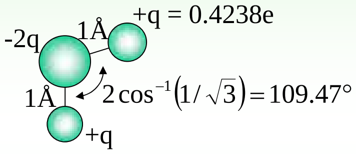
19.6 torr Vacuum, 18 MΩ de-ionized water
Surface roughness, Ra, value of 0.02 μm
Modified RCA cleaning (1 part NH_4OH, 3 parts H_2O_2, and 15 parts H_2O)

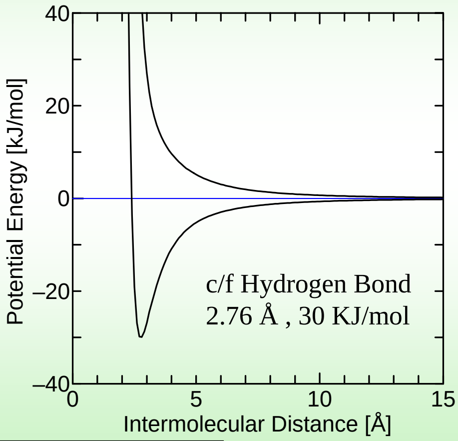


System Configuration
(water droplet on fcc(111) platinum surface)

SPC/E H. J. C. Berendsen, et al. (1987)

$$\phi = 4\varepsilon\left\{\left(\frac{\sigma}{r_{OO}}\right)^{12} - \left(\frac{\sigma}{r_{OO}}\right)^{6}\right\} + \sum_i \sum_j \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$





Cut-off Length
25 Å

Water-Water Potential

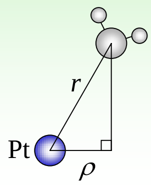
E. Spohr & K. Heinzinger (1988)

$$\phi_{H_2O-Pt} = \phi_{O-Pt}(r_{OPt}, \rho_{OPt}) + \phi_{H-Pt}(r_{H_1Pt}) + \phi_{H-Pt}(r_{H_2Pt})$$

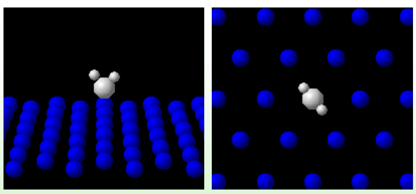
$$\phi_{O-Pt} = [a_1 \exp(-b_1 r) - a_2 \exp(-b_2 r)] f(\rho) + a_3 \exp(-b_3 r)[1 - f(\rho)]$$

$$\phi_{H-Pt} = a_4 \exp(-b_4 r)$$

$$f(\rho) = \exp(-c\rho^2)$$



a_1 = 1.8942×10^{-16} J,	b_1 = 1.1004 Å^{-1}
a_2 = 1.8863×10^{-16} J,	b_2 = 1.0966 Å^{-1}
a_3 = 10^{-13} J,	b_3 = 5.3568 Å^{-1}
a_4 = 1.742×10^{-19} J,	b_4 = 1.2777 Å^{-1}
c = 1.1004 Å $^{-1}$	



Water-Platinum Potential (SH Potential)

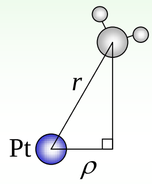
S.-B. Zhu and M. R. Philpott (1994)

$$\phi_{\mathrm{H_2O\text{-}surf}} = \phi_{\mathrm{H_2O\text{-}cond}} + \phi_{\mathrm{an}}(\mathbf{r}_\mathrm{O}) + \phi_{\mathrm{isr}}(\mathbf{r}_\mathrm{O}) + \sum_{\mathrm{H}} \left[\phi_{\mathrm{an}}(\mathbf{r}_\mathrm{H}) + \phi_{\mathrm{isr}}(\mathbf{r}_\mathrm{H})\right]$$

$$\phi_{\mathrm{H_2O\text{-}cond}} = \sum_{l,k} \frac{q_l q_k}{2 r_{lk}}$$

$$\phi_{\mathrm{an}}(\mathbf{r}_p) = 4\varepsilon_{p\text{-Pt}} \sum_j \left[\left(\frac{\sigma_{p\text{-Pt}}^{\;2}}{(\alpha\rho_{pj})^2 + z_{pj}^{\;2}} \right)^6 - \left(\frac{\sigma_{p\text{-Pt}}^{\;2}}{(\rho_{pj}/\alpha)^2 + z_{pj}^{\;2}} \right)^3 \right]$$

$$\phi_{\mathrm{isr}}(\mathbf{r}_p) = -4\varepsilon_{p\text{-Pt}} \sum_j \frac{c_{p\text{-Pt}}\,\sigma_{p\text{-Pt}}^{\;10}}{r_{pj}^{\;10}}$$

