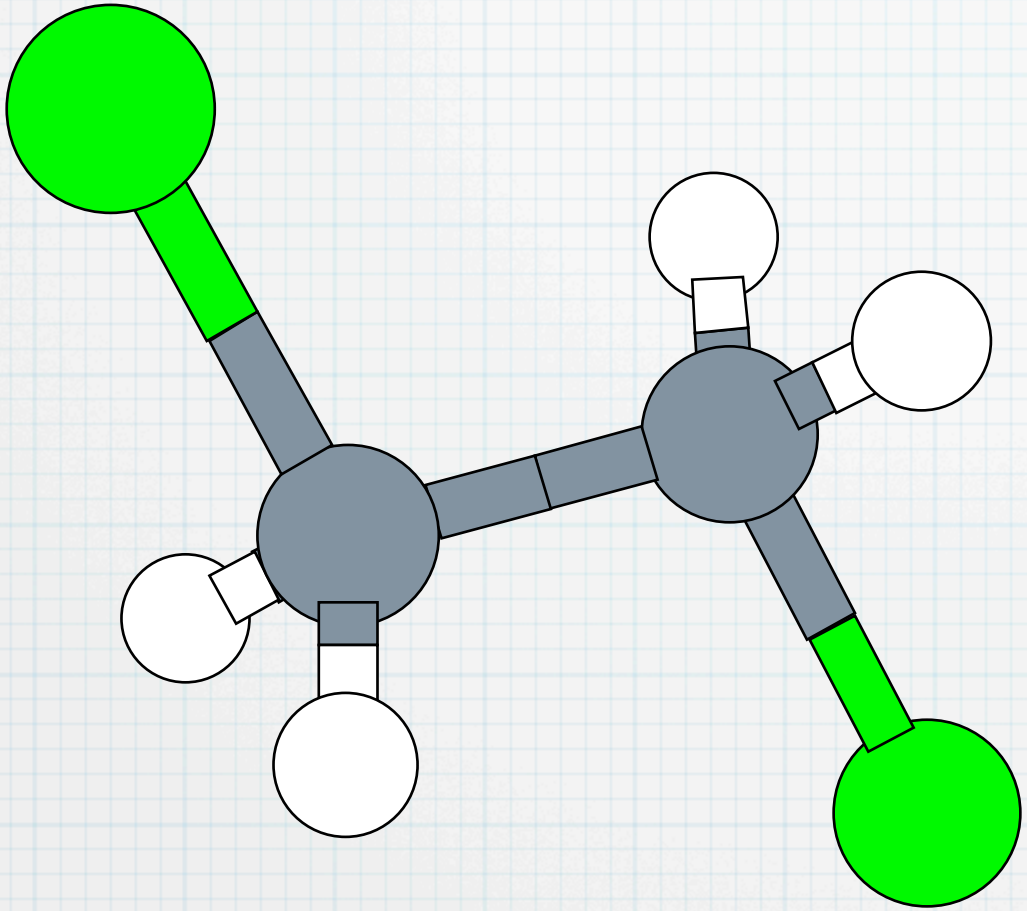
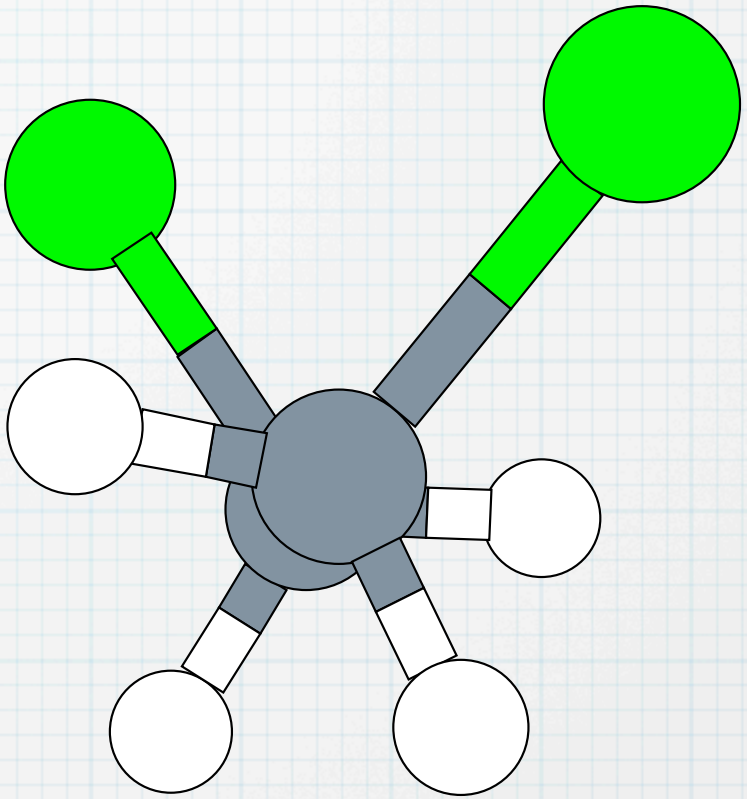
1,2-DCE MD calculation



Trans



Gauche

1,2-ジクロロエタン CH_2ClCH_2Cl	C—C	1.531	C—Cl	1.790
	C—H	1.11	∠CCCl	109.0
	∠CCH	113		
	トランス形 73%, ゴーシュ形 27%(室温)			

trans DCE ab-initio cal.: in vacuum

P B3LYP/6-311+G** SCF=(Tight, MaxCycle=199) Pop=MK Opt=(Verytight)

Trans in vaccum

SCF Done: E(RB+HF-LYP) = -999.101195164 A.U.

Dipole moment (field-independent basis, Debye):

X= 0.0000 Y= 0.0000 Z= 0.0000 Tot= 0.0000

Charges from ESP fit,

Charge= 0.00000

Dipole= -0.0002 0.0004 0.0000 Tot= 0.0004

1	C	-0.140250
2	C	-0.147544
3	H	0.151597
4	H	0.151597
5	H	0.153429
6	H	0.153428
7	Cl	-0.161613
8	Cl	-0.160645

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.666423	1.350983	0.000047
2	6	0	-2.496026	-0.153972	-0.000044
3	1	0	-3.185388	1.697689	-0.890453
4	1	0	-3.185290	1.697593	0.890641
5	1	0	-1.977159	-0.500583	-0.890638
6	1	0	-1.977061	-0.500679	0.890457
7	17	0	-1.028387	2.137183	-0.000001
8	17	0	-4.134063	-0.940171	0.000004

Optimized Parameters
(Angstroms and Degrees)

Name	Definition	Value	Derivative Info.
R1	R(1,2)	1.5146	-DE/DX = 0.0
R2	R(1,3)	1.0874	-DE/DX = 0.0
R3	R(1,4)	1.0874	-DE/DX = 0.0
R4	R(1,7)	1.8169	-DE/DX = 0.0
R5	R(2,5)	1.0874	-DE/DX = 0.0
R6	R(2,6)	1.0874	-DE/DX = 0.0
R7	R(2,8)	1.8169	-DE/DX = 0.0
A1	A(2,1,3)	111.7432	-DE/DX = 0.0
A2	A(2,1,4)	111.7432	-DE/DX = 0.0
A3	A(2,1,7)	109.1796	-DE/DX = 0.0
A4	A(3,1,4)	109.9579	-DE/DX = 0.0
A5	A(3,1,7)	106.9936	-DE/DX = 0.0
A6	A(4,1,7)	106.9937	-DE/DX = 0.0
A7	A(1,2,5)	111.7432	-DE/DX = 0.0
A8	A(1,2,6)	111.7432	-DE/DX = 0.0
A9	A(1,2,8)	109.1796	-DE/DX = 0.0
A10	A(5,2,6)	109.9579	-DE/DX = 0.0
A11	A(5,2,8)	106.9936	-DE/DX = 0.0
A12	A(6,2,8)	106.9936	-DE/DX = 0.0
D1	D(3,1,2,5)	56.3113	-DE/DX = 0.0
D2	D(3,1,2,6)	-180.0	-DE/DX = 0.0
D3	D(3,1,2,8)	-61.8443	-DE/DX = 0.0
D4	D(4,1,2,5)	180.0	-DE/DX = 0.0
D5	D(4,1,2,6)	-56.3113	-DE/DX = 0.0
D6	D(4,1,2,8)	61.8443	-DE/DX = 0.0
D7	D(7,1,2,5)	-61.8443	-DE/DX = 0.0
D8	D(7,1,2,6)	61.8444	-DE/DX = 0.0
D9	D(7,1,2,8)	-180.0	-DE/DX = 0.0

gauche DCE ab-initio cal. : in vaccum

SCF Done: E(RB+HF-LYP) = -999.098668932 A.U.

gauche - trans = 0.0687 eV = 798 K
trans : gaush = 14 : 1

Dipole moment (field-independent basis, Debye):
X= 0.0000 Y= 0.0000 Z= 2.9237 Tot= 2.9237

! Optimized Parameters !
! (Angstroms and Degrees) !

Name	Definition	Value	Derivative Info.
R1	R(1,2)	1.5117	-DE/DX = 0.0
R2	R(1,3)	1.0881	-DE/DX = 0.0
R3	R(1,4)	1.0907	-DE/DX = 0.0
R4	R(1,7)	1.8095	-DE/DX = 0.0
R5	R(2,5)	1.0881	-DE/DX = 0.0
R6	R(2,6)	1.0907	-DE/DX = 0.0
R7	R(2,8)	1.8095	-DE/DX = 0.0
A1	A(2,1,3)	111.6849	-DE/DX = 0.0
A2	A(2,1,4)	109.1663	-DE/DX = 0.0
A3	A(2,1,7)	112.949	-DE/DX = 0.0
A4	A(3,1,4)	109.554	-DE/DX = 0.0
A5	A(3,1,7)	106.948	-DE/DX = 0.0
A6	A(4,1,7)	106.3597	-DE/DX = 0.0
A7	A(1,2,5)	111.6849	-DE/DX = 0.0
A8	A(1,2,6)	109.1663	-DE/DX = 0.0
A9	A(1,2,8)	112.949	-DE/DX = 0.0
A10	A(5,2,6)	109.554	-DE/DX = 0.0
A11	A(5,2,8)	106.948	-DE/DX = 0.0
A12	A(6,2,8)	106.3597	-DE/DX = 0.0
D1	D(3,1,2,5)	171.5295	-DE/DX = 0.0
D2	D(3,1,2,6)	-67.1696	-DE/DX = 0.0
D3	D(3,1,2,8)	50.9296	-DE/DX = 0.0
D4	D(4,1,2,5)	-67.1696	-DE/DX = 0.0
D5	D(4,1,2,6)	54.1314	-DE/DX = 0.0
D6	D(4,1,2,8)	172.2306	-DE/DX = 0.0
D7	D(7,1,2,5)	50.9296	-DE/DX = 0.0
D8	D(7,1,2,6)	172.2306	-DE/DX = 0.0
D9	D(7,1,2,8)	-69.6702	-DE/DX = 0.0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.412402	0.633448	0.896553
2	6	0	0.412402	-0.633448	0.896553
3	1	0	-1.476824	0.420231	0.821879
4	1	0	-0.214921	1.189316	1.813985
5	1	0	1.476824	-0.420231	0.821879
6	1	0	0.214921	-1.189316	1.813985
7	17	0	0.000319	1.744063	-0.471167
8	17	0	-0.000319	-1.744063	-0.471167

Charges from ESP fit, RMS= 0.00271 RRMS= 0.18267:
Charge= 0.00000
Dipole= 0.0011 -0.0006 3.0651 Tot= 3.0651

