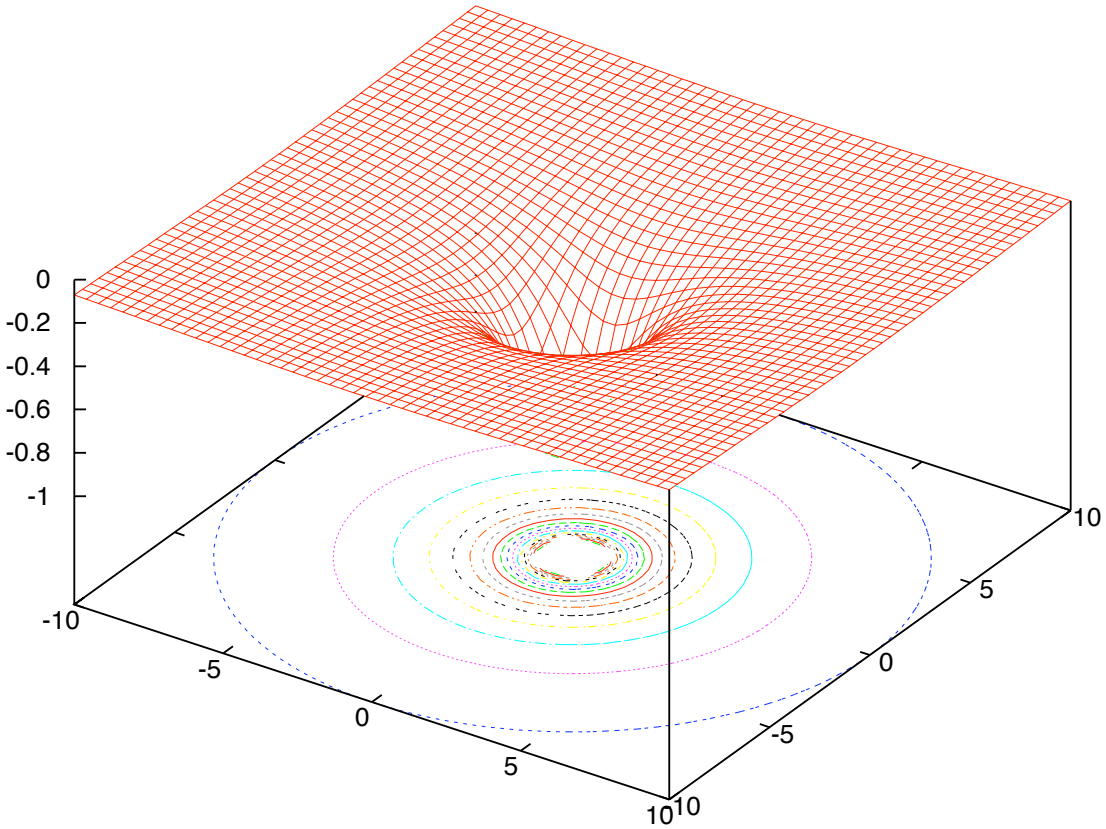
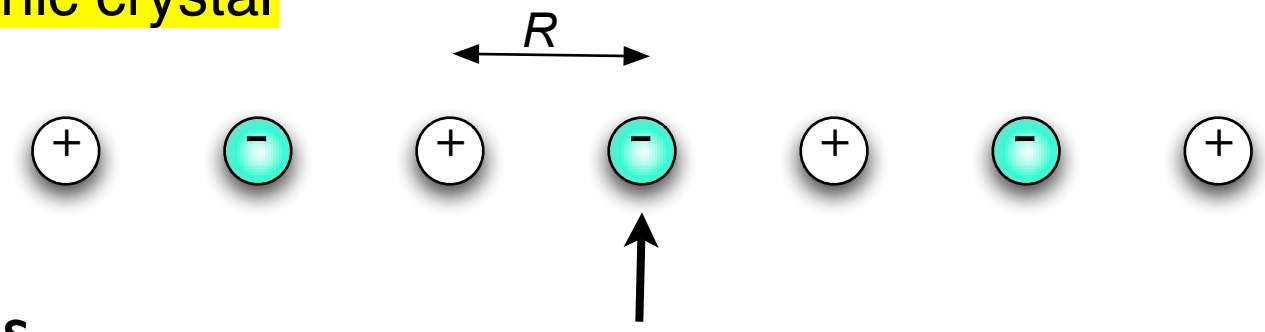
Long-range electrostatic interaction



- First we learn what means "long range"? It is very important concept for simulation. !!

Consider 1D ionic crystal



$2N$ ions

N cations: $q_+ = e$

N anions: $q_- = -e$

We can cal. the coulomb interaction U_0 which involve the ↑ anion

(2 means int. to left and right is the same)

$$\frac{4\pi\epsilon_0 U_0}{e^2} = 2\left(-\frac{1}{R}+\frac{1}{2R}-\frac{1}{3R}+\frac{1}{4R}-\ldots\right) = -\frac{2}{R}\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\ldots\right)$$