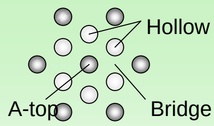


$\alpha = 0.8$

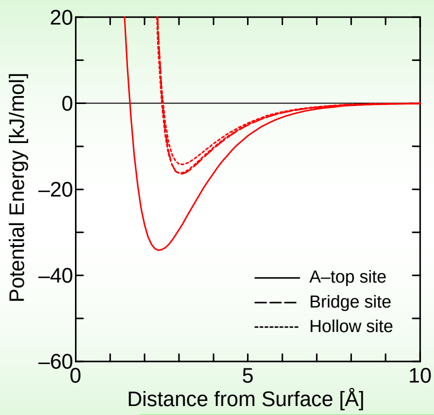
$\sigma_{\text{O-Pt}} = 2.70$ Å, $\varepsilon_{\text{O-Pt}} = 6.64\times10^{-21}$ J, $c_{\text{O-Pt}} = 1.28$

$\sigma_{\text{H-Pt}} = 2.55$ Å, $\varepsilon_{\text{H-Pt}} = 3.91\times10^{-21}$ J, $c_{\text{H-Pt}} = 1.2$

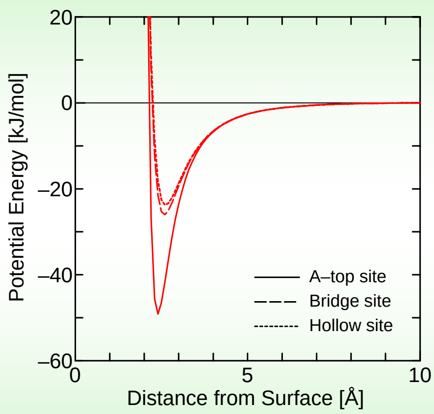
Water-Platinum Potential (ZP Potential)



