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	作成者: Hosoya, Masahiko, Nakamoto, Makoto, Kina,
	Chikako, Miyazato, Mikato
	メールアドレス:
	所属:
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Prediction of Crystal Structures Using a Piecewise Linear Interatomic Potential

Masahiko Hosoya*, Makoto Nakamoto **, Chikako Kina*** and Mikako Miyazato ****

Department of Physics and Earth Sciences, Faculty of Science, University of the Ryukyus Nishihara, Okinawa 903-0213, Japan

Abstract

As an interatomic potential of atoms, we propose a piecewise linear one which provides the best prediction of crystal structure. The potential composed of plain parameters has an enormous advantage of limiting the possible structures into a finite number of discrete ones. Its usefulness is shown by an example of twodimensional monoatomic crystals at an absolute-temperature of zero.

1. Introduction

It is one of the most important targets of condensed matter physics to relate the structure of a crystal to the microscopic feature of interatomic potentials of constituent atoms[1]. However such works are still a long way off. One obstacle may lie in the fact that only analytical functions have been chosen as interatomic potentials so far. Since most of well-known potentials such as Lennard-Jones's or Morse's one are too simple to draw various crystal structures of, they must be modified by some additional terms. The resultant potentials are obscured with many incomprehensible parameters. Then, if the sufficient use of a computer is taken into consideration, we should abandon the analytical nature of a potential and use the function which can be handled more easily. The simplest function that meets the above demand is a piecewise linear function. The purpose of this paper is to show how this function is useful.[2][3][4][5][6]

2. Potential

2.1 Piecewise Linear Interatomic Potentials Let us consider what type of crystal appears

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when cohesive or attractive energy of the atoms is given by a piecewise linear potential V(r). Its typical shape is shown in Fig. 1. It is linear except at the positions specified by r_i , so it may have a locally minimal or maximal value at r_i . Parameter r_0 is always the shortest distance between the atoms, while the other r_i are arbitrarily chosen. As a simple example in the 2-dimensional case, we choose them in Fig. 1 as $r_1=1.5r_0$, $r_2=2r_0$, $r_3=2.5r_0$. Each of the potential energy values at r_i is set to V_0, V_1, V_2 and V_3 . V(r) is assumed to have a positive infinite value for $r<r_0$, and zero for $r>r_3$. The latter assumption means $V_3=0$. For further simplicity, let us fix $V_0=-1$. Then we have the simplest V(r) which contains only two parameters V_1 and V_2 .



Fig. 1. A piecewise linear interatomic potential used in this work.

^{*} Retired in 2006. Present address: Syuri-Kinzyoutyou 3-40-2, Naha, Okinawa 903-0815, Japan. E-mail : cpfyq230@ybb.ne.jp.

^{**} Present address: Okinawa Prefectural Government, Izumizaki 1-2-2, Naha, Okinawa 900-0021, Japan

^{***} Present address: Urasoe Technical High School, Kyouzuka 1-1-1, Urasoe, Okinawa 901-2111, Japan.

^{****} Present address: OKINAWA FUJITSU SYSTEMS ENGINEERING LIMITED, Kumoji 1-12-12, Naha, Okinawa 900-0015, Japan.

The present work was presented in several academic meetings. Main reports were listed in References.

2.2 Remarkable Advantage of Piecewise Linear Potentials

Our work is to determine which configuration of atoms has the minimal energy under the potential given. Even if we assume the atoms make a crystal, possible structures are infinite.



Fig. 2. Invariant positions of the potential.

However a piecewise linear potential has a convenient feature that allows us to avoid this difficulty. When any two piecewise linear potentials are summed up, the positions of their inflection points are conserved as in Fig.2. If we add any two piecewise linear potentials, for example V_A and V_B , the minimal value of $V_{\scriptscriptstyle A}$ + $V_{\scriptscriptstyle B}\,$ appears at $x_{\scriptscriptstyle A}$ or $x_{\scriptscriptstyle B}\,$ which originally indicates the minimum value of V_A or V_{B} respectively. Therefore, we need not look for all domains of x to find the position of the minimal value of $V_A + V_B$. We only have to compare its values at x_A and x_B with each other. Similarly, when we select more than two potentials, for exampe V_A , V_{B} and V_{C} , ..., we can find the minimum value of their sum only by comparing a finite number of values with each other. This simplifies our work tremendously.

3. Two dimensional crystals

3.1 Cohesive energy of a crystal

Let us concentrate on the problem using the simplest case. The atoms are assumed to make a crystal lattice. We only are concerned with the twodimensional monoatomic crystals which have one atom per primitive cell. The energy of the entire crystal is the sum of two-body potentials.