$$= -\frac{2}{R}\ln 2$$

$$\ln(1+x) \simeq x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots$$

The interaction is the same for all $2N$ ions, then

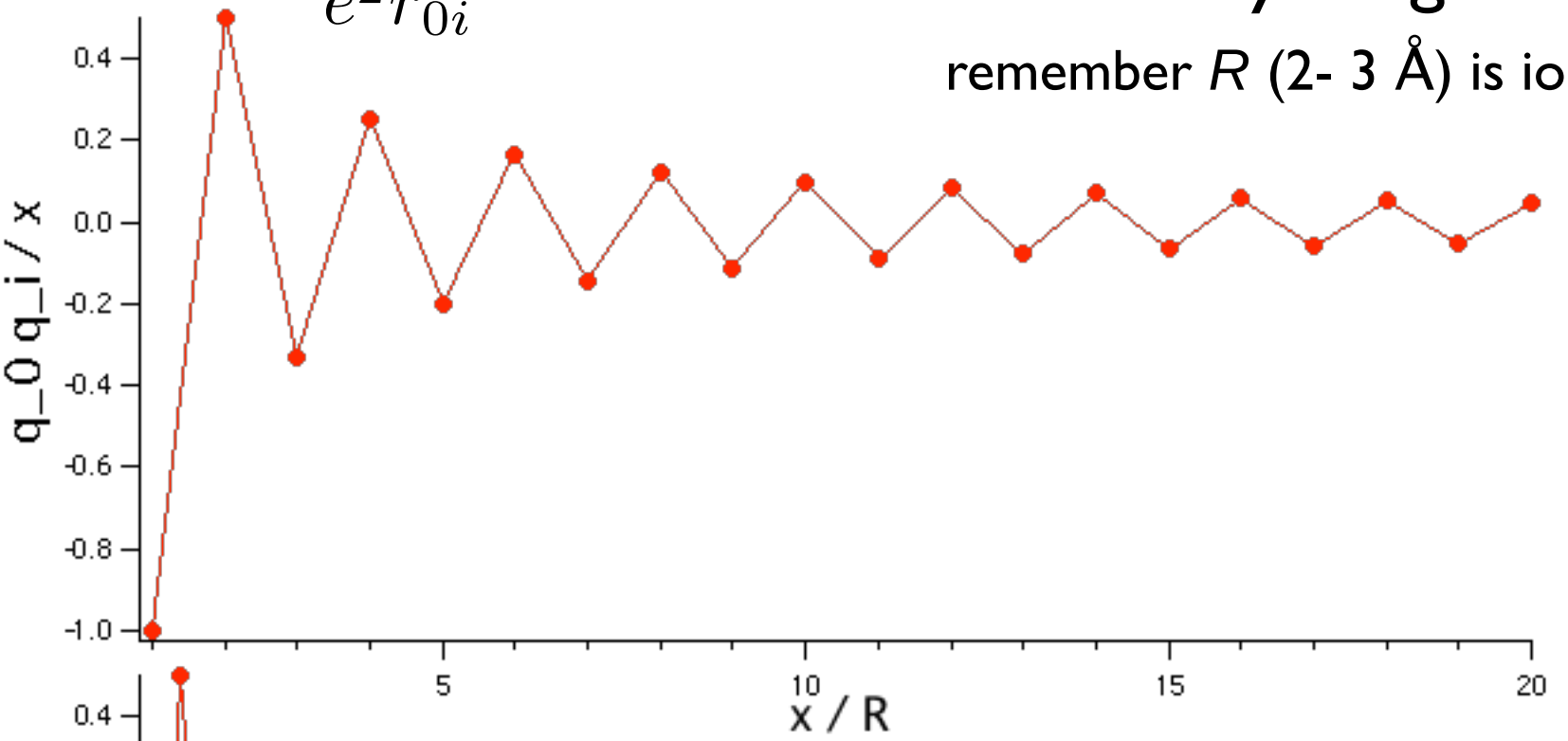
$$U = \frac{1}{2}\sum_{i,j}\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} = \frac{1}{2}2NU_0 = -N\frac{e^2}{4\pi\epsilon_0}\frac{2\ln 2}{R}$$

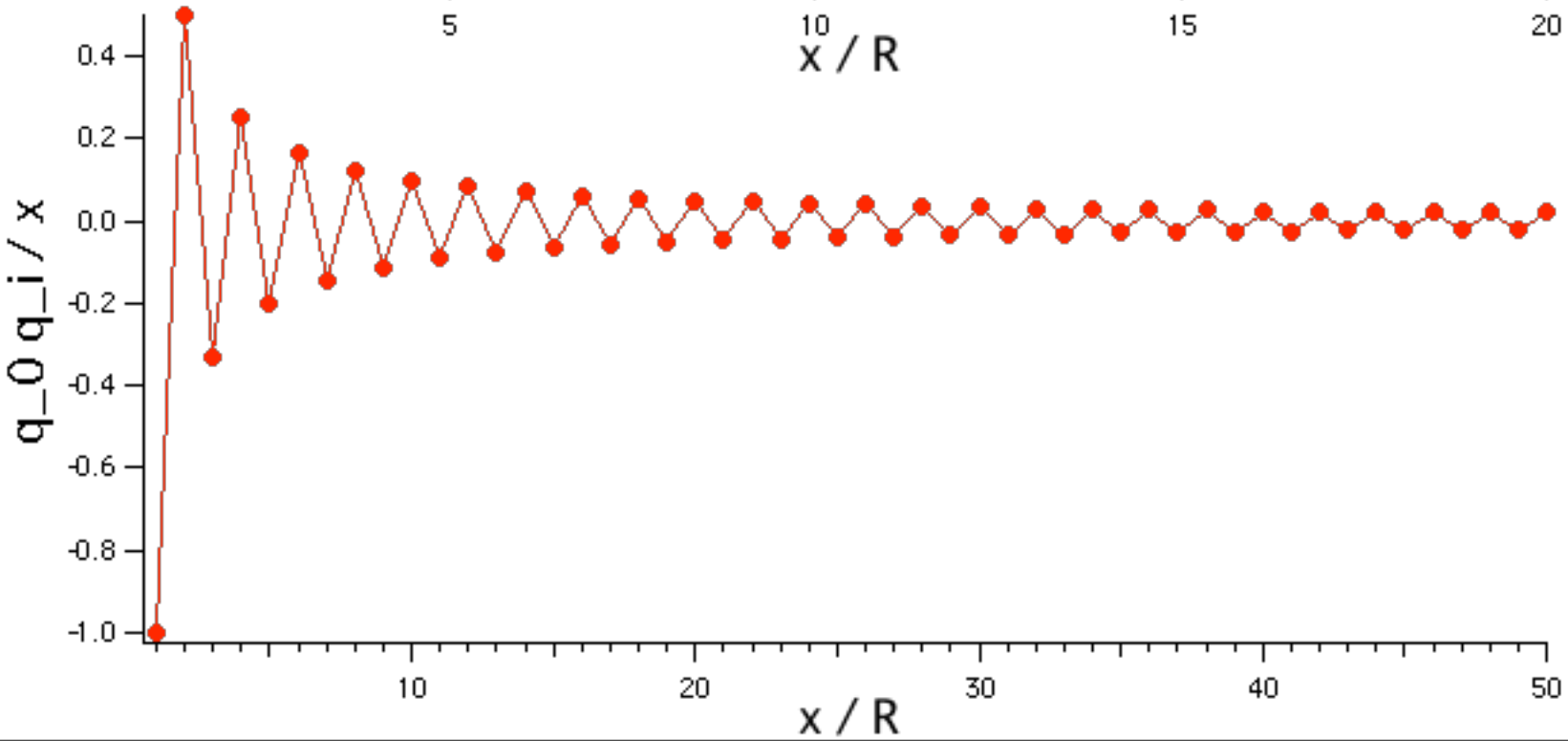
Madelung constant

If we plot $\frac{q_0 q_i}{e^2 r_{0i}}$

very long-range !!