S-H Potential

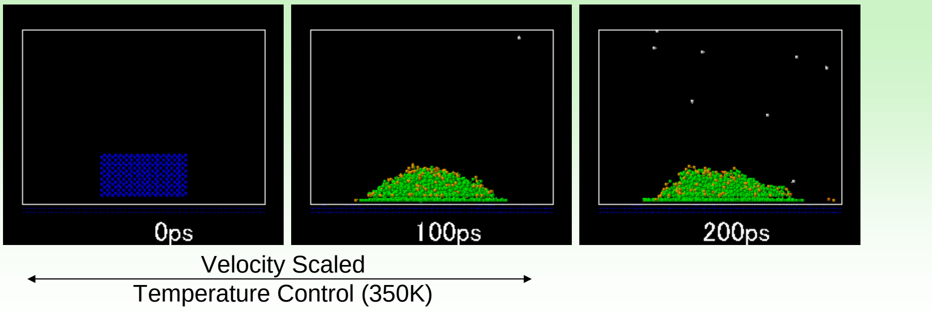


Z-P Potential

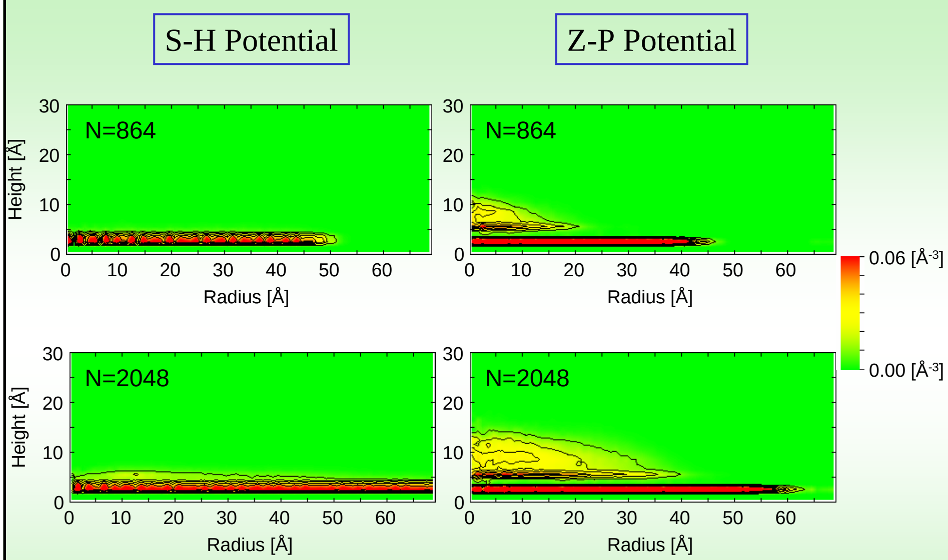


Experiment(STM)
Morgensterm et. al. (1996) 400 meV = 40 kJ/mol

Comparison of Water-Platinum Potential

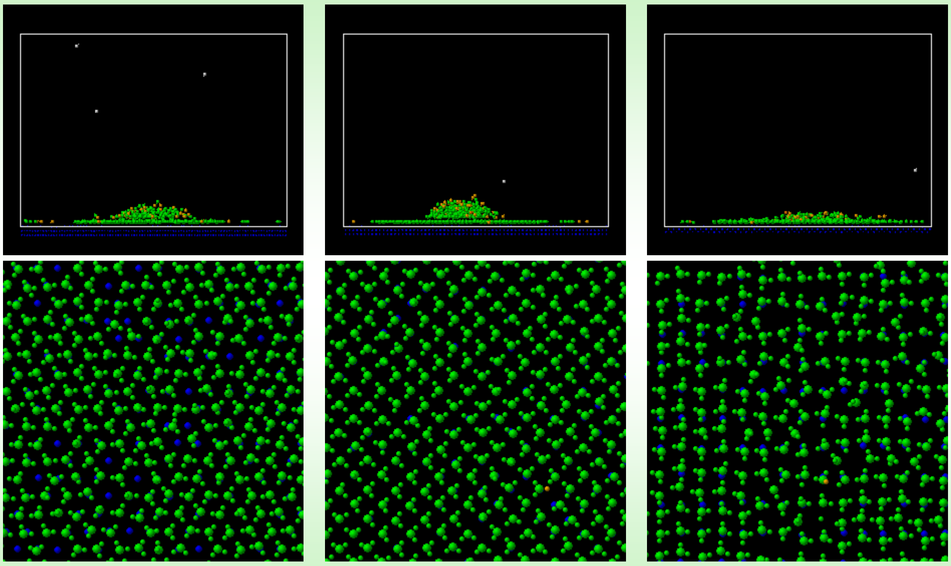


Snapshots of Water Droplet on Platinum Surface
(N=2048, fcc(111), ZP Potential)

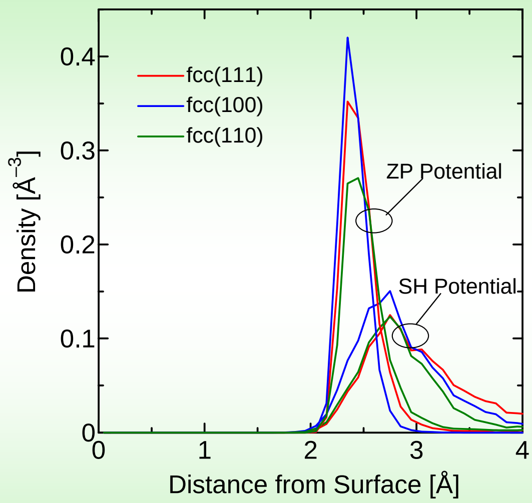


Two Dimensional Density Profiles of Water Droplet
on fcc(111) Platinum Surface

(111) (Pt: 0.150 Å^{-2}) (100) (Pt: 0.130 Å^{-2}) (110) (Pt: 0.093 Å^{-2})