In Fig.3 for example, the atom at the origin interacts on only the black atoms within the circle having the radius r_3 . If the number of such lattice



points is n, the energy per one atom is

$$V_{atom} = \frac{1}{n} \sum_{(i,j)} V(r(i,j)) ,$$

where r(i,j) means the distance from the origin to the lattice point (i,j) and summation is performed over n lattice points. Our purpose is to figure out a way where the structure to minimize V_{atom} .

3.2 Specification of two-dimensional crystals

A crystal for the present model is specified by two primitive translation vectors **a** and **b**. We can assume that **a** to lie on x-axis and its length is r_0 without losing generality. Therefore the crystal is described by the two components (x_2 , y_2) of **b** as in Fig. 4.



Fig. 4. Primitive translation vectors specifying the crystal.

3.3 Range of search

We do not need to scan the entire area spanned by (x_2, y_2) . Firstly, V(r) is a periodic function of x_2 with the period r_0 , for x_2+r_0 has the same lattice as indicated by x_2 . Secondly, V(r) is an even function with respect to x_2 , because the mirrored lattice should have the same energy. It accompanies

another mirror symmetry at $x_2=r_0/2$ which equalizes a value of V at $x_2=r_0/2-\Delta x$ to that at $x_2=r_0/2+\Delta x$, because the value at $x_2=r_0/2+\Delta x$ is the same to that at $x_2=-r_0/2-\Delta x$ by parity, and the latter is equivalent to that at $x_2=-r_0/2-\Delta x$ by periodicity. Then V has the shape as shown in Fig.5, which indicates that the area $0 \le x_2 \le r_0/2$ is sufficient.



Fig. 5. Symmetry of the potential.

Furthermore V (r) is invalid in the areas $x_2^2+y_2^2<r_0^2$ and $x_2^2+y_2^2>r_3^2$ by our assumption. Therefore only the dotted area in Fig.6 is sufficient enough to exhaust all the eligible lattices.



Fig. 6. Scanning area of (x_2, y_2) .

3.4 Possible lattices



Fig. 7. Possible lattice points affecting the energy of the crystal.

When we scan x_2 and y_2 in the above region, 20 lattice points contained in the dotted areas in Fig.7 can affect the total energy of the crystal, for they move in the interior of circle with the radius r_3 . Only half of them are sufficient for calculation by symmetry, which are numbered from 1 to 10. The following indices should be assigned to them.

 $\begin{array}{c} (1) (-2, 1), (2) (-1, 1), (3) (0, 1), (4) (1, 1), (5) (2, 1), \\ (6) (-2, 2), (7) (-1, 2), (8) (0, 2), (9) (1, 2), (10) (2, 2). \\ \end{array}$ The distance R (i, j) from the origin to lattice point (i, j) is given as follows.

$$\begin{split} & R(0,1) = SQR(x_2^2 + y_2^2) \\ & R(1,1) = SQR((x_2 + r_0)2 + y_2^2) \\ & R(-1,1) = SQR((x_2 - r_0)2 + y_2^2) \\ & R(0,2) = SQR((2x_2)^2 + (2y_2)^2) \\ & R(2,1) = SQR((x_2 + 2r_0)^2 + y_2^2) \\ & R(1,2) = SQR((2x_2 + r_0)^2 + (2y_2)^2) \\ & R(-1,2) = SQR((2x_2 - r_0)^2 + (2y_2)^2) \\ & R(-2,1) = SQR((2x_2 - 2r_0)^2 + (2y_2)^2) \\ & R(2,2) = SQR((2x_2 + 2r_0)^2 + (2y_2)^2) \\ & R(-2,2) = SQR((2x_2 - 2r_0)^2 + (2y_2)^2) \\ & R(-2,2) = SQR((2x_2 - 2r_0)^2 + (2y_2)^2) \end{split}$$

Here SQR means square root.

As has been stated in 2.2, a minimal value of the total energy is obtained at the position where any individual two-body potential has a minimum value. In other words, this means a minimal value occurs whenever a lattice point lies on a circle with the radius r_0 , r_1 , r_2 or r_3 . In addition, it also occurs where x_2 is 0 or $r_0/2$, as suggested in Fig. 5. Therefore the energy of the crystal can have a minimal value if it fulfills one of the following six kinds of conditions.

- (1) $R(I,J)=r_0$
- (2) $R(I,J)=r_1$
- (3) $R(I,J)=r_2$
- (4) $R(I,J)=r_3$
- (5) $x_2=0$
- (6) $x_2 = r_0/2$

Since the ten lattice points must be tested, the total number of conditions (1) to (4) is 40. Adding conditions (5) and (6), we can see 42 conditions in all. Let us use the following symbols to express these conditions simply.