remember *R* (2- 3 Å) is ion-ion distance

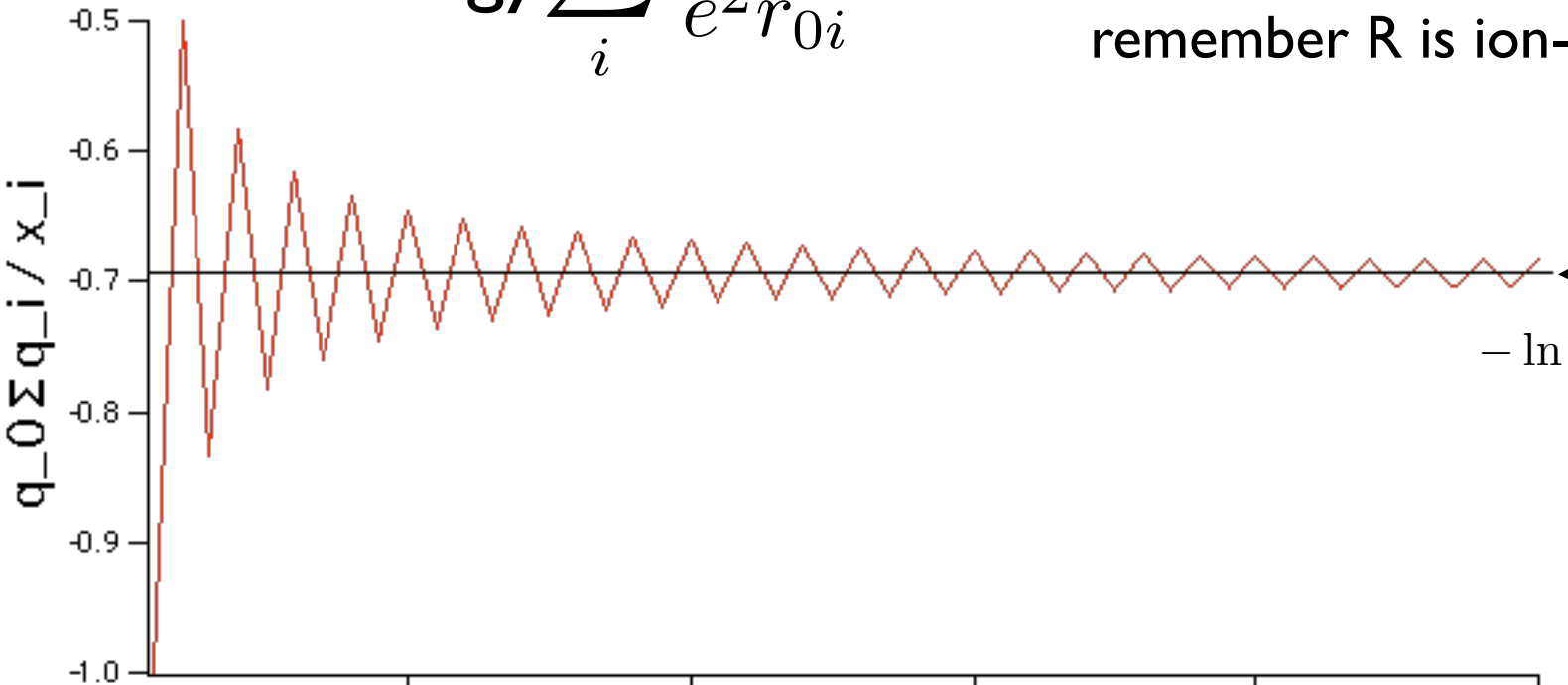




If we plot total energy $\sum_i \frac{q_0 q_i}{e^2 r_{0i}}$

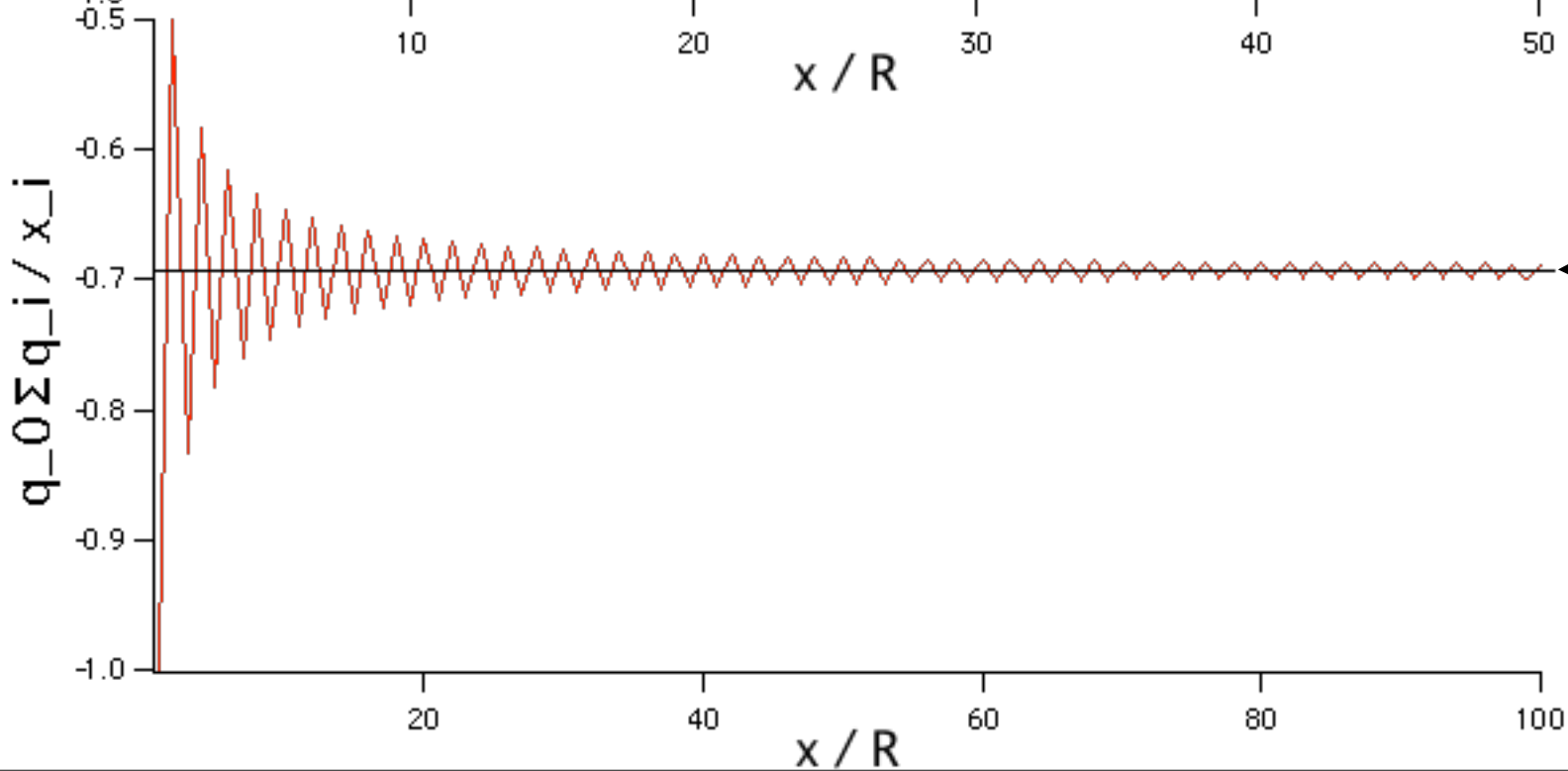
slow convergence!!

remember R is ion-ion distance



$-\ln 2$

$-\ln 2 = -0.693147$



$-\ln 2$

- So if we simply use the cut-off (I. Benjamin use 3 nm cutoff) we may get not-accurate (sometimes wrong) answer!!

- Some special care should be taken to handle the long range interaction!!