1	C	-0.210818
2	C	-0.187963
3	H	0.179542
4	H	0.161413
5	H	0.174044
6	H	0.156443
7	Cl	-0.134562
8	Cl	-0.138099

trans DCE ab-initio cal.: in DCE

P B3LYP/6-311+G** SCF=(Tight, MaxCycle=199) Pop=MK Opt=(Verytight) SCRF=(PCM,Solvent=DiChloroEthane)

Gauche DCE in DCE Variational PCM results

==========

<psi(f)| H |psi(f)> (a.u.) = -999.100665

<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -999.105782

Total free energy in solution: with all non electrostatic terms

(a.u.) = -999.102685

(Polarized solute)-Solvent (kcal/mol) = -3.21

Cavitation energy (kcal/mol) = 10.82

Dispersion energy (kcal/mol) = -9.76

Repulsion energy (kcal/mol) = 0.88

Total non electrostatic (kcal/mol) = 1.94

Dipole moment (field-independent basis, Debye):

X= 0.0000 Y= 0.0000 Z= 0.0008 Tot= 0.0008

Charges from ESP fit, RMS= 0.00279 RRMS= 0.25610:

Dipole= -0.0003 0.0010 0.0009 Tot= 0.0013

1 C -0.127995

2 C -0.133489

3 H 0.162514

4 H 0.162519

5 H 0.163971

6 H 0.163947

7 Cl -0.196074

8 Cl -0.195394

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.671814	1.349987	0.000121
2	6	0	-2.490634	-0.152978	-0.000002
3	1	0	-3.184281	1.700475	-0.893659
4	1	0	-3.183826	1.700541	0.894125
5	1	0	-1.978231	-0.503369	-0.893854
6	1	0	-1.978560	-0.503631	0.893931
7	17	0	-1.027013	2.139935	-0.000343
8	17	0	-4.135439	-0.942918	-0.000306

! Optimized Parameters !

! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.
! R1	R(1,2)	1.5138	-DE/DX = 0.0 !
! R2	R(1,3)	1.0883	-DE/DX = 0.0 !
! R3	R(1,4)	1.0882	-DE/DX = 0.0 !
! R4	R(1,7)	1.8247	-DE/DX = 0.0 !
! R5	R(2,5)	1.0883	-DE/DX = 0.0 !
! R6	R(2,6)	1.0883	-DE/DX = 0.0 !
! R7	R(2,8)	1.8247	-DE/DX = 0.0 !
! A1	A(2,1,3)	112.0886	-DE/DX = 0.0 !
! A2	A(2,1,4)	112.0977	-DE/DX = 0.0 !
! A3	A(2,1,7)	108.7798	-DE/DX = 0.0 !
! A4	A(3,1,4)	110.4504	-DE/DX = 0.0 !
! A5	A(3,1,7)	106.5498	-DE/DX = 0.0 !
! A6	A(4,1,7)	106.5508	-DE/DX = 0.0 !
! A7	A(1,2,5)	112.091	-DE/DX = 0.0 !
! A8	A(1,2,6)	112.0954	-DE/DX = 0.0 !
! A9	A(1,2,8)	108.7795	-DE/DX = 0.0 !
! A10	A(5,2,6)	110.4504	-DE/DX = 0.0 !
! A11	A(5,2,8)	106.5534	-DE/DX = 0.0 !
! A12	A(6,2,8)	106.5474	-DE/DX = 0.0 !
! D1	D(3,1,2,5)	55.1532	-DE/DX = 0.0 !
! D2	D(3,1,2,6)	-179.9754	-DE/DX = 0.0 !
! D3	D(3,1,2,8)	-62.4135	-DE/DX = 0.0 !
! D4	D(4,1,2,5)	-179.9755	-DE/DX = 0.0 !
! D5	D(4,1,2,6)	-55.104	-DE/DX = 0.0 !
! D6	D(4,1,2,8)	62.4579	-DE/DX = 0.0 !
! D7	D(7,1,2,5)	-62.4078	-DE/DX = 0.0 !
! D8	D(7,1,2,6)	62.4637	-DE/DX = 0.0 !
! D9	D(7,1,2,8)	-179.9745	-DE/DX = 0.0 !

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gauche DCE ab-initio cal.: in DCE

P B3LYP/6-311+G** SCF=(Tight, MaxCycle=199) Pop=MK Opt=(Tight) SCRF=(PCM,Solvent=DiChloroEthane)

Trans in DCE Variational PCM results
=====0.022 eV = 261.5 K trans : gauche = 1 : 0.42

<psi(f)| H |psi(f)> (a.u.) = -999.097322
<psi(f)|H+V(f)/2|psi(f)> (a.u.) = -999.105161
Total free energy in solution: with all non electrostatic terms

(a.u.) = -999.101857

(Polarized solute)-Solvent (kcal/mol) = -4.92

Cavitation energy (kcal/mol) = 10.84
Dispersion energy (kcal/mol) = -9.62
Repulsion energy (kcal/mol) = 0.85
Total non electrostatic (kcal/mol) = 2.07

Dipole moment (field-independent basis, Debye):
X= 0.0000 Y= 0.0000 Z= 3.8279 Tot= 3.8279
Charges from ESP fit, RMS= 0.00262 RRMS= 0.13952:
Dipole= -0.0025 0.0003 3.9469 Tot= 3.9469

1	**C**	**-0.200412**
2	**C**	**-0.180907**
3	**H**	**0.192555**
4	**H**	**0.186865**
5	**H**	**0.187347**
6	**H**	**0.182669**
7	**Cl**	**-0.182611**
8	**Cl**	**-0.185506**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.413548	0.630461	0.902144
2	6	0	0.413548	-0.630461	0.902144
3	1	0	-1.480490	0.424342	0.835481
4	1	0	-0.201716	1.196748	1.810425
5	1	0	1.480490	-0.424342	0.835481
6	1	0	0.201716	-1.196748	1.810425
7	17	0	-0.011466	1.736655	-0.487103
8	17	0	0.011466	-1.736655	-0.487103

! Optimized Parameters !
! (Angstroms and Degrees) !

! Name	Definition	Value	Derivative Info.
! R1	R(1,2)	1.508	-DE/DX = 0.0 !
! R2	R(1,3)	1.0887	-DE/DX = 0.0 !
! R3	R(1,4)	1.0911	-DE/DX = 0.0 !
! R4	R(1,7)	1.8208	-DE/DX = 0.0 !
! R5	R(2,5)	1.0887	-DE/DX = 0.0 !
! R6	R(2,6)	1.0911	-DE/DX = 0.0 !
! R7	R(2,8)	1.8208	-DE/DX = 0.0 !
! A1	A(2,1,3)	112.2845	-DE/DX = 0.0 !
! A2	A(2,1,4)	109.1162	-DE/DX = 0.0 !
! A3	A(2,1,7)	112.7603	-DE/DX = 0.0 !
! A4	A(3,1,4)	109.8459	-DE/DX = 0.0 !
! A5	A(3,1,7)	106.5416	-DE/DX = 0.0 !
! A6	A(4,1,7)	106.0786	-DE/DX = 0.0 !
! A7	A(1,2,5)	112.2845	-DE/DX = 0.0 !
! A8	A(1,2,6)	109.1162	-DE/DX = 0.0 !
! A9	A(1,2,8)	112.7603	-DE/DX = 0.0 !
! A10	A(5,2,6)	109.8459	-DE/DX = 0.0 !
! A11	A(5,2,8)	106.5416	-DE/DX = 0.0 !
! A12	A(6,2,8)	106.0786	-DE/DX = 0.0 !
! D1	D(3,1,2,5)	172.4115	-DE/DX = 0.0 !
! D2	D(3,1,2,6)	-65.5596	-DE/DX = 0.0 !
! D3	D(3,1,2,8)	52.0396	-DE/DX = 0.0 !
! D4	D(4,1,2,5)	-65.5596	-DE/DX = 0.0 !
! D5	D(4,1,2,6)	56.4693	-DE/DX = 0.0 !
! D6	D(4,1,2,8)	174.0685	-DE/DX = 0.0 !
! D7	D(7,1,2,5)	52.0396	-DE/DX = 0.0 !
! D8	D(7,1,2,6)	174.0685	-DE/DX = 0.0 !
! D9	D(7,1,2,8)	-68.3322	-DE/DX = 0.0 !

Basically you can make the potential from the quantum chemical (QC) calculation.

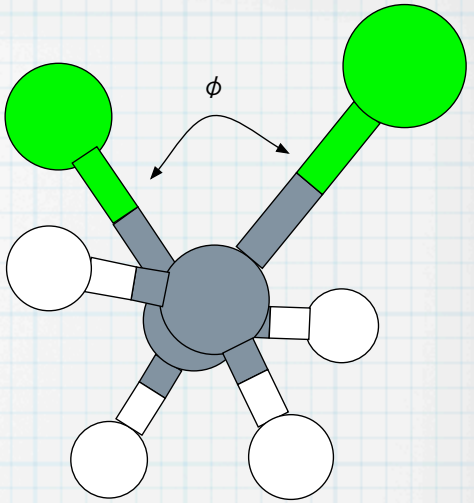
0) get the optimized structure

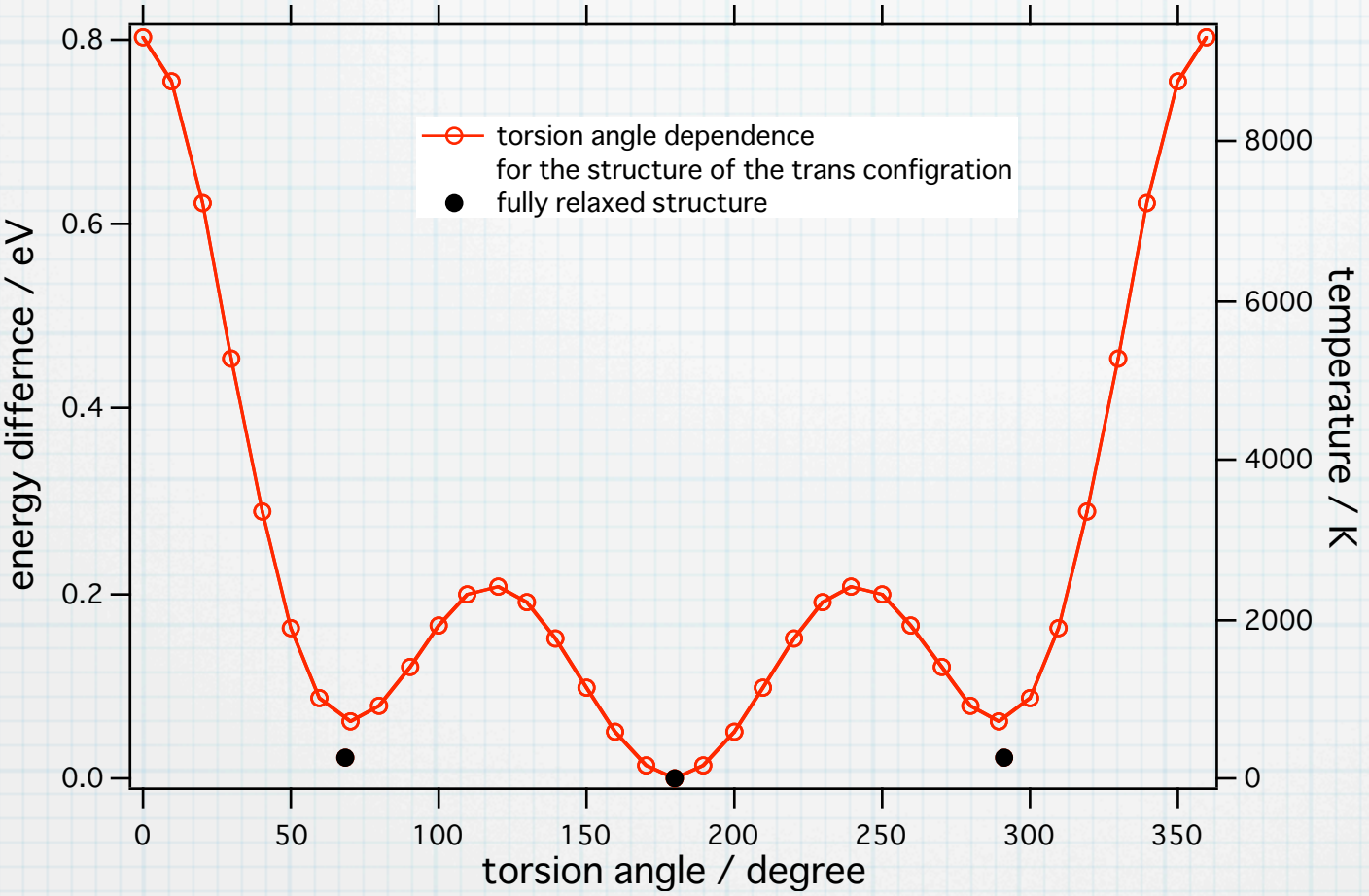
intermolecular potential
1) it is better to use the QC cal. in the solvent (maybe!!)
2) the electrostatic potential fit (ESP) charges can be used.
3) LJ potential can not obtained!! from QC cal.