Comparison of Surface Structure (Z-P Potential, N=864)

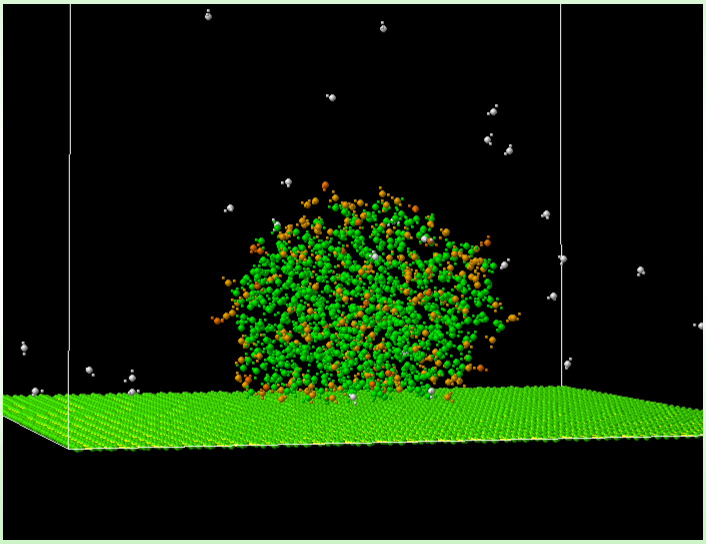


SH Potential
(111) 0.113 Å^{-2} (75%)
(100) 0.125 Å^{-2} (96%)
(110) 0.094 Å^{-2} (102%)

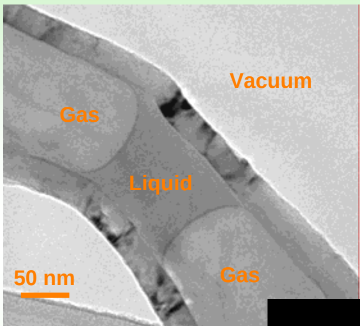
ZP Potential
(111) 0.132 Å^{-2} (88%)
(100) 0.130 Å^{-2} (100%)
(110) 0.117 Å^{-2} (127%)