Ewald method

I want to skip the formulation.
If you like, please refer pp.35-42 of

http://www.users.kudpc.kyoto-u.ac.jp/~d54649/web_material/MDselfstudy.pdf

(Prof. Kano told me that one of the B4 students in his lab always say that she is happy when she handles equations!)

But One very important thing:

short range part ☞direct Coulomb sum (***R*** space)

long range part ☞ ***k***-space sum (reciprocal space)

(long range ***r*** ⇔ short range ***k***)

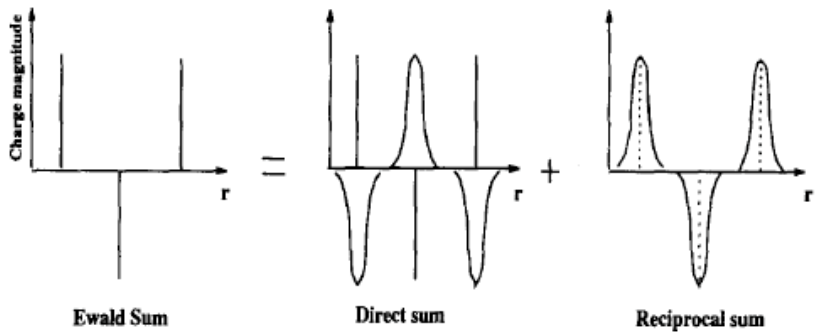


Fig. 2. The Ewald sum components of a one-dimensional point-charge system. The vertical lines are (+/−) unit charges, and the Gaussians are also normalized to unity.

In the Ewald method the electrostatic potential becomes

$$V_{\mathrm{I-I}} = \frac{e^2}{4\pi\epsilon_0}\left\{\frac{1}{2}\frac{4\pi}{\Omega_{cell}}\sum_{\mathbf{G}\neq 0}\frac{1}{|\mathbf{G}|^2}e^{-\frac{|\mathbf{G}|^2}{4\kappa^2}}\underbrace{\left[\left[\sum_{i=1}^{N}Z_i\cos(\mathbf{G}\cdot\mathbf{r}_i)\right]^2+\left[\sum_{i=1}^{N}Z_i\sin(\mathbf{G}\cdot\mathbf{r}_i)\right]^2\right]}_{|S(\mathbf{G})|^2}\right.$$

$$+\frac{1}{2}\sum_i\sum_j Z_iZ_j\left[\sum_{\mathbf{R}}{}'\frac{1}{x}\mathrm{erfc}(\kappa x)\Big|_{x=|\mathbf{R}+\mathbf{r}_j-\mathbf{r}_i|}\right.$$

$$\left.\left.-\frac{2\kappa}{\sqrt{\pi}}\delta_{ij}-\frac{\pi}{\kappa^2\Omega_{cell}}\right]\right\}$$

The practical points: we should give

1) cutoff of ***G*** sum

2) cutoff ***R*** sum

3) ***κ*** value

Don't worry! In DL-POLY these parameters are optimized inside the program, so just set,

ewald precision 1d-6

(If you don't like it, you can set "ewald sum *κ k1 k2 k3*")

MD Simulations of High Temperature Molten Salts

cf. S. Okazaki, Y. Miyamoto, and I. Okada, PRB, 45, 1992, 2055-2062
LiCl and LiCl-CsCl

Potential : Coulomb + Born-Huggins-Meyer (Tosi-Fumi potential)

$$\phi_{ij}(r) = \underbrace{\frac{z_i z_j e^2}{r}}_{\text{Coulomb}} + \underbrace{A_{ij} b \exp\left(\frac{\sigma_i^0 + \sigma_j^0 - r}{\rho}\right) - \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8}}_{\text{BHM}}$$

Tosi-Fumi potential parameters for alkali-halides

	σ_+^0(pm)	σ_-^0(pm)	ρ(pm)	c_{++}	c_{--}	c_{+-}	d_{++}	d_{--}	d_{+-}
LiF	81.6	117.9	29.9	0.073	14.5	0.8	0.03	17.0	0.6
LiCl		158.5	34.2		111.0	2.0		223.0	2.4
LiBr		171.6	35.3		185.0	2.5		423.0	3.3
LiI		190.7	43.0		378.0	3.3		1060.0	5.3
NaF	117.0		33.0	1.68	16.5	4.5	0.8	20.0	3.8
NaCl			31.7		116.0	11.2		233.0	13.9
NaBr			34.0		196.0	13.0		450.0	19.0
NaI			38.6		392.0	19.1		1100.0	31.0
KF	146.3		33.8	24.3	18.6	19.5	24.0	22.0	21.0
KCl			33.7		124.5	48.0		250.0	73.0
KBr			33.5		206.0	60.0		470.0	99.0
KI			35.5		403.0	82.0		1130.0	156.0
RbF	158.7		32.8	59.4	18.9	31.0		23.0	40.0
RbCl			31.8		130.0	79.0		260.0	134.0
RbBr			33.5		215.0	99.0		490.0	180.0
RbI			33.7		428.0	135.0		1200.0	280.0
CsF	172.0		28.2	152.0	19.1	52.0		23.0	78.0

$b = 0.338 \times 10^{-19}$ J

c, d の単位はそれぞれ 10^{-79} Jm^6, 10^{-99} Jm^8 である。

添字の +, − はそれぞれ陽イオン種, 陰イオン種を示す。

A はボーリング定数で $A_{ij} = (z_i/n_i) + (z_j/n_j) + 1$ である。

ただし n_i, n_j はそれぞれのイオンの最外殻電子数である。

岡田勲　溶融塩の分子動力学シミュレーション

計算物理学と計算化学　８章　134-157 KAIBUNDO

LiCl molten salts: physical properties

無機塩	T_m / K
LiCl	883

ρ / 10^3 kg m^{-3}
LiCl 1.884 - 4.328x10^{-4} T (910-1050 K)
金属データブック

1.463 g cm^{-3} at 973 K
fcc cubic lattice 5.774 Å

solid-> LiCl | 20 | 2.068

fcc cubic lattice 5.14 Å

化合物	T / K	η / mPa s
LiCl	900	1.40
	920	1.32
	940	1.25
	960	1.19
	980	1.13
	1000	1.08
	1020	1.03
	1040	0.989
	1060	0.949
	1080	0.912
	1100	0.877

[G.J. Janz, "NIST Standard Reference. Database 27", (1991)]

融解塩	イオン	D_0/10^{-7} m^2 s^{-1}	Q / kJ mol^{-1}	温度 T / K
LiCl	Li+	1.23	18.00	883～1033
	Cl-	0.71	18.43	883～1033