the intra-moecular potential
4) bond length potential can be obtained from QC cal if the other degree of freedom is fixed.
5) bond angle potential can be obtained from QC cal if the other degree of freedom is fixed.
6) torsion angle potential can be obtained from QC cal if the other degree of freedom is fixed.
7) scaled intra-molecular 1-4 non-bonded interaction should be take into acount!

I will show the one example:
torsion angle potential Cl-C-C-Cl of DCE

Cl-C-C-Cl torsion angle potential of DCE in DCE





exp: energy diff. trans- gauche in DCE 0.31 kcal mol-1 = 13.4 meV = 156 K cal. 262 K

in vacuum 1.20 kcal mol-1 = 52.0 meV = 604 K cal. 798 K

OPLS-AA force field for 1,2-DCE

Table. OPLS All-Atom Potential Function Parameters for 1,2-Dichloroethane

Non-Bonded Parameters*			
Atom	q(e)	σ(Å)	ϵ(kcal/mol)
C	-0.006	3.500	0.066
H	0.103	2.500	0.030
Cl	-0.200	3.400	0.300

Bond Stretching Parameters		
Bond	r_0(Å)	k(kcal/mol-Å^2)
C-H	1.090	340.0
C-C	1.529	268.0
C-Cl	1.781	245.0

Angle Bending Parameters		
Angle	θ_0(deg)	k(kcal/mol-rad^2)
C-C-H	110.7	37.5
H-C-H	107.8	33.0
C-C-Cl	109.8	69.0
H-C-Cl	107.6	51.0

Torsional Parameters	
Angle	V's(kcal/mol)
HCCH	V_3 = 0.318
HCCCl	V_3 = 0.400
ClCCCl	V_0 = 0.250 V_1 = -0.250

* Intramolecular 1,4-non-bonded interactions are scaled by 0.5.

The Importance of Polarization for Dipolar Solutes in Low-Dielectric Media: 1,2-Dichloroethane and Water in Cyclohexane

William L. Jorgensen,* Nora A. McDonald, Massimo Selmi, and Paul R. Rablen

Department of Chemistry, Yale University
New Haven, Connecticut 06520-8107

化 合 物	θ / °C	ρ / g cm^{-3}
1,2-ジクロロエタン	0	1.2824

1,2-ジクロロエタン CH_2ClCH_2Cl	C—C	1.531	C—Cl	1.790
	C—H	1.11	∠CCCl	109.0
	∠CCH	113		
	トランス形 73%, ゴーシュ形 27%(室温)			

$ClH_2C\text{-}CH_2Cl$

C:12.011

H:1.0079

Cl:35.453

12.011×2 + 1.0079×4 + 35.453×2 =
98.9596 g mol^{-1}

1.2824 / 98.9596 = 0.012959 mol cm-3
= 0.007804 # Å^{-3}

1 molecule = 128.14 Å^3

256 molecules = 32803.74 Å^3
= (32.01163 Å)^3

4×(4×4×4) = 256

32.01163 / 4 = 8.00291 Å

center of mass: fcc lattice
random orientation

crystal

T. B. Reed and W. N. Lipscomb, Acta Cryst. 1953, 6, 45.

$a = 4{\cdot}66 \pm 0{\cdot}03$, $b = 5{\cdot}42 \pm 0{\cdot}02$, $c = 7{\cdot}88 \pm 0{\cdot}02$ Å,
$\beta = 103{\cdot}5 \pm 0{\cdot}5°$

$$x^{Cl} = 0{\cdot}320 \pm 0{\cdot}001,\ y_{Cl} = 0{\cdot}281 \pm 0{\cdot}001,$$
$$z_{Cl} = 0{\cdot}084 \pm 0{\cdot}001\ ,$$

$$x_C = 0{\cdot}100 \pm 0{\cdot}004,\ y_C = -0{\cdot}012 \pm 0{\cdot}004 \text{ and}$$
$$z_C = 0{\cdot}084 \pm 0{\cdot}004\ .$$

These parameters refer to the positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$ (*Internationale Tabellen*, 1935). They lead to the molecular parameters C–C=1·49±0·04 Å, C–Cl=1·80±0·02 Å, Cl···Cl=4·24±0·02 Å and ∠ C–C–Cl=105·5±0·5°. Our values

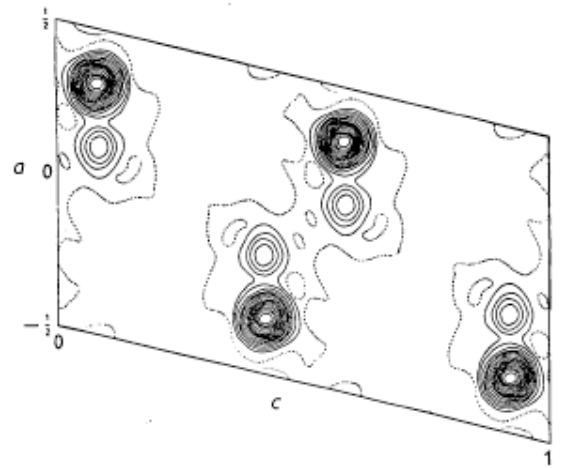


Fig. 2. Projection of the electron density along the b axis. Contours are at 2 e.Å^{-2}. The two-electron contour is broken.

and $V = 194$ Å^3. These values may be compared with $a = 5{\cdot}04$, $b = 5{\cdot}56$, $c = 8{\cdot}00$ Å and $\beta = 109{\cdot}5°$ for the unit cell at −50° C., which is larger by 18 Å^3.

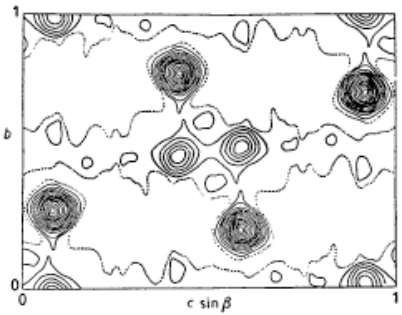


Fig. 4. Projection of the electron density along the a axis. Contours are in intervals of 2 e.Å^{-2}. The two-electron contour is broken.

5. **bonds** n

where n is the number of flexible chemical bonds in the molecule. Each of the subsequent n records contains:

bond key	a4	see table 4.7
index 1	integer	first atomic site in bond
index 2	integer	second atomic site in bond
variable 1	real	potential parameter see table 4.7
variable 2	real	potential parameter see table 4.7
variable 3	real	potential parameter see table 4.7
variable 4	real	potential parameter see table 4.7

The meaning of these variables is given in table 4.7. This directive (and associated data records) need not be specified if the molecule contains no flexible chemical bonds. See the note on the atomic indices appearing under the **shell** directive above.

Table 4.7: Chemical bond potentials

key	potential type	Variables (1-4)				functional form
harm **-hrm**	Harmonic	k	r_0			$U(r) = \frac{1}{2}k(r-r_0)^2$
mors **-mrs**	Morse	E_0	r_0	k		$U(r) = E_0[\{1-\exp(-k(r-r_0))\}^2 - 1]$
12-6 **-126**	12-6	A	B			$U(r) = \left(\frac{A}{r^{12}}\right) - \left(\frac{B}{r^6}\right)$
rhrm **-rhm**	Restraint	k	r_0	r_c		$U(r) = \frac{1}{2}k(r-r_0)^2 \quad \lvert r-r_0\rvert \le r_c$ $U(r) = \frac{1}{2}kr_c^2 + kr_c(\lvert r-r_0\rvert - r_c) \quad \lvert r-r_0\rvert > r_c$
quar **-qur**	Quartic	k	r_0	k'	k''	$U(r) = \frac{k}{2}(r-r_0)^2 + \frac{k'}{3}(r-r_0)^3 + \frac{k''}{4}(r-r_0)^4$
buck **-bck**	Buckingham	A	ρ	C		$U(r) = Aexp(-r/\rho) - C/r^6$

Note: bond potentials with a dash (-) as the first character of the keyword, do not contribute to the *excluded atoms list* (see section 2.1). In this case DL_POLY_2 will also calculate the nonbonded pair potentials between the described atoms, unless these are deactivated by another potential specification.

OPLS-AA force field

$$E_{\text{bond}} = \sum_{\text{bonds}} K_r(r - r_{\text{eq}})^2$$

$$k = 2K_r$$

OPLS:

optimized potentials
for liquid simulations
by W. L. Jorgensen et al.

AA: All-Atom

8. **angles *n***

where n is the number of valence angle bonds in the molecule. Each of the n records following contains:

angle key	a4	potential key. See table 4.8
index 1	integer	first atomic index
index 2	integer	second atomic index (central site)
index 3	integer	third atomic index
variable 1	real	potential parameter see table 4.8
variable 2	real	potential parameter see table 4.8

The meaning of these variables is given in table 4.8. See the note on the atomic indices appearing under the **shell** directive above. This directive (and associated data records) need not be specified if the molecule contains no angular terms.

Table 4.8: Valence Angle potentials

key	potential type	Variables (1-4)				functional form†
harm **-hrm**	Harmonic	k	θ_0			$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2$
quar **-qur**	Quartic	k	θ_0	k'	k''	$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 + \frac{k'}{3}(\theta - \theta_0)^3 + \frac{k''}{4}(\theta - \theta_0)^4$
thrm **-thm**	Truncated harmonic	k	θ_0	ρ		$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]$
shrm **-shm**	Screened harmonic	k	θ_0	ρ_1	ρ_2	$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 \exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]$
bvs1 **-bv1**	Screened Vessal[24]	k	θ_0	ρ_1	ρ_2	$U(\theta) = \frac{k}{8(\theta-\theta_0)^2}\left\{[(\theta_0 - \pi)^2 - (\theta - \pi)^2]^2\right\}$ $\exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]$
bvs2 **-bv2**	Truncated Vessal[25]	k	θ_0	a	ρ	$U(\theta) = k[\theta^a(\theta - \theta_0)^2(\theta + \theta_0 - 2\pi)^2 - \frac{a}{2}\pi^{a-1}$ $(\theta - \theta_0)^2(\pi - \theta_0)^3] \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]$
hcos **-hcs**	Harmonic Cosine	k	θ_0			$U(\theta) = \frac{k}{2}(cos(\theta) - cos(\theta_0))^2$
cos **-cos**	Cosine	A	δ	m		$U(\theta) = A[1 + cos(m\theta - \delta)]$
mmsb **-msb**	MM Stretch-bend	A	θ_0	d_{ab}	d_{ac}	$U(\theta) = A(\theta - \theta_0)(r_{ab} - d_{ab})(r_{ac} - d_{ac})$

†θ is the a-b-c angle.