Density of Monolayer

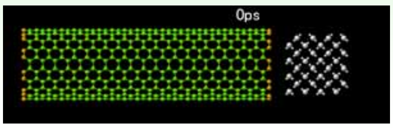
Water Droplet on Graphite

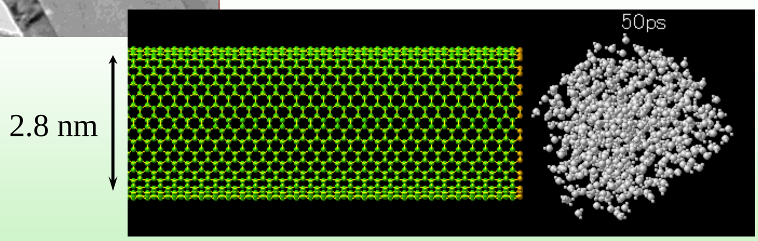


Liquid in Carbon Nanotube

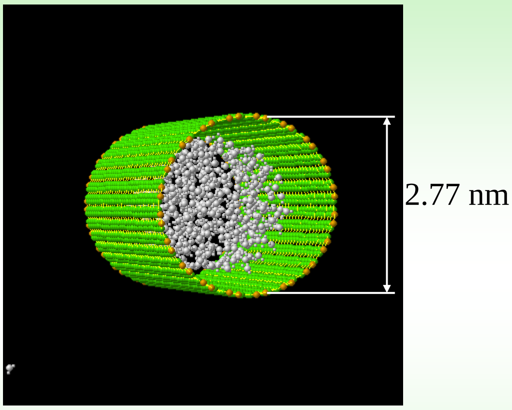


Y. Gogotsi et al., APL (2001).





T. Kimura & S. Maruyama (2002).

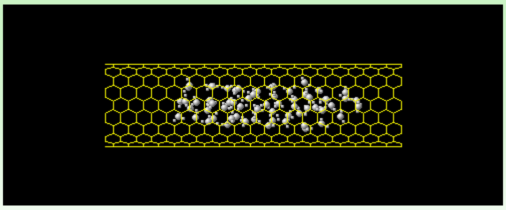


Water
SPC/E

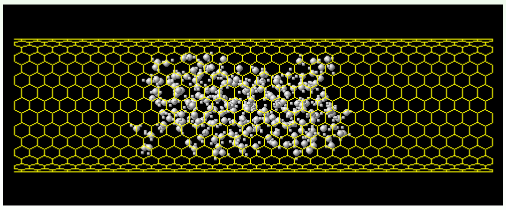
Carbon
Rigid

Water-Carbon
Lennard-Jones(O-C)
$\varepsilon = 1.08\times10^{-21}$ J
$\sigma = 0.316$ nm

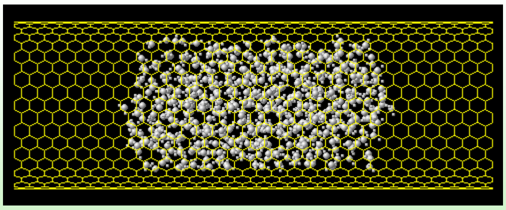
Molecular Dynamics Simulation of Water in Carbon Nanotube



64 water in (10,10)
d=1.39 nm



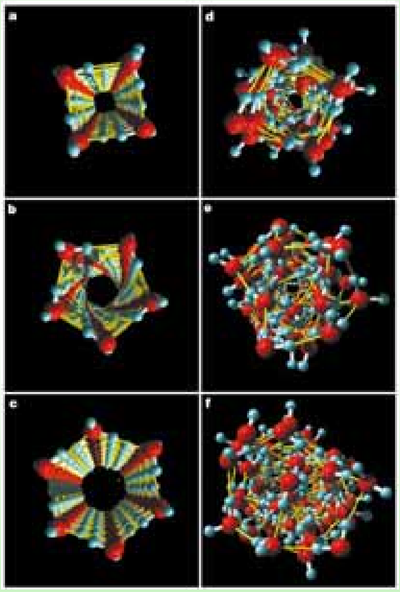
216 water in (16,16)
d=2.22 nm



512 water in (20,20)
d=2.77 nm

Molecular Dynamics Simulation of Water in Carbon Nanotube

Molecular Dynamics Simulation of Ice Water in Carbon Nanotube



K. Koga, et al., *Nature*, 2001

(14,14) D=1.11 nm ?

(15,15) D=1.19 nm ?

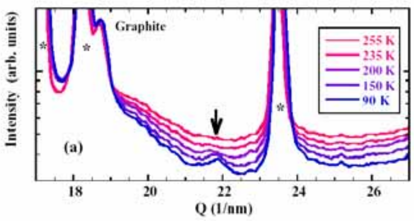
(16,16) D=1.26 nm ?

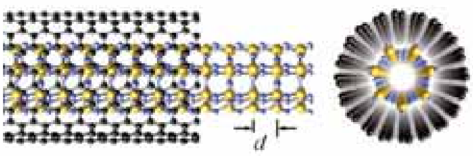
50~500 MPa

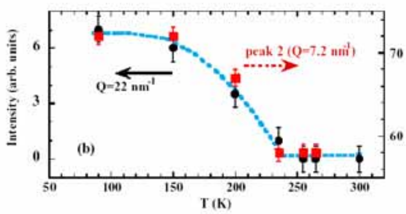
Ice Water in Carbon Nanotube

"Phase Transition in Confined Water Inside Carbon Nanotubes"
Y. Maniwa, et al., *J. Phys. Soc. Jpn.*, 2002.