Li$^+$ 1.3D-8 m^{2}s^{-1} at 973K
Cl$^-$ 0.7D-8 m^{2}s^{-1} at 973K

LiCl potential parameters

A_{ij} : Pauling parameter

$$(?? = \frac{z_i}{n_i} + \frac{z_j}{n_j} + 1)$$

Li+ Li+	~~2~~	1.25
Li+ Cl-	~~4/3~~	1
Cl- Cl-	~~2/3~~	0.75

$$z_{\mathrm{Li^+}} = 1,\ z_{\mathrm{Cl^-}} = -1$$
$$n_{\mathrm{Li^+}} = 2,\ n_{\mathrm{Cl^-}} = 6$$
$$n_{\mathrm{Li^+}} = 8??,\ n_{\mathrm{Cl^-}} = 8??$$

$$b = 0.338 \times 10^{-19}\mathrm{J} = 20.35\ \mathrm{kJ\ mol^{-1}}$$

$$\sigma^0_{\mathrm{Li^+}} = 0.816\ \text{Å},\ \sigma^0_{\mathrm{Cl^-}} = 1.585\ \text{Å},\ \rho_{\mathrm{LiCl}} = 0.342\ \text{Å}$$

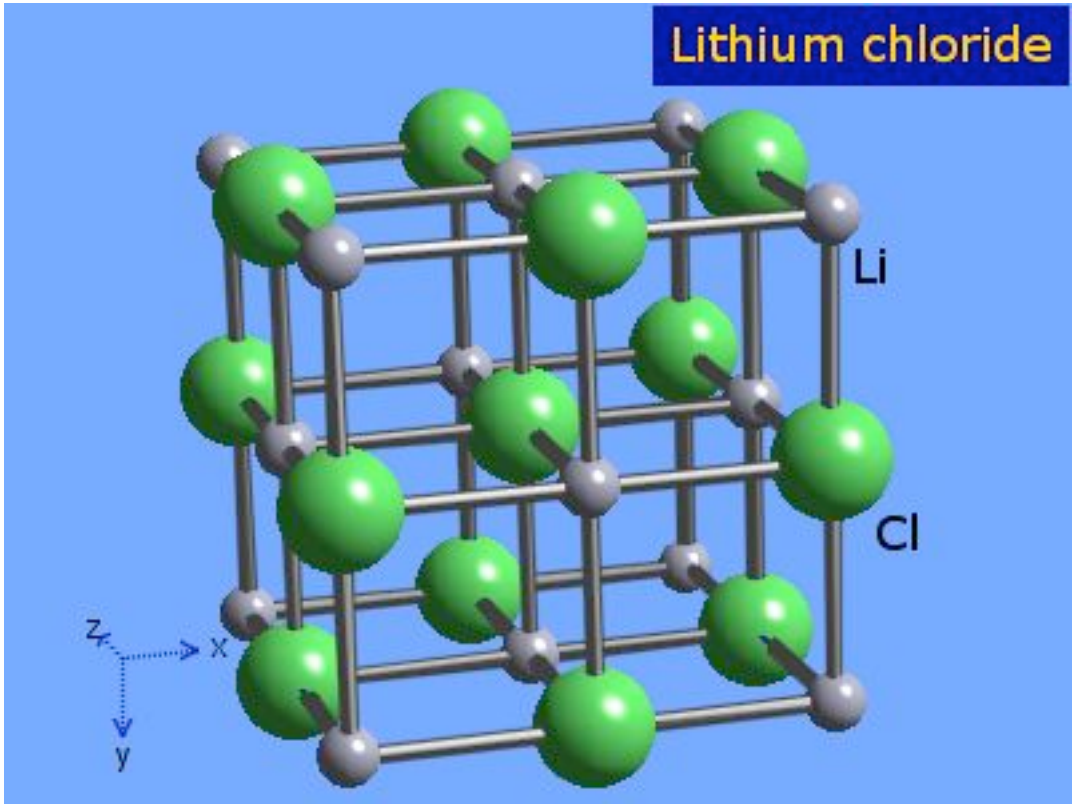
	c / 10^{-79} J m^6	d 10^{-99} J m^8
Li+ Li+	0.073	0.03
Li+ Cl-	2.0	2.4
Cl- Cl-	111.0	223.0

$$1.0 \times 10^{-79}\ \mathrm{J\ m^6} = 1.0 \times 10^{-19}\mathrm{J\ Å^6} = 60.221\ \mathrm{kJ\ mol^{-1}\ Å^6}$$
$$1.0 \times 10^{-99}\ \mathrm{J\ m^8} = 1.0 \times 10^{-19}\mathrm{J\ Å^8} = 60.221\ \mathrm{kJ\ mol^{-1}\ Å^8}$$

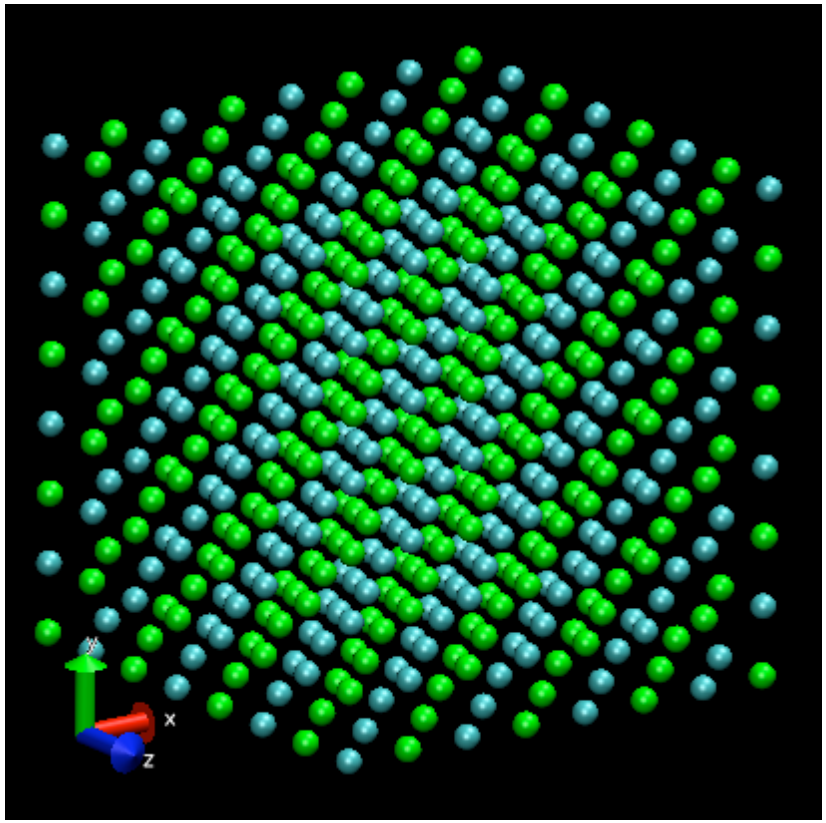
DL-POLY parameters (Please check the values!)

key	potential type	Variables (1-5)					functional form
bhm	Born-Huggins -Meyer	A	B	σ	C	D	$U(r) = A\ \exp[B(\sigma - r)] - \frac{C}{r^6} - \frac{D}{r^8}$