Note: valence angle potentials with a dash (-) as the first character of the keyword, do not contribute to the *excluded atoms list* (see section 2.1). In this case DL_POLY_2 will calculate the nonbonded pair potentials between the described atoms.

OPLS-AA force field

$$E_{\text{angle}} = \sum_{\text{angles}} K_\theta(\theta - \theta_{\text{eq}})^2$$

$$k = 2K_\theta$$

9. **dihedrals** ***n***

where n is the number of dihedral interactions present in the molecule. Each of the following n records contains:

dihedral key	a4	potential key. See table 4.9
index 1	integer	first atomic index
index 2	integer	second atomic index
index 3	integer	third atomic index
index 4	integer	fourth atomic index
variable 1	real	potential parameter see table 4.9
variable 2	real	potential parameter see table 4.9
variable 3	real	potential parameter see table 4.9
variable 4	real	1-4 electrostatic interaction scale factor.
variable 5	real	1-4 Van der Waals interaction scale factor.

The meaning of the variables 1-3 is given in table 4.9. The variables 4 and 5 specify the scaling factor for the 1-4 electrostatic and Van der Waals nonbonded interactions respectively. This directive (and associated data records) need not be specified if the molecule contains no dihedral angle terms. See the note on the atomic indices appearing under the **shell** directive above.

Table 4.9: Dihedral Angle Potentials

key	potential type	Variables (1-4)				functional form‡
cos	Cosine	A	δ	m		$U(\phi) = A\,[1 + \cos(m\phi - \delta)]$
harm	Harmonic	k	ϕ_0			$U(\phi) = \frac{1}{2}k(\phi - \phi_0)^2$
hcos	Harmonic cosine	k	ϕ_0			$U(\phi) = \frac{k}{2}(cos(\phi) - cos(\phi_0))^2$
cos3	Triple cosine	A_1	A_2	A_3		$U(\phi) = \frac{1}{2}A_1(1 + cos(\phi)) + \frac{1}{2}A_2(1 - cos(2\phi))$ $+\frac{1}{2}A_3(1 + cos(3\phi))$
ryck	Ryckaert-Bellemans	A				$U(\phi) = A(a_0 + a_1 cos\phi - a_2 cos^2\phi + a_3 cos^3\phi +$ $a_4 cos^4\phi + a_5 cos^5\phi)$ $[a_0 \rightarrow a_5$ pre-set]
rbf	Fluorinated Ryckaert-Bellemans	B				$U(\phi) = B(b_0 - b_1 cos\phi - b_2 cos^2\phi - b_3 cos^3\phi +$ $b_4 cos^4\phi + b_5 cos^5\phi + b_6 exp(-b_7(\phi - \pi))$ $[b_0 \rightarrow b_6$ pre-set]
opls	OPLS	A_0	A_1	A_2	A_3	$U(\phi) = A_0 + \frac{1}{2}(A_1(1 + cos(\phi)) + A_2(1 - cos(2\phi))$ $+A_3(1 + cos(3\phi)))$

‡ϕ is the a-b-c-d dihedral angle.

OPLS-AA force field

$$E_{\text{torsion}}(\phi^i) = \sum_i \left\{ \frac{V_0^i}{2}[1 + \cos(f_0^i)] + \frac{V_1^i}{2}[1 + \cos(\phi^i + f_1^i)] + \frac{V_2^i}{2}[1 - \cos(2\phi^i + f_2^i)] + \frac{V_3^i}{2}[1 + \cos(3\phi^i + f_3^i)] \right\}$$

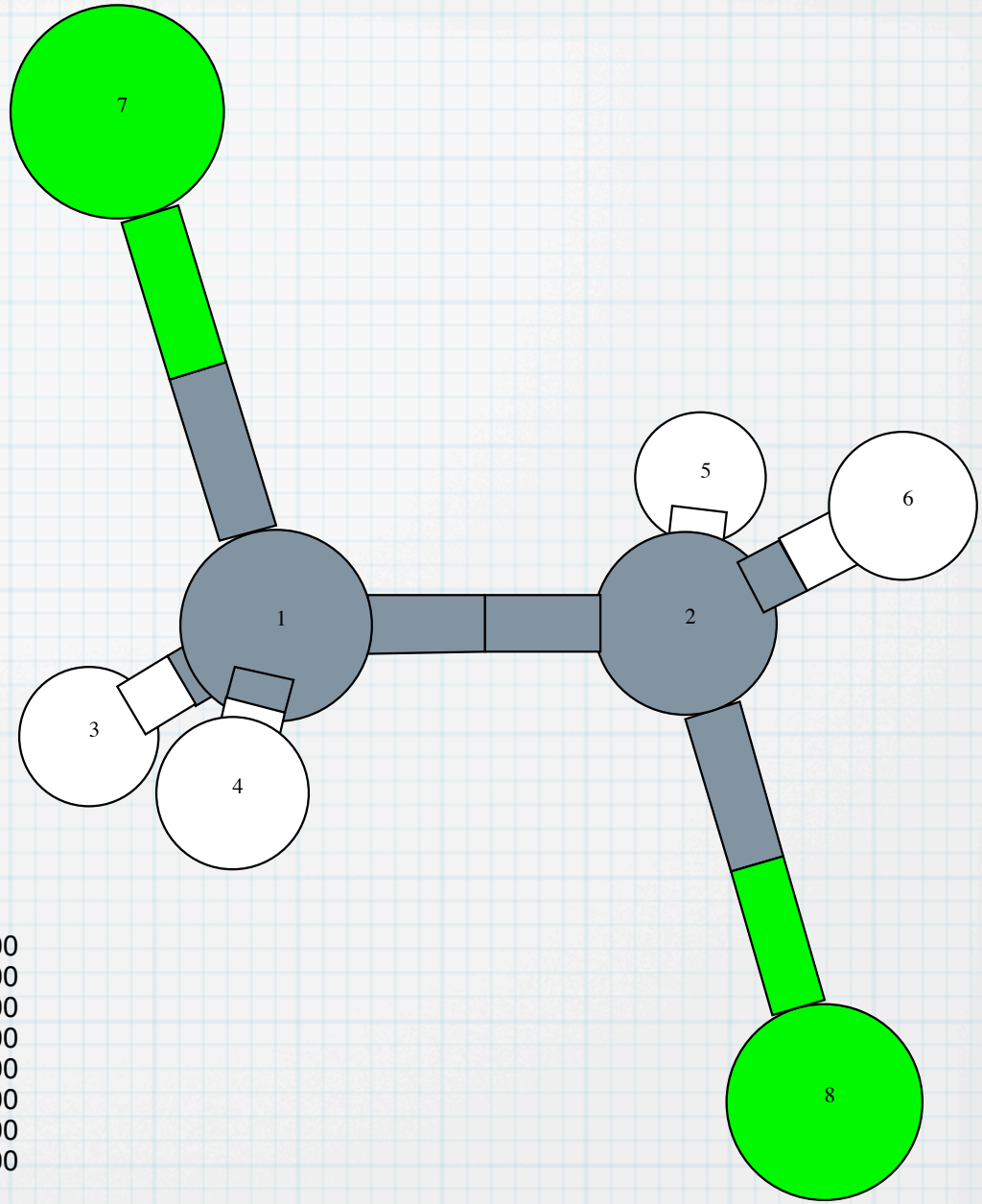
when $V_0^i, f_0^i, f_1^i, f_2^i, f_3^i = 0$

$$E_{\text{torsion}}(\phi^i) = \sum_i \left\{ \frac{V_1^i}{2}[1 + \cos(\phi^i)] + \frac{V_2^i}{2}[1 - \cos(2\phi^i)] + \frac{V_3^i}{2}[1 + \cos(3\phi^i)] \right\}$$

→cos3

FIELD

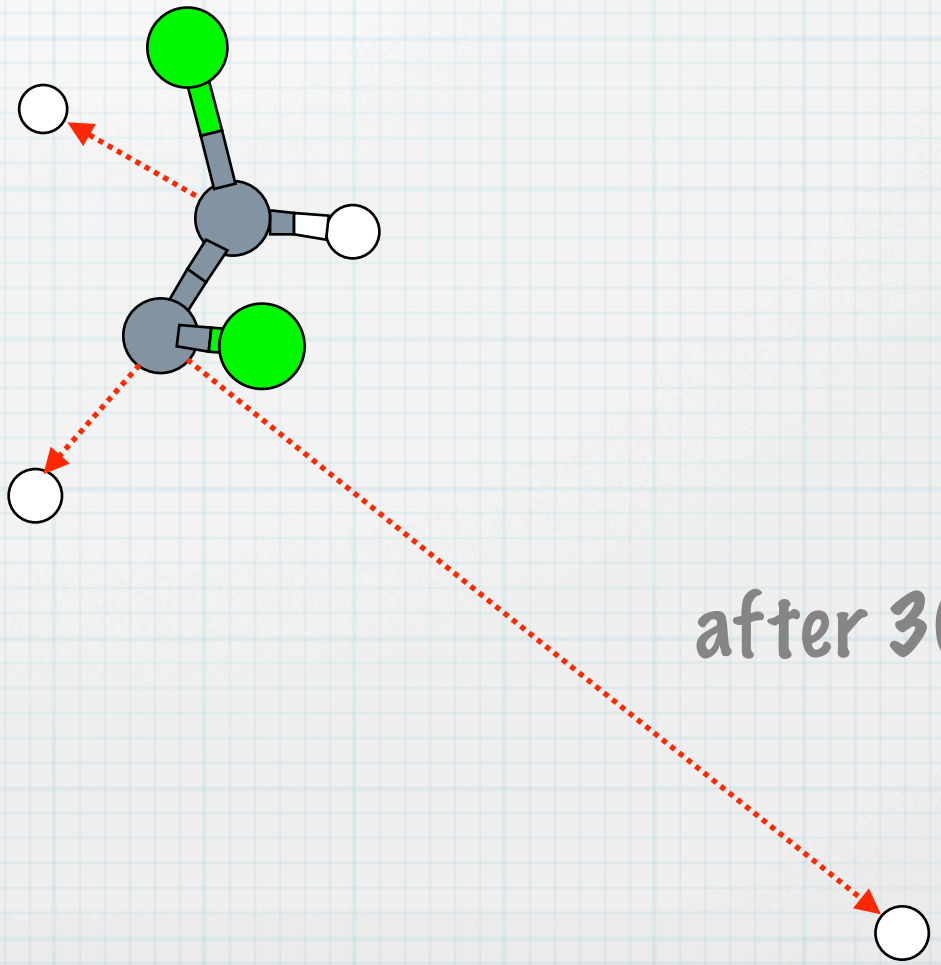
```
DCE all atom
units kJ
molecular types 1
DCE
nummols 1
atoms  8
C          12.011      -0.006    2
H           1.0079      0.103    4
Cl         35.4530     -0.200    2
bonds 7
harm    1    3   2845.12  1.0900
harm    1    4   2845.12  1.0900
harm    2    5   2845.12  1.0900
harm    2    6   2845.12  1.0900
harm    1    2   2242.62  1.5290
harm    1    7   2050.16  1.7810
harm    2    8   2050.16  1.7810
angles 12
harm    1    2    5    313.8        110.70
harm    1    2    6    313.8        110.70
harm    2    1    3    313.8        110.70
harm    2    1    4    313.8        110.70
harm    3    1    4    276.1        107.80
harm    5    2    6    276.1        107.80
harm    1    2    8    577.4        109.80
harm    2    1    7    577.4        109.80
harm    3    1    7    426.8        107.60
harm    4    1    7    426.8        107.60
harm    5    2    8    426.8        107.60
harm    6    2    8    426.8        107.60
dihedrals 9
OPLS     3    1    2    5    0.00000  0.00000  0.0000  1.3305  0.5000     0.5000
OPLS     3    1    2    6    0.00000  0.0000   0.0000  1.3305  0.5000     0.5000
OPLS     4    1    2    5    0.00000  0.00     0.0000  1.3305  0.5000     0.5000
OPLS     4    1    2    6    0.00000  0.0      0.0000  1.3305  0.5000     0.5000
OPLS     3    1    2    8    0.00000  0.00     0.0000  1.6736  0.5000     0.5000
OPLS     4    1    2    8    0.00000  0.0      0.0000  1.6736  0.5000     0.5000
OPLS     5    2    1    7    0.00000  0.00     0.0000  1.6736  0.5000     0.5000
OPLS     6    2    1    7    0.00000  0.0000   0.000   1.6736  0.5000     0.5000
OPLS     7    1    2    8    1.046    1.046    0.0000  0.0000  0.5000     0.5000
finish
vdw 6
     C      C    lj  0.276144     3.5
     C      H    lj  0.186176     3.0
     C      Cl   lj  0.588741     3.45
     H      H    lj  0.12552      2.5
     H      Cl   lj  0.396929     2.95
    Cl      Cl   lj  1.2552       3.4
close
```