X-ray diffraction
water adsorption in single-walled carbon nanotube

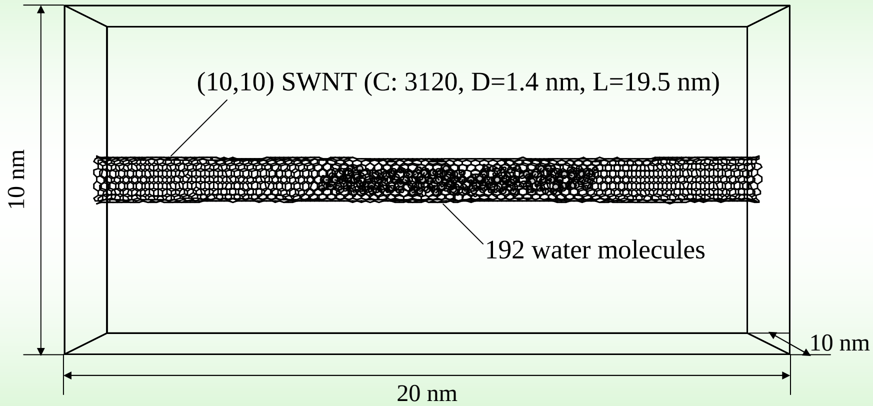






phase transition at 235K

System Configuration



Water: SPC/E
Carbon: Brenner

C-C Potential Function

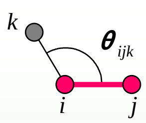
Total Energy E_b:

$$E_b = \sum_i \sum_{j(<i)} \left\{ V_R(r_{ij}) - B^*_{ij} V_A(r_{ij}) \right\}$$

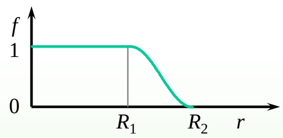
$$V_R(r) = f(r) \frac{D_e}{S-1} \exp\left\{ -\beta \sqrt{2S} (r - R_e) \right\} \qquad V_A(r) = f(r) \frac{D_e S}{S-1} \exp\left\{ -\beta \sqrt{\frac{2}{S}} (r - R_e) \right\}$$

$$B^*_{ij} = \frac{B_{ij} + B_{ji}}{2}, \quad B_{ij} = \left[1 + \sum_{k(\neq i,j)} \left\{ G_c(\theta_{ijk}) f(r_{ik}) \right\} \right]^{-\delta}$$

$$G_c(\theta) = a_0 \left(1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + (1 + \cos\theta)^2} \right)$$



Cut-off function



Potential parameters

$D_e =$	6.325 eV	$S =$	1.29	$\beta =$	1.5Å^{-1}	$R_e =$	1.315Å
$\delta =$	0.80469	$a_0 =$	0.011304	$c_0 =$	19	$d_0 =$	2.5
$R_1 =$	1.7Å	$R_2 =$	2.0Å				

D. W. Brenner, *Phys. Rev. B*, **42** (1990) 9458.

Water-Carbon Potential

Lennard-Jones interaction

$$\phi(r) = 4\varepsilon_{CO}\left\{\left(\frac{\sigma_{CO}}{r_{CO}}\right)^{12} - \left(\frac{\sigma_{CO}}{r_{CO}}\right)^{6}\right\}$$

$\varepsilon_{CO}=0.108\times10^{-21}$J
$\sigma_{CO}=3.19\times10^{-10}$m

Quadrupole interaction(carbon atoms and partial charges on water)

$$\phi(r) = \frac{1}{3}\frac{q}{4\pi\varepsilon_0}\sum_{\alpha,\beta}\Theta_{\alpha,\beta}\frac{3r_\alpha r_\beta - r^2\delta_{\alpha\beta}}{r^5}$$

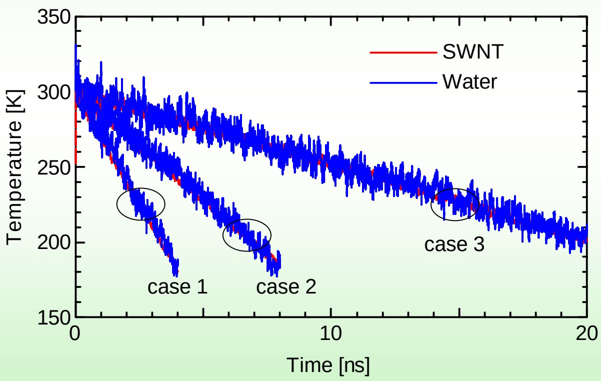
$-2\Theta_{x'x'} = -2\Theta_{y'y'} = \Theta_{z'z'} = -3.03\times10^{-40}$C

Walther, J. H., et al. (2001)