	A kJ mol^{-1}	B Å^{-1}	σ Å	C kJ mol^{-1} Å^6	D kJ mol^{-1} Å^8
Li^+ - Li^+	25.44	2.924	1.632	4.40	1.81
Li^+ - Cl^-	20.35	2.924	2.401	120.44	144.53
Cl^- - Cl^-	15.26	2.924	3.170	6684.57	13429.36



start configuration
NaCl structure:
Li fcc + 1-basis Li-Cl



256 Li cation
+
256 Cl anion

CONFIG

```
LiCl Tosi-Fumi  coulomb 973 K
         2           1
    23.0949137651        .0000000000        .0000000000
      .0000000000      23.0949137651        .0000000000
      .0000000000        .0000000000      23.0949137651
    Li     1
   -11.5474568825     -11.5474568825     -11.5474568825
   -10.6165397575      -9.2381425951       2.3127320988
      .0000000000        .0000000000        .0000000000
    Cl     2
    -8.6605926619     -11.5474568825     -11.5474568825
    -3.8343057133       3.3861251245       -.2857354079
      .0000000000        .0000000000        .0000000000
    Li     3
    -8.6605926619      -8.6605926619     -11.5474568825
    -2.4627326782     -10.9204233616     -10.5006199708
      .0000000000        .0000000000        .0000000000
    Cl     4
   -11.5474568825      -8.6605926619     -11.5474568825
      .3993300091       8.0160734289      -5.3483995294
      .0000000000        .0000000000        .0000000000
    ...
    Li   511
     5.7737284413       8.6605926619       8.6605926619
    10.1377456936     -13.0366025747       9.8671728482
      .0000000000        .0000000000        .0000000000
    Cl   512
     8.6605926619       8.6605926619       8.6605926619
      .7285484771       1.4579165760        .5758900933
      .0000000000        .0000000000        .0000000000
```

FIELD

```
LiCl Tosi-Fumi+Ewald
units  kJ
molecules 1
LiCl
nummols 256
atoms 2
     Li    6.941      1.00
     Cl   35.453     -1.00
finish
vdW 3
     Li      Li bhm      25.44   2.924   1.632    4.40     1.81
     Li      Cl bhm      20.35   2.924   2.401   120.44   144.53
     Cl      Cl bhm      15.26   2.924   3.170  6684.57 13429.36
close
```

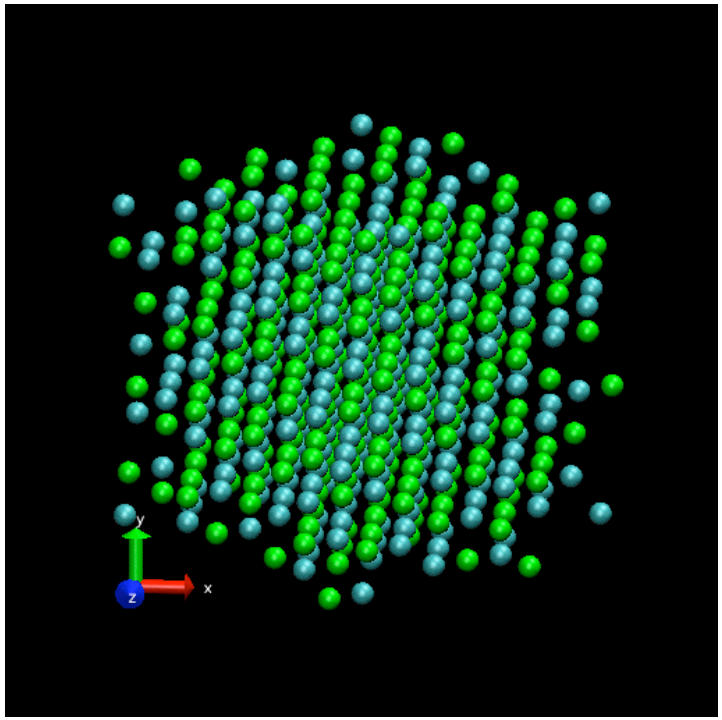
CONTROL

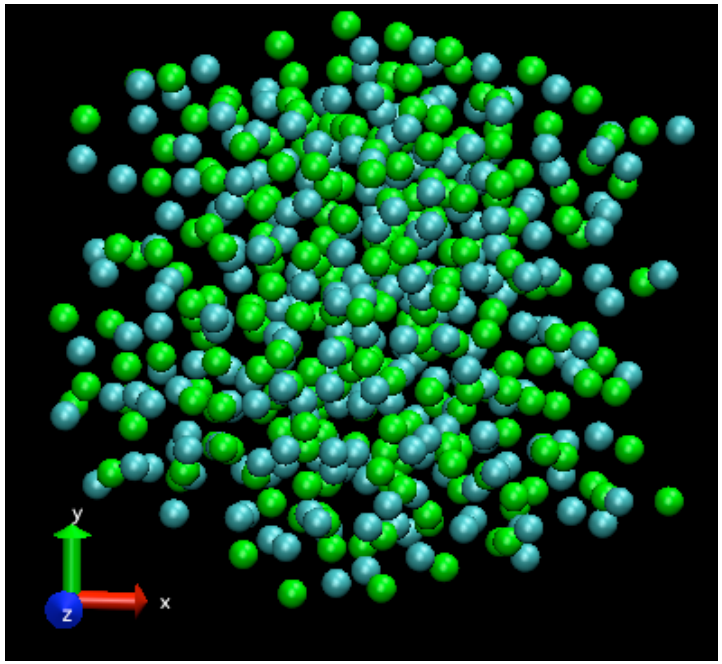
```
LiCl Tosi-Fumi+Ewald
units  kJ
molecules 1
LiCl
nummols 256
atoms 2
     Li    6.941      1.00
     Cl   35.453     -1.00
finish
vdW 3
     Li     Li bhm     25.44   2.924   1.632     4.40     1.81
     Li     Cl bhm     20.35   2.924   2.401   120.44   144.53
     Cl     Cl bhm     15.26   2.924   3.170  6684.57 13429.36
close
```

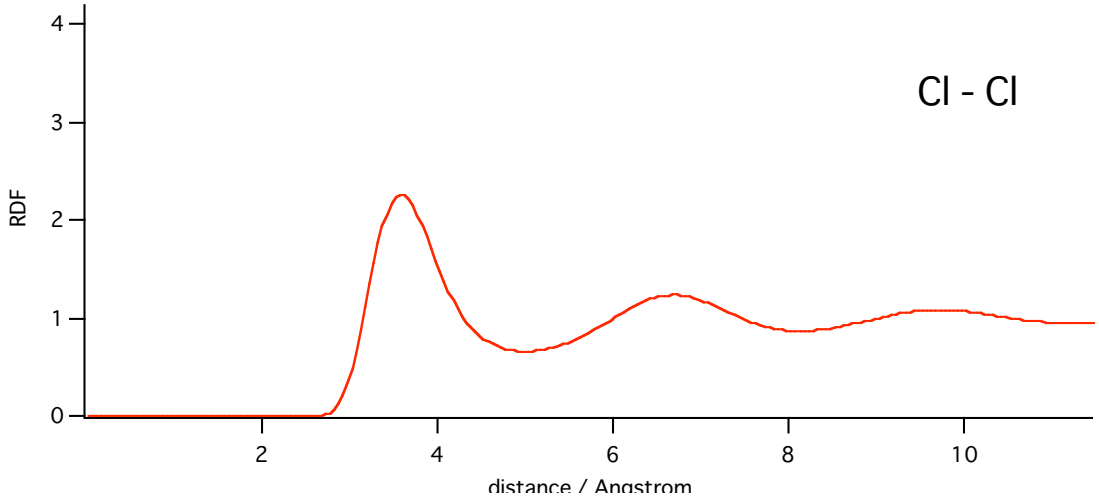
You can download the three input files and the CONFIG generation program DLPOLY_LiClinput.f from /home/d/d54649/DL_POLY/data_LiCl_TosiFumiEwald