OPLS does not work!! Use cos3

Please remember that all bonds, angles, and torsion should be specified. Otherwise, ↓

```
DCE all atom
units kJ
molecular types 1
DCE
nummols 1
atoms  8
C          12.011      -0.006    2
H           1.0079      0.103    4
Cl         35.4530     -0.200    2
bonds 3
harm    1    3   2845.12  1.0900
harm    1    2   2242.62  1.5290
harm    1    7   2050.16  1.7810
angles 4
harm    1    2    5    313.8        110.70
harm    3    1    4    276.1        107.80
harm    1    2    8    577.4        109.80
harm    3    1    7    426.8        107.60
dihedrals 3
cos3    3    1    2    5    0.00000   0.0000   1.3305   0.5000   0.5000
cos3    3    1    2    8    0.00000   0.0000   1.6736   0.5000   0.5000
cos3    7    1    2    8   -1.046     0.0000   0.0000   0.5000   0.5000
finish
vdw 6
     C      C    lj  0.276144     3.5
     C      H    lj  0.186176     3.0
     C      Cl   lj  0.588741     3.45
     H      H    lj  0.12552      2.5
     H      Cl   lj  0.396929     2.95
    Cl      Cl   lj  1.2552       3.4
close
```

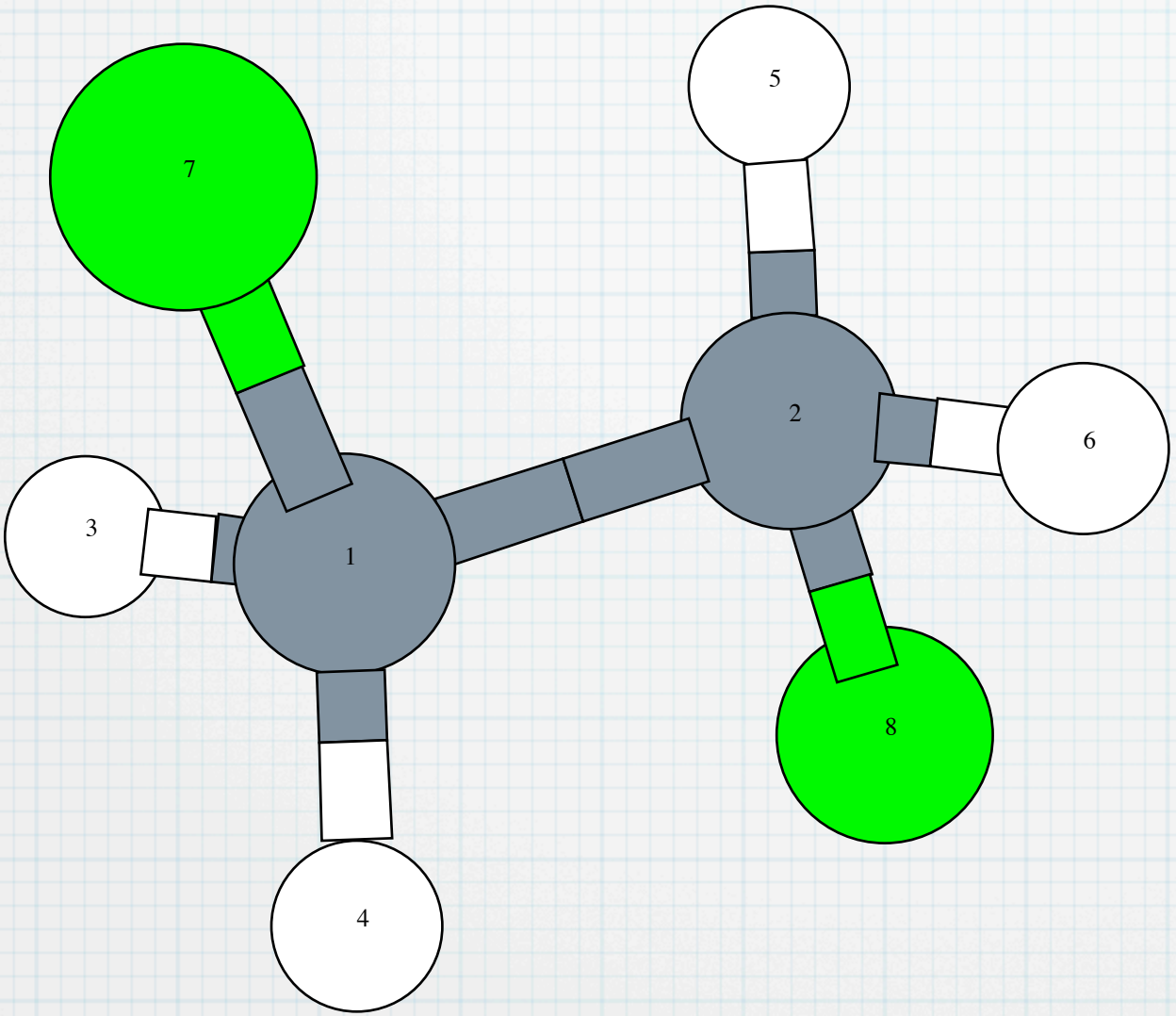


FIELD check cal.

structure relaxation of single molecule
from all atom model potential

0 K, single molecule simulation
intra-molecule potential check

MD result: NVE 0.5 K, 1 molecule cos3



bond / Angstrom

1-3	1.0910
1-4	1.0904
2-5	1.0916
2-6	1.0905
1-2	1.5314
1-7	1.7824
2-8	1.7829

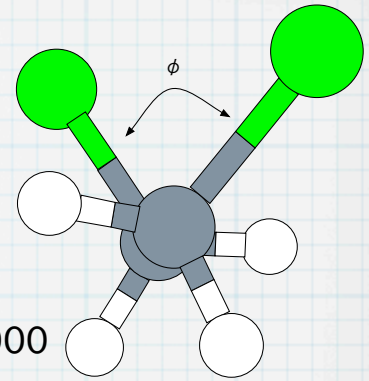
angle / degree

125	111.37
126	111.30
213	111.26
214	111.44
314	108.03
526	108.27
128	110.06
217	110.13
317	107.83
417	108.02
528	107.71
628	108.00

torsion / degree

3125	60.15
3126	181.07
4125	180.79
4126	301.71
3128	300.77
4128	61.40
5217	300.64
6217	61.56
7128	181.26

Cl-C-C-Cl torsion angle potential of DCE in DCE



FP cal. :
from the structure of the trans configration
FP cal. :fully relaxed structure
MD force field

energy differnce / eV

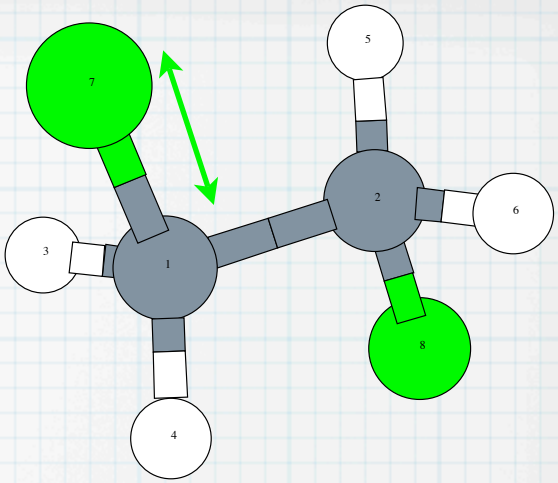
temperature / K

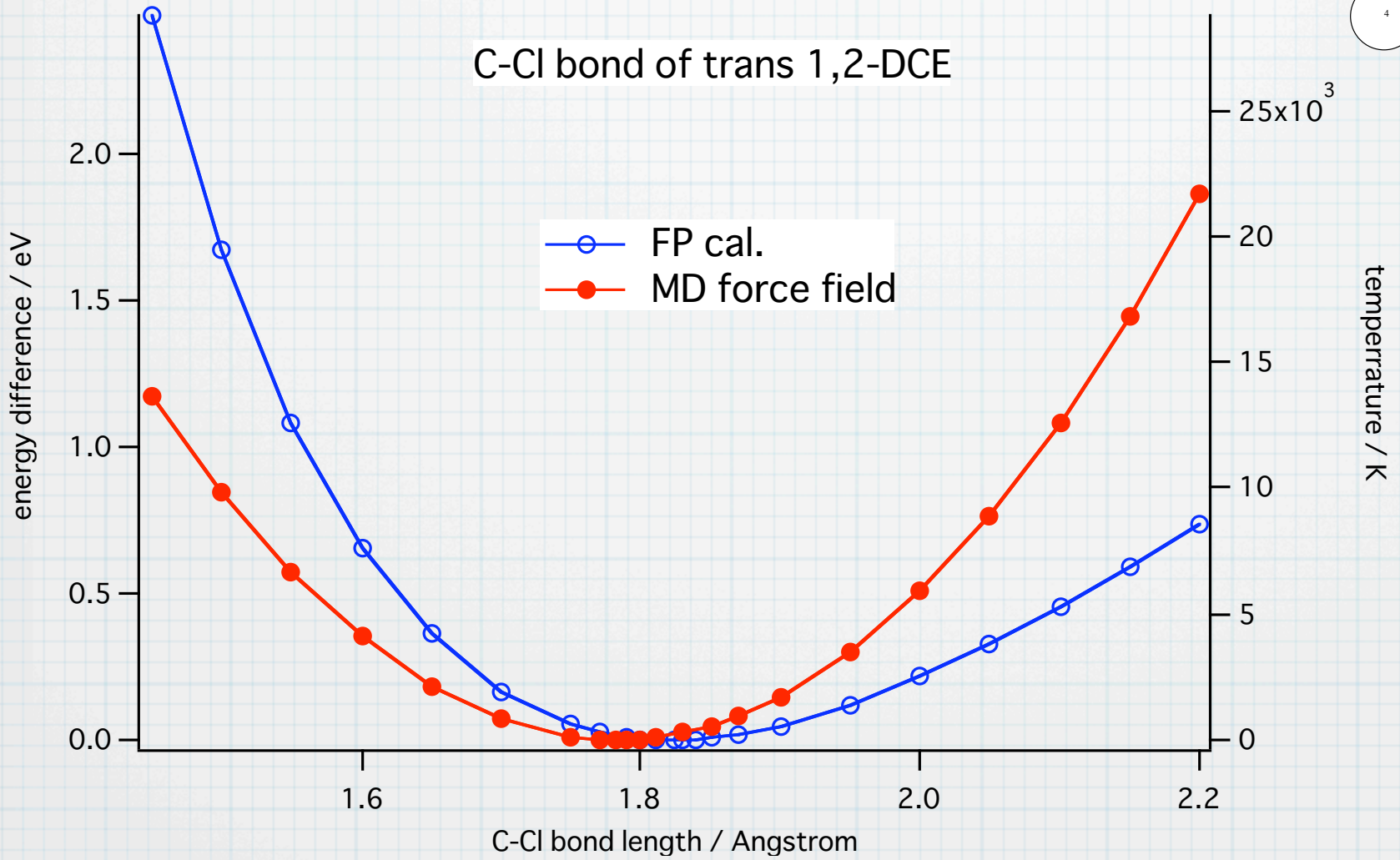
torsion angle / degree

exp: energy diff. trans- gauche in DCE 0.31 kcal mol-1 = 13.4 meV = 156 K cal. 262 K