Time Variations of Temperature

PV

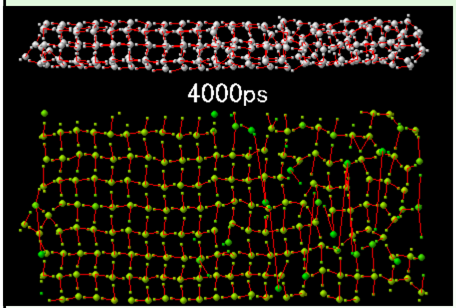
50 ps**まで：系全体に温度制御**(300 K)
50 ps**以降：**SWNT**のみ温度制御（一定熱流速）**



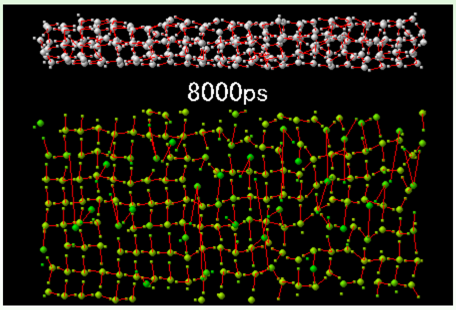
case 1
Q = -5.0×10^{-9} W
case 1
Q = -2.5×10^{-9} W
case 3
Q = -1.0×10^{-9} W

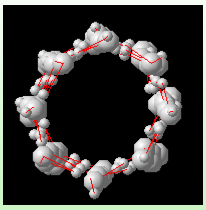
Final Shape of Ice Nanotube in SWNT

case 1

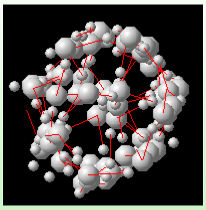


case 2





0.68 nm



Critical Radius & Free Energy

Area $A = 4\pi r^2$

Volume $V = \frac{4}{3}\pi r^3$

Surface tension γ

Free Energy of Cluster $\Delta G = \gamma A + \Delta g V$

Free energy difference
In solid and vapor for unit volume
Assumption of ideal gas
$\Delta g = -\rho_l k_B T \ln(\frac{\rho}{\rho_e})$

Number of molecules $n = \rho_l V$

Supersaturation Ratio $S = \frac{\rho}{\rho_e}$

$$r^* = \frac{2\gamma}{\rho_l k_B T \ln S}$$

$$n^* = \frac{32\pi\gamma^3 f}{3\rho_l^2 (k_B T \ln S)^3}$$

$$\Delta G^* = \frac{16\pi\gamma^3 f}{3(\rho_l k_B T \ln S)^2}$$

Critical Radius & Free Energy

Area $A = 4\pi r^2$

Volume $V = \frac{4}{3}\pi r^3$

Surface tension γ

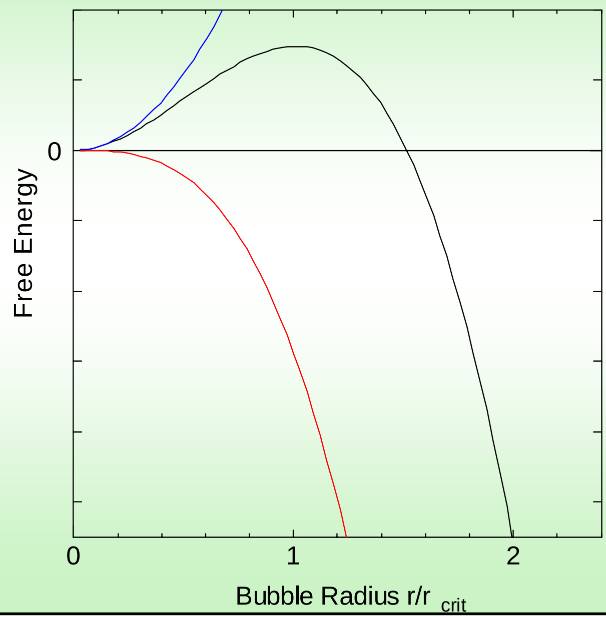
Free Energy of Cluster $= \gamma A + \Delta g V + \Delta G_L$