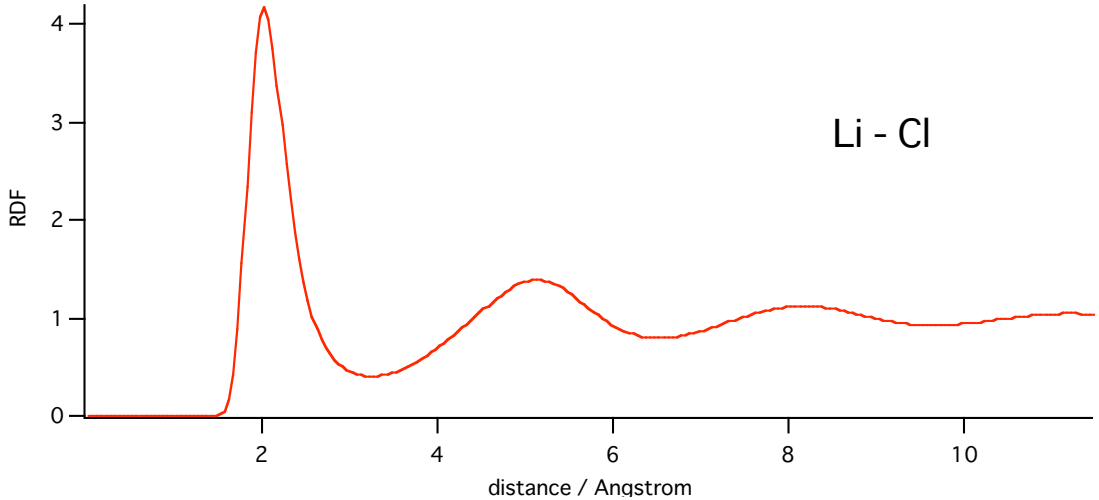
Please sftp d54649@sakura.kudpc.kyoto-u.ac.jp

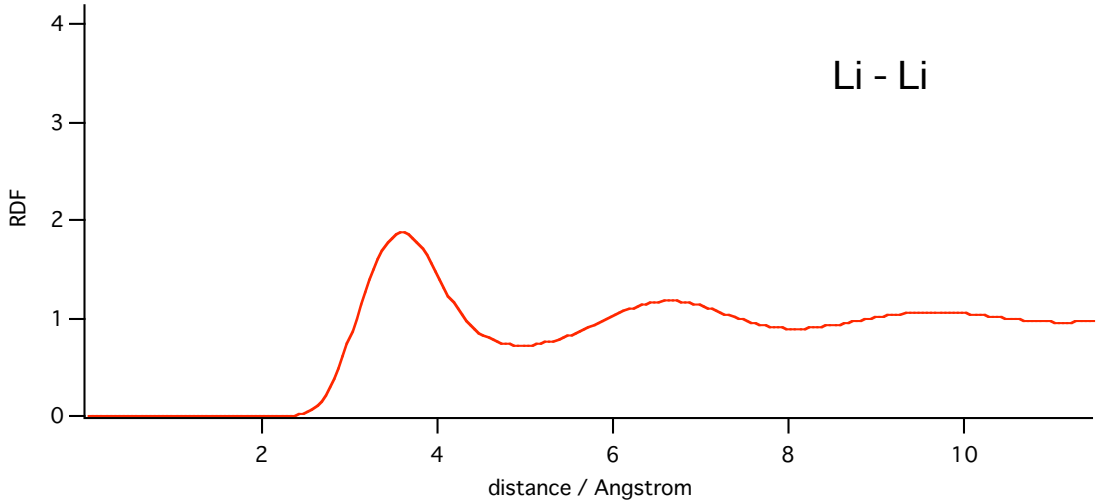
results






Cl - Cl
RDF
0
1
2
3
4
2
4
6
8
10
distance / Angstrom


Li - Cl
RDF
0
1
2
3
4
2
4
6
8
10
distance / Angstrom


Li - Li
RDF
0
1
2
3
4
2
4
6
8
10
distance / Angstrom

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

ion	D
Li^+	9.0 x10^-9
Cl^-	7.5 x10^-9

exp

Li^+ 1.3D-8 m^2s^{-1} at 973K

Cl^- 0.7D-8 m^2s^{-1} at 973K

So what's ? ===>

It seems very easy to run the simulation!! ===>

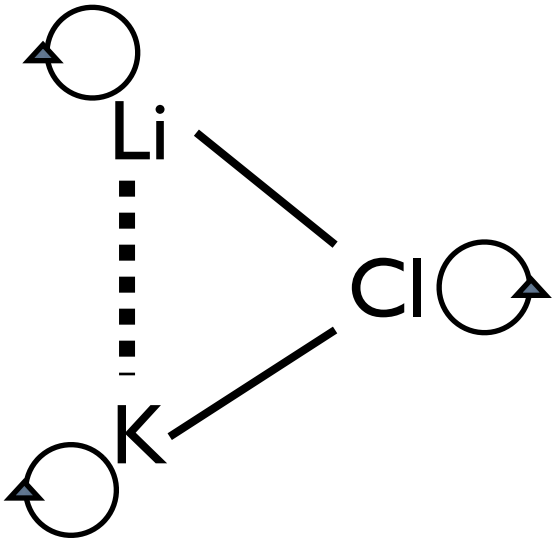
The analysis of the calculation results are very important. ===>

Thermal average, space-time correlation and so on.

mixing system

M.Y. did not cal. this system.
Please do it
by yourself if you have an interest.

- LiCl-KCl case ?
- Li-K ?



J. Phys. Chem. Ref. Data, Vol. 4, No. 4, 1975

KCl-LiCl

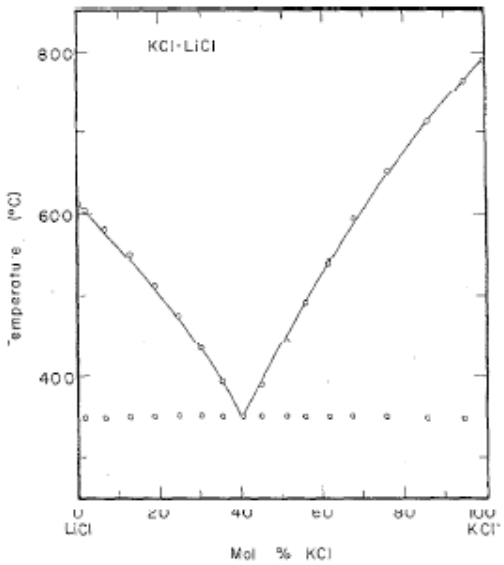


FIGURE 68. Temperature composition phase diagram for KCl-LiCl.