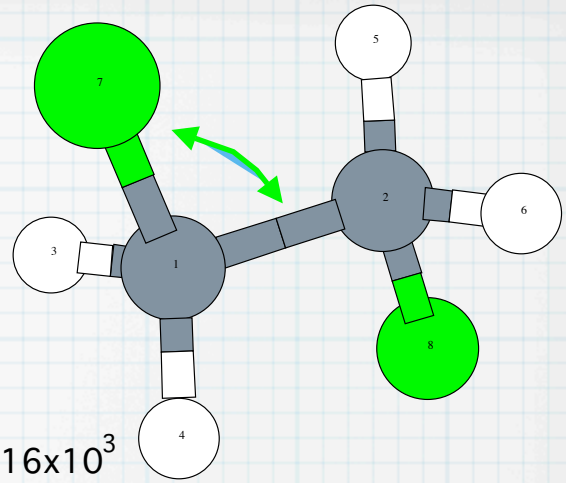
in vacuum 1.20 kcal mol-1 = 52.0 meV = 604 K cal. 798 K

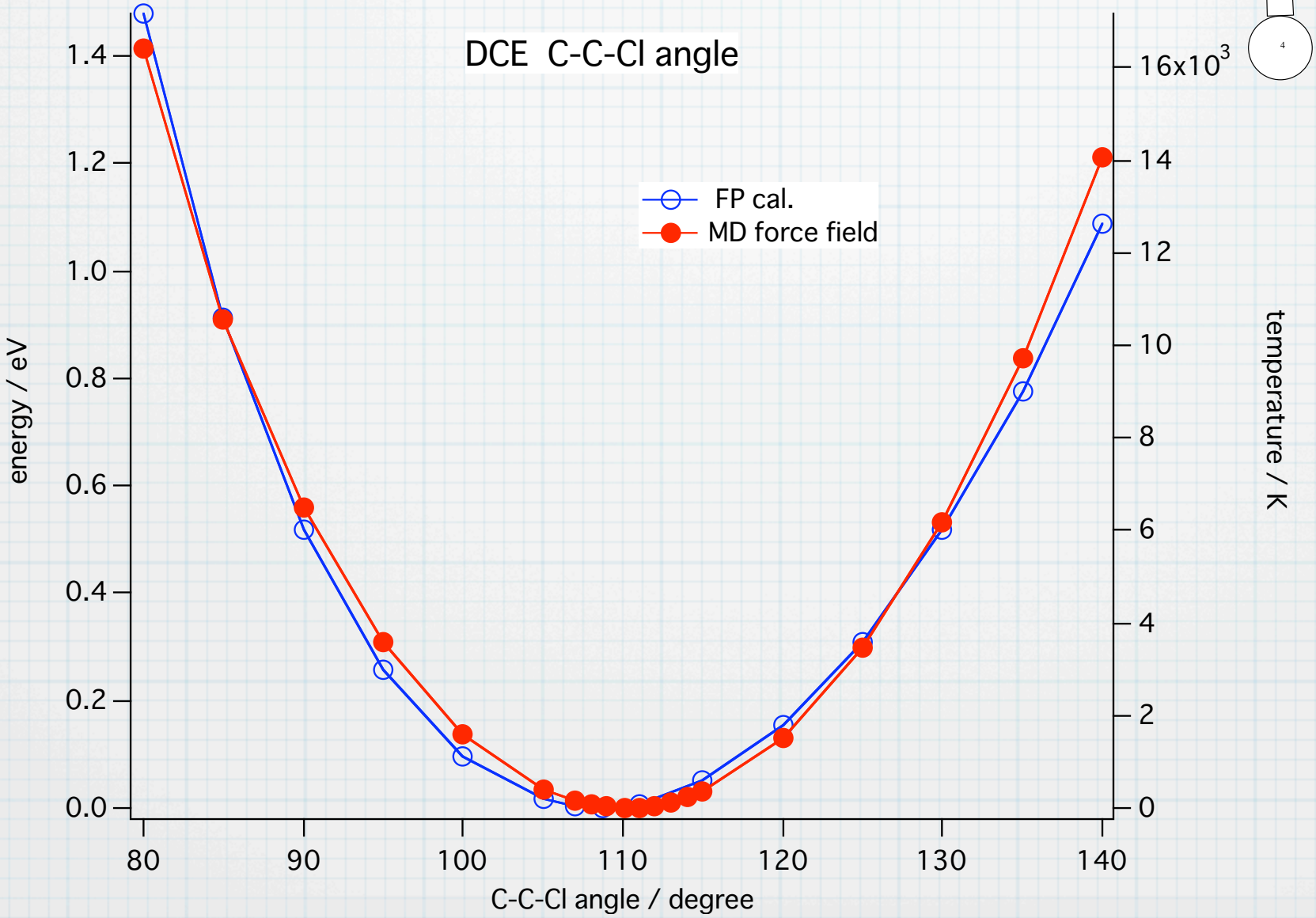
C-Cl bond length potential of DCE in DCE