Free Energy Gain by Compression of Liquid

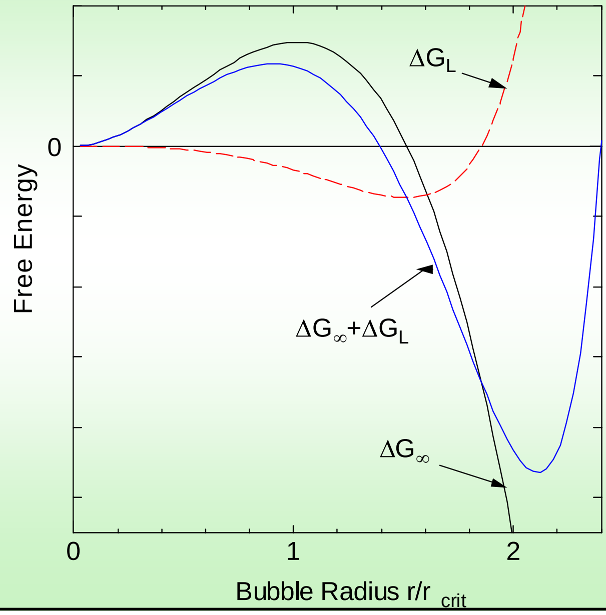
$$\Delta g_L (L^3 - \frac{3}{4}\pi r^3)$$

$$\Delta g_L = f(\frac{\rho_L}{\rho_{sat}}) = f\left(\frac{V_{sat}}{V_L}\right) = f\left(\frac{L^3 - \frac{4}{3}\pi r_{sat}^3}{L^3 - \frac{4}{3}\pi r^3}\right)$$

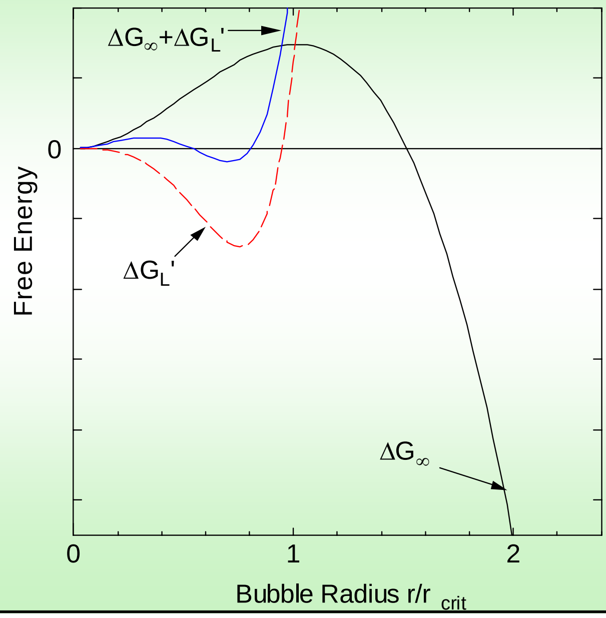
Note on Stability of Nano-Bubble



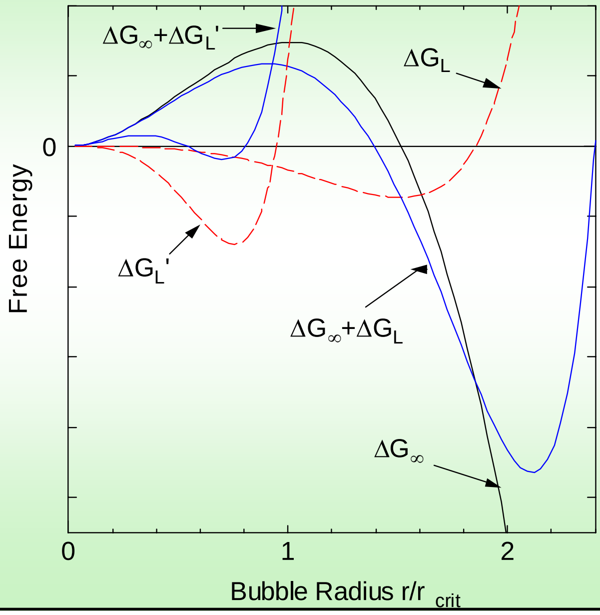
Note on Stability of Nano-Bubble



Note on Stability of Nano-Bubble



Note on Stability of Nano-Bubble



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