S. Zhemchuzhngi and F. Rambath, Izv. Spb. Politekhnicheskogo Institute, **12**, 349 (1909); Zh. Russ. Fiz.-Khim. Ova Chast Fiz. **41**, 1755 (1909); S. Zemeszuzny and F. Rambach, Z. Anorg. Chem., **65**, 403 (1910).

TABLE 393. KCl-LiCl: Specific conductance (ohm^{-1} cm^{-1})

	Mol percent LiCl						
T	100	81.77	70.36	58.80	40.45	19.96	0
670				1.227			
690				1.360			
710				1.490			
730			1.976	1.615			
750			2.133	1.737			
770			2.280	1.854			
790			2.416	1.967			
810		3.150	2.541	2.076			
830		3.271	2.656	2.181			
850		3.386	2.760	2.281			
870		3.495	2.854		1.890		
890		3.599			1.992		
910	5.819				2.087		
930	5.940				2.177		
950	6.054				2.260		
970	6.161				2.337		
990	6.261				2.408	2.109	
1010	6.353				2.472	2.176	
1030	6.439					2.239	
1050	6.517					2.298	
1070						2.354	2.225
1090						2.406	2.279
1110						2.454	2.329
1130							2.376
1150							2.420
1170							2.460
1190							2.497

TABLE 395. KCl-LiCl: Density (g cm^{-3})

	Mol percent LiCl											
T	100	90	80	70	60	50	40	30	20	10	0	59.5
720					1.646							
740				1.622	1.636							1.636
760			1.598	1.612	1.625							1.626
780			1.588	1.602	1.615	1.627						1.615
800			1.578	1.591	1.604	1.616						1.605
820		1.552	1.568	1.581	1.594	1.605						1.594
840		1.542	1.558	1.571	1.583	1.595						1.584
860		1.533	1.548	1.562	1.573	1.584	1.595					1.574
880		1.523	1.539			1.574	1.584					1.564
900	1.496	1.514				1.563	1.573	1.583				
920	1.487	1.505				1.553	1.562	1.572				
940	1.478	1.496				1.543	1.552	1.561				
960	1.469						1.541	1.550				
980	1.460						1.531	1.539	1.548			
1000	1.451						1.521	1.528	1.536			
1020	1.443							1.518	1.525	1.534		
1040	1.434							1.507	1.514	1.522		
1060								1.497	1.503	1.510	1.520	
1080									1.492	1.499	1.507	
1100									1.481	1.487	1.495	
1120									1.471	1.476	1.483	
1140										1.465	1.471	
1160										1.454	1.460	
1180											1.447	
1200											1.436	

TABLE 398. KCl-LiCl: Viscosity (cp)

	Mol percent LiCl							
T	100	80	60	50	40	30	20	0
890			1.46					
900	1.60		1.42					
910	1.54	1.40	1.38					
920	1.49	1.36	1.33		1.45	1.47		
930	1.43	1.32	1.29	1.35	1.40	1.42		
940	1.38	1.28	1.25	1.31	1.36	1.38		
950	1.33	1.24	1.22	1.27	1.32	1.34		
960	1.29	1.21	1.18	1.23	1.28	1.31		
970	1.24	1.18	1.15	1.20	1.24	1.27	1.36	
980	1.20	1.15	1.12	1.17	1.21	1.24	1.32	
990	1.17	1.12	1.09	1.13	1.18	1.20	1.28	
1000	1.13	1.09	1.06	1.10	1.14	1.17	1.24	
1010	1.10	1.06	1.03	1.08	1.11	1.14	1.21	
1020	1.07	1.04	1.01	1.05	1.09	1.12	1.18	
1030	1.05	1.01	0.99	1.02	1.06	1.09	1.14	
1040	1.02	0.99	0.97	1.00	1.03	1.06	1.11	
1050	1.01	0.97	0.95	0.97	1.01	1.04	1.09	
1060	0.99	0.95	0.93	0.95	0.98	1.01	1.06	
1070	0.98	0.93	0.92	0.93	0.96	0.99	1.03	
1080						0.97	1.01	
1090								1.04
1100								1.01
1110								0.99
1120								0.96
1130								0.94
1140								0.92
1150								0.89

TABLE 401. KCl-LiCl: Surface tension (dyn cm^{-1})

	Mol percent LiCl									
T	90	79	69	58	50	40	30	22	15	10
660				135.22						
680				133.57						
700				131.92						
720				130.28						
740				128.63						
760				126.98						
780			127.30	125.33	124.31					
800			125.74	123.69	122.70					
820			124.17	122.04	121.08					
840		123.88	122.61	120.39	119.46					
860		122.46	121.04	118.75	117.85					
880	123.96	121.04	119.47	117.10	116.23	115.09				
900	122.61	119.62		115.45	114.61	113.40				
920	121.26	118.20		113.81	113.00	111.71	110.97			
940	119.90	116.78			111.38	110.02	109.23			
960	118.56	115.36			109.77	108.33	107.49			
980	117.20	113.94			108.15	106.64	105.75	106.40		
1000	115.85	112.52			106.53	104.95	104.01	104.57		
1020	114.50	111.10			104.92	103.25	102.28	102.73	102.95	
1040	113.15						100.54	100.90	101.25	101.03
1060	111.80						98.80	99.07	99.56	99.37
1080									97.86	97.71
1100									96.16	96.04

無機塩	T_m / K
LiCl	883
KCl	1043

ρ / 10^3 kg m^{-3}

LiCl 1.884 - 4.328x10^{-4} T (910-1050 K)

KCl 2.136 - 5.832x10^{-4} T (910-1050 K)

LiCl(58.8)-KCl(41.2) 2.0286-5.2676x10^{-4} T (680-860 K)

金属データブック

化合物	T / K	η / mPa s
LiCl	900	1.40
	920	1.32
	940	1.25
	960	1.19
	980	1.13
	1000	1.08
	1020	1.03
	1040	0.989
	1060	0.949
	1080	0.912
	1100	0.877

化合物	T / K	η / mPa s
KCl	1110	0.938
	1120	0.908
	1130	0.887
	1140	0.866
	1150	0.847
	1160	0.828

[G.J. Janz, "NIST Standard Reference. Database 27", (1991)]

融解塩	イオン	D0/10-7 m2 s-1	Q/kJ mol-1	温度 T/ K
KCl	K+	1.80	28.79	1070～1260
	Cl-	1.80	29.83	1065～1260
LiCl	Li+	1.23	18.00	883～1033
	Cl-	0.71	18.43	883～1033

For the mixing rule, please refer to
B. Larson et al.
Mol. Phys. 1973, 26, 1521-1532