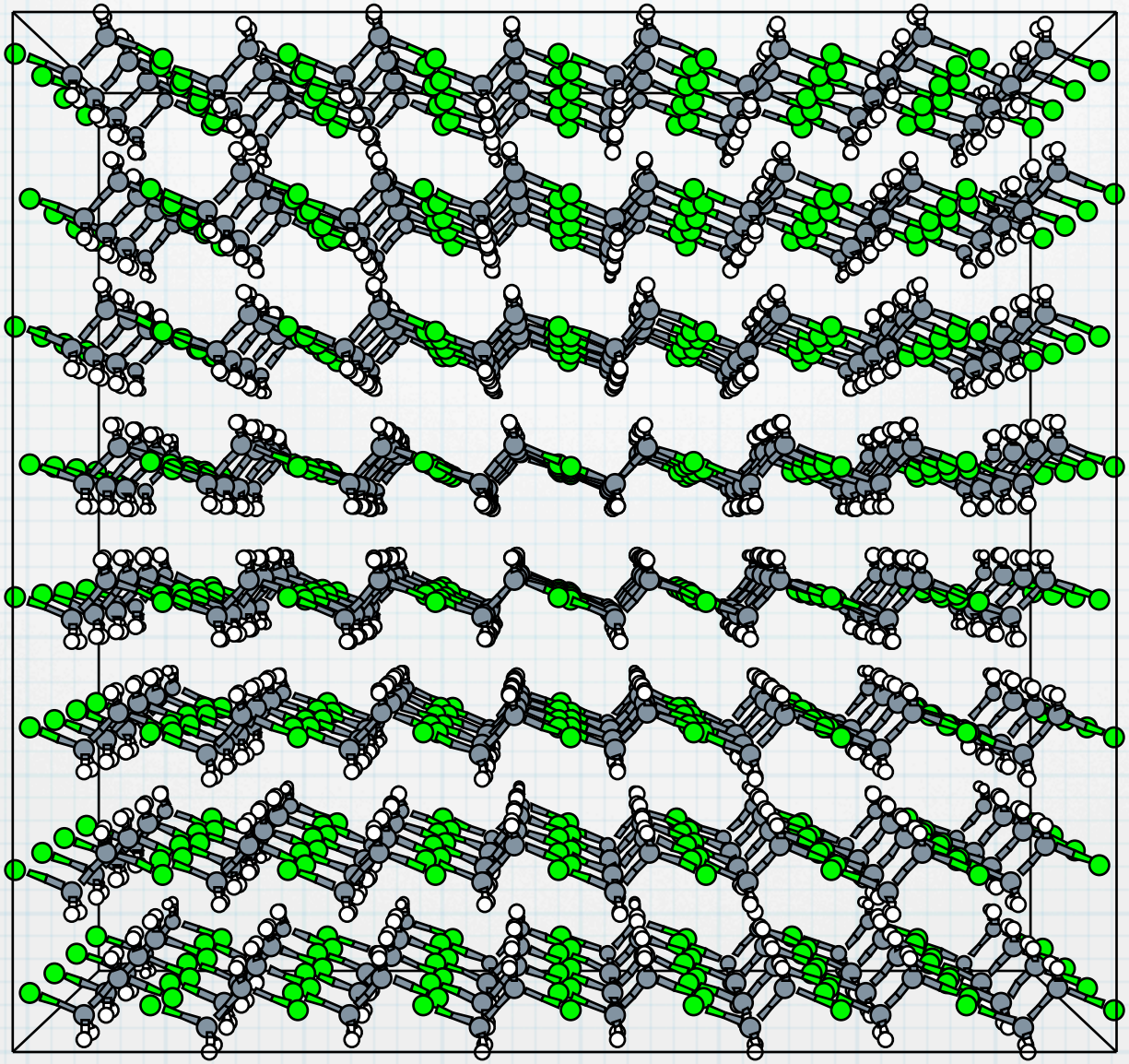


C-C-Cl bond anglel potential of DCE in DCE





Now we move to 356 mol. system. initial configuration



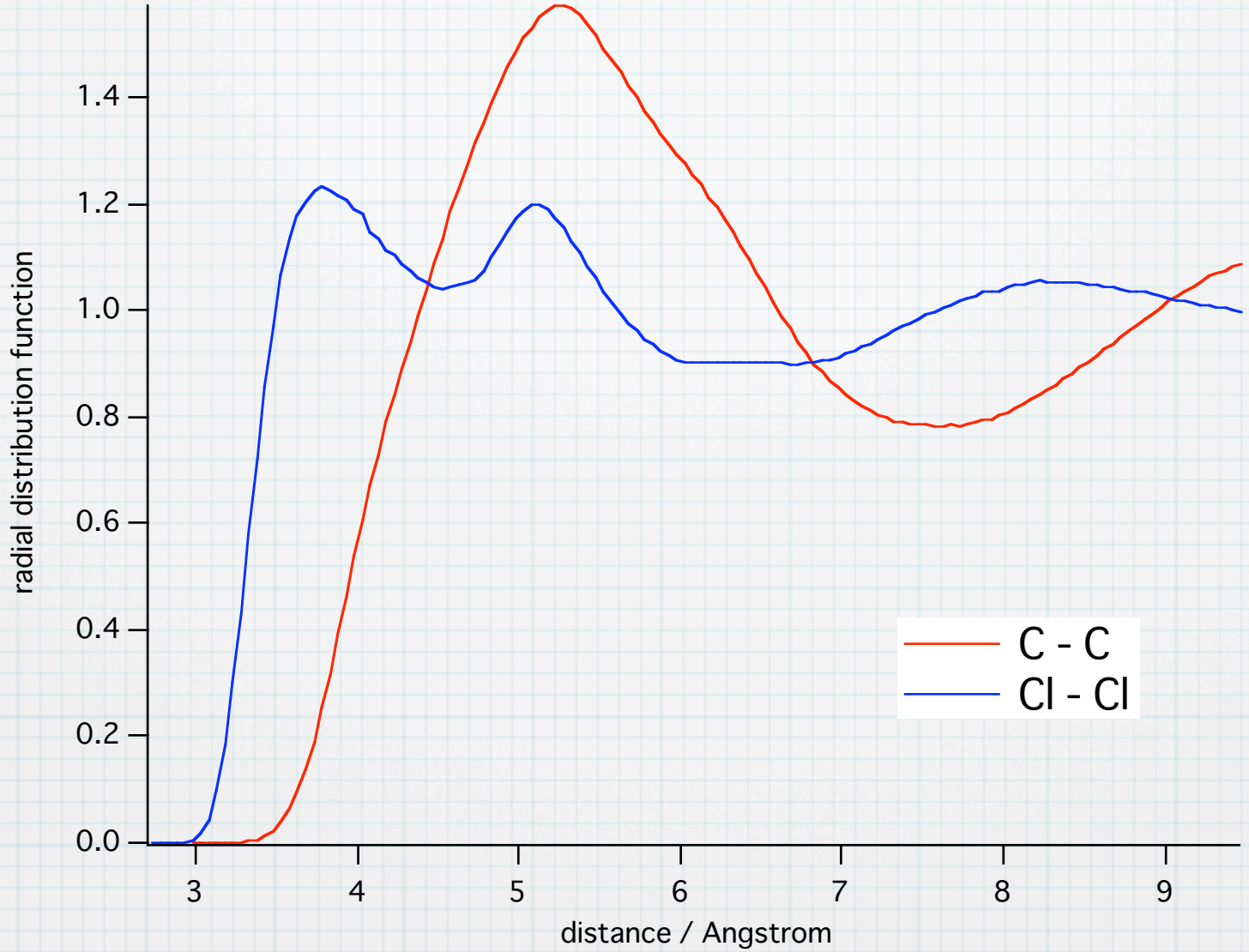
NVE simulation: results self-diffusion

```
DCE NVE 256 mol.

integrator velocity verlet
temperature       300.0
ensemble nve

steps          1500000
equilibration   500000
multiple step        1
scale               10
print               50
stack              100
stats               10
rdf                  1
traj     1   100  0

timestep        0.0001
cutoff          9.50
delr width      0.5000
ewald precision 1d-6
shake tolerance  1.0E-5
quaternion tolerance  1.0E-5
print rdf

job time         300000.00
close time         1000.00

finish
```

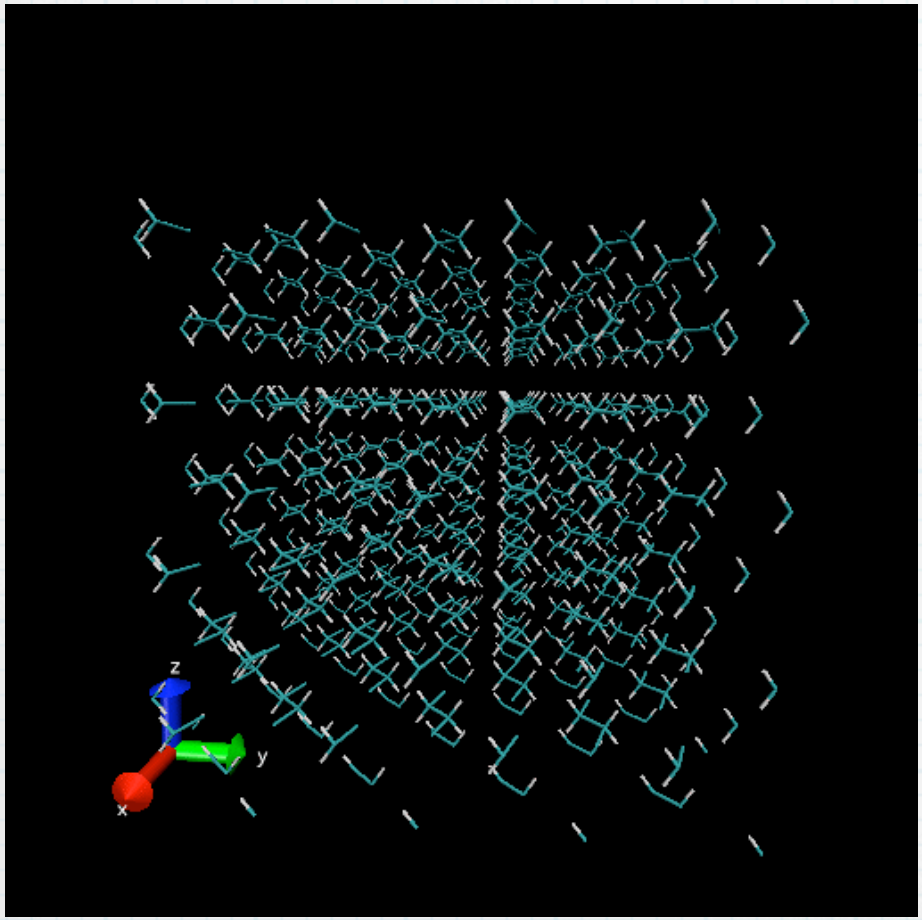
```
run terminated after 1500000 steps. final averages calculated over 1000000 steps.

-------------------------------------------------------------------------------------------------------------------------------

    step     eng_tot    temp_tot     eng_cfg     eng_vdw     eng_cou     eng_bnd     eng_ang     eng_dih     eng_tet
time(ps)     eng_pv    temp_rot     vir_cfg     vir_vdw     vir_cou     vir_bnd     vir_ang     vir_con     vir_tet
cpu  (s)     volume    temp_shl     eng_shl     vir_shl       alpha        beta       gamma     vir_pmf       press

-------------------------------------------------------------------------------------------------------------------------------
 1500000  4.3299E+03  3.0077E+02 -3.3486E+03 -6.8950E+03 -1.9603E+03  2.1842E+03  3.1003E+03  2.2218E+02  0.0000E+00
  150.000  6.4082E+03  0.0000E+00  9.1222E+03 -6.5921E+03  1.9600E+03  1.3754E+04  0.0000E+00  0.0000E+00  0.0000E+00
******** 3.2791E+04  0.0000E+00  0.0000E+00  0.0000E+00  9.0000E+01  9.0000E+01  9.0000E+01  0.0000E+00  1.0387E+00

 r.m.s.   5.2674E-01  3.8798E+00  9.9063E+01  6.7939E+01  6.0573E+01  7.0591E+01  9.4880E+01  3.2248E+01  0.0000E+00
fluctn.   1.5009E+03  0.0000E+00  4.5155E+03  1.1320E+03  6.0584E+01  4.2374E+03  0.0000E+00  0.0000E+00  0.0000E+00
          0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  0.0000E+00  7.5013E-01
-------------------------------------------------------------------------------------------------------------------------------


      Approximate 3D Diffusion  coefficients (10^-9 m^2 / s)

      atom       D
      C       1.0027E+00
      H       9.9311E-01
      Cl      1.0486E+00


        Average pressure tensor                          r.m.s. fluctuations

       1.0153E+00 -2.7400E-02 -7.6797E-03          1.1143E+00  7.1434E-01  7.1722E-01
      -2.7400E-02  1.0548E+00  1.1290E-02          7.1434E-01  1.0973E+00  6.9323E-01
      -7.6797E-03  1.1290E-02  1.0460E+00          7.1722E-01  6.9323E-01  1.1083E+00

       trace/3.   1.0387E+00
```

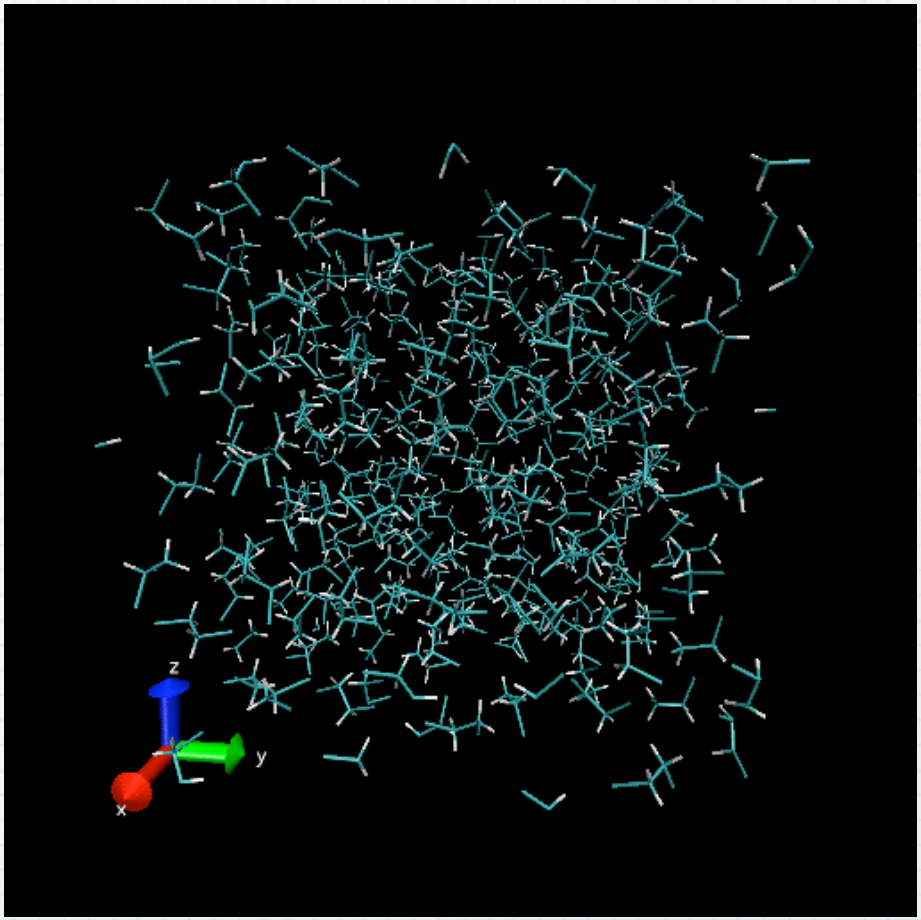
Self-diffusion const. of 1,2-DCE 1.692E-9 m2 s-1 298.15 K 0.1 MPa
0.985E-9 m2 s-1 298.15 100.8 MPa
rho 1245.98 kg m-3 at 298.15 K
R. Malhotra, W. E. Price, L. A. Woolf and A. J. Easteal
Thermodynamic and transport properties of 1, 2-dichloroethane
International Journal of Thermophysics
Volume 11, Number 5 / 1990年9月 835-861

NVE simulation: RDF



NVE simulation: animation





NPT simulation: results

DCE NVE 256 mol.

integrator velocity verlet
temperature 300.0
ensemble npt hoover 0.1 0.2

steps 1500000
equilibration 500000
multiple step 1
scale 10
print 50
stack 100
stats 10
rdf 1
traj 1 100 0

timestep 0.0001
cutoff 9.50
delr width 0.5000
ewald precision 1d-6
shake tolerance 1.0E-5
quaternion tolerance 1.0E-5
print rdf
pres 0.001

job time 300000.00
close time 1000.00

finish

run terminated after 1500000 steps. final averages calculated over 1000000 steps.

step	eng_tot	temp_tot	eng_cfg	eng_vdw	eng_cou	eng_bnd	eng_ang	eng_dih	eng_tet
time(ps)	eng_pv	temp_rot	vir_cfg	vir_vdw	vir_cou	vir_bnd	vir_ang	vir_con	vir_tet
cpu (s)	volume	temp_shl	eng_shl	vir_shl	alpha	beta	gamma	vir_pmf	press
1500000	5.6388E+03	3.0000E+02	-2.6014E+03	-6.1940E+03	-1.7966E+03	2.1290E+03	3.0296E+03	2.3051E+02	0.0000E+00
150.000	5.0597E+03	0.0000E+00	1.5311E+04	-3.3301E+03	1.7958E+03	1.6845E+04	0.0000E+00	0.0000E+00	0.0000E+00
********	3.6001E+04	0.0000E+00	0.0000E+00	0.0000E+00	9.0000E+01	9.0000E+01	9.0000E+01	0.0000E+00	2.1809E-03
r.m.s.	5.8095E+01	5.4122E+00	2.4561E+02	2.1253E+02	9.3930E+01	9.5145E+01	9.6932E+01	3.4834E+01	0.0000E+00
fluctn.	1.5768E+03	0.0000E+00	4.6418E+03	1.0358E+03	9.4067E+01	4.4672E+03	0.0000E+00	0.0000E+00	0.0000E+00
	9.1542E+02	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	7.0717E-01

Approximate 3D Diffusion coefficients (10^-9 m^2 / s)

atom	D
C	**2.2328E+00**
H	**2.2248E+00**
Cl	**2.2788E+00**

Average pressure tensor

-1.0661E-02	1.2868E-02	-1.3885E-03
1.2868E-02	2.1396E-02	2.8010E-03
-1.3885E-03	2.8010E-03	-4.1919E-03

r.m.s. fluctuations

1.0312E+00	6.2499E-01	6.3513E-01
6.2499E-01	1.0251E+00	6.3548E-01
6.3513E-01	6.3548E-01	1.0273E+00

trace/3. 2.1809E-03

Average cell vectors

33.0171898095	.0000000000	.0000000000
.0000000000	33.0171898095	.0000000000
.0000000000	.0000000000	33.0171898095

r.m.s. fluctuations

2.7817E-01	0.0000E+00	0.0000E+00
0.0000E+00	2.7817E-01	0.0000E+00
0.0000E+00	0.0000E+00	2.7817E-01

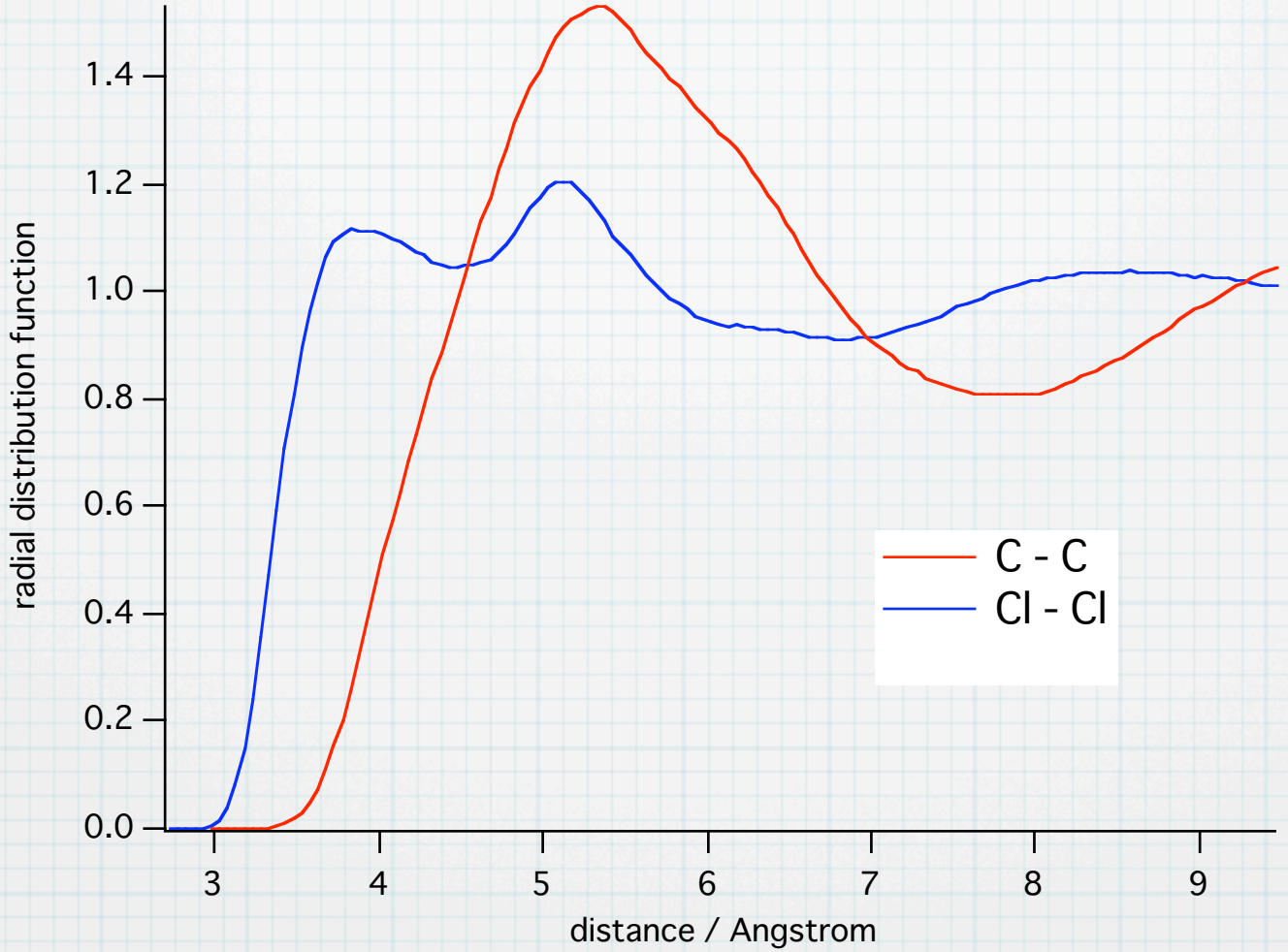
rho_cal: 1168.8 kg m-3

Self-diffusion const. of 1,2-DCE **1.692E-9 m2 s-1 298.15 K 0.1 MPa**
0.985E-9 m2 s-1 298.15 100.8 MPa

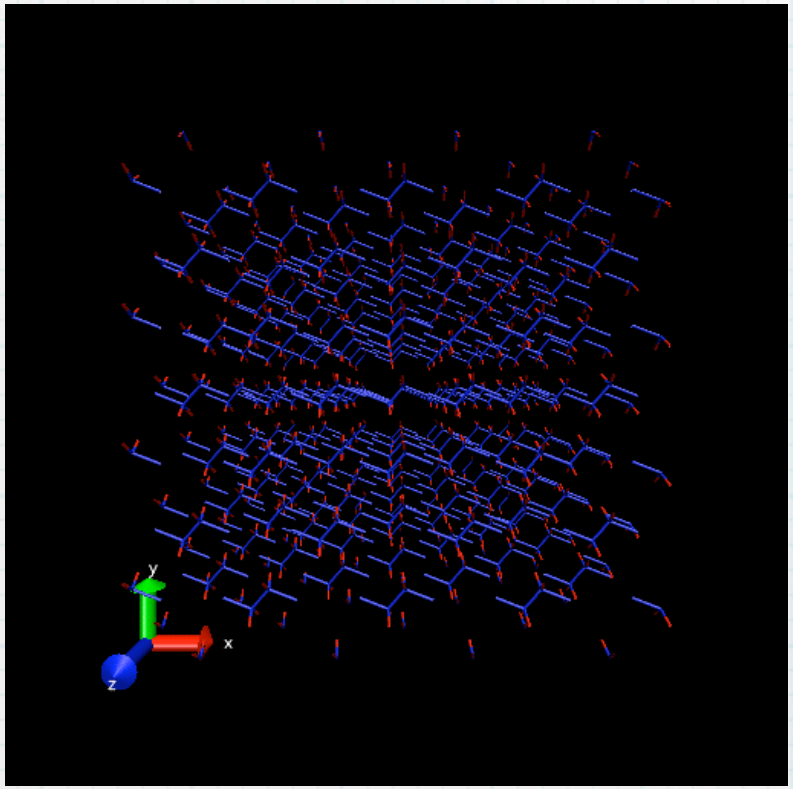
rho 1245.98 kg m-3 at 298.15 K

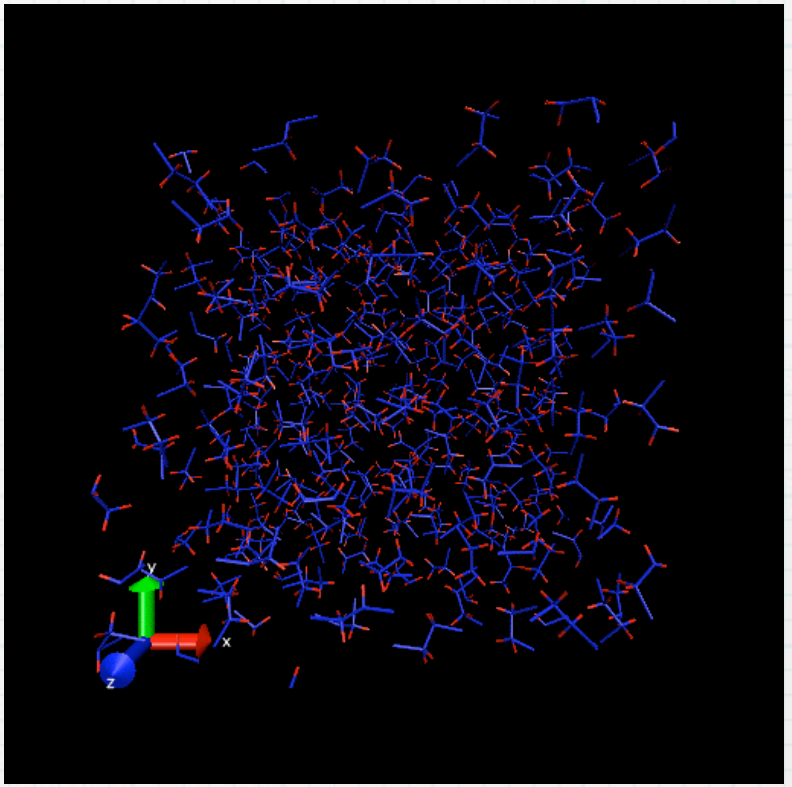
R. Malhotra, W. E. Price, L. A. Woolf and A. J. Easteal
Thermodynamic and transport properties of 1, 2-dichloroethane
International Journal of Thermophysics
Volume 11, Number 5 / 1990年9月 835-861

NPT simulation



NPT simulation





This is the end of the tutorial.

I hope now you can start to simulate the system that you have interest.

One more very important thing!!

You can find the force field parameter sets from the following site.

ftp://dasher.wustl.edu/pub/tinker/params

You can get Amber, OPLS-AA, Charmm, Dang and etc.

Thank you for your attention.
Good luck!!

2007/08/23 M. Y.