 $C(I,J;k) : R(I,J)=r_k$ L0 : x₂=0

L1 :
$$x_2 = r_0/2$$

Here the initials C and L have been adopted from "circle" and "line" respectively.

Since we have two degrees of freedom x_2 and y_2 , the energy of the crystal can have a minimal value whenever any two of 42 conditions are fulfilled at the same time. In the dotted area of Fig.3, such intersections occur at the following 41 points where r_0 is taken to be 1. The result means that the number of possible phases is 41 at most. The merit stated in the last part of Section 2 works efficiently.

TABLE I. SPECIAL VECTORS FOR A CRYSTAL TO BE STABLE

Phase.: x2,y2; condition 1, condition 2 1:0,1;L0,C(0,1;0) 2: 0, 1.11803; L0,C(1,1;1) 3: 0, 1.14564; L0,C(1,2;3) 4: 0, 1.25; L0,C(0,2;3) 5: 0, 1.5; L0,C(2,1;3) 6: 0, 1.73205; L0,C(1,1;2) 7: 0, 2; L0,C(0,1;2) 8: 0, 2.29129; L0,C(1,1;3) 9: 0, 2.5; L0,C(0,1;3) 10: 0.5, 0.866025; L1,C(0,1;0) 11: 0.5, 1; L1,C(-1,2;2) 12: 0.5, 1.14564; L1,C(-2,2;3) 13: 0.5, 1.25; L1,C(-1,2;3) 14: 0.5, 1.32288; L1,C(1,1;2) 15: 0.5, 1.41421; L1,C(0,1;1) 16: 0.5, 1.93649; L1,C(0,1;2) 17: 0.5, 2; L1,C(1,1;3) 18: 0.5, 2.44949; L1,C(0,1;3) 19: 0.125, 0.992157; C(0,1;0),C(1,1;1) 20: 0.21875, 0.975781; C(0,1;0),C(-2,2;3) 21: 0.25, 0.968246; C(0,1;0),C(-1,2;2) 22: 0.3125, 0.949918; C(0,1;0),C(2,1;3) 23: 0.28125, 0.975781; C(-1,2;2),C(1,2;3) 24: 0.2625, 0.990502; C(-2,1;2),C(1,2;3) 25: 0.25, 1; C(1,2;3),C(-2,2;3) 26: 0.3, 0.979796; C(2,1;3),C(-1,2;2) 27: 0.28125, 1.02269; C(2,1;3),C(-2,1;2) 28: 0.020833, 1.13632; C(-1,1;1),C(1,2;3) 29: 0.0625, 1.17094; C(-1,1;1),C(-1,2;3) 30: 0.390625, 1.1874; C(0,2;3),C(-2,1;2) 31: 0.4375, 1.24844; C(-1,2;3),C(-2,1;2)

32: 0.1875, 1.21031; C(2,1;3),C(-1,2;3) 33: 0.25, 1.22474; C(0,2;3),C(-1,2;3) 34: 0.15625, 1.2402; C(-1,1;1),C(0,2;3) 35: 0.166667, 1.24722; C(-1,1;1),C(2,1;3) 36: 0.171875, 1.23813; C(2,1;3),C(0,2;3) 37: 0.4375, 1.39054; C(-1,1;1),C(1,1;2) 38: 0.375, 1.45237; C(0,1;1),C(1,1;2) 39: 0.125, 1.65359; C(1,1;2),C(-2,1;3) 40: 0.375, 1.89984; C(-1,1;2),C(-2,1;3) 41: 0.4375, 1.95156; C(0,1;2),C(-2,1;3)

3.5 Phase Diagram

Thereforewe can get the most probable lattice immediately by comparing the 41 phases with each other. The result in Fig.8 was obtained with the program shown in the Appendix. Only seven phases appeared, one of which (10) is hexagonal, three((3, 4 and 9) are rectangular, and the other three (29, 32 and 34) are oblique. As was expected, the closepacked structure 10 is most prominent.



Fig. 8. Phase diagram of the two-dimensional crystal.

4. Conclusion

A piecewise linear potential has proved its usefulness in the simple example of twodimensional monoatomic crystals. The advantage of conserving the inflection points exceeds the sacrifice of losing the analyzability of potential.

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Appendix

The phase diagram in Fig. 8 was produced by the following BASIC program. It was written for N88BASIC by NEC and F-BASIC by Fujitsu, but may be operated in any BASIC with slight modulation.

1000 'SAVE "PDPWL2D.BAS",A
1010 '
1020 'PHASE DIAGRAM CALCULATED ON A
PIECEWISE
1030 'LINEAR INTERATOMIC POTENTIAL
ENERGY
1040 '(ENGLISH VERSION OF
"SOUZU2DF.BAS")
1050 '
1060 PROGRAM\$="PDPWL2D.BAS"
1070 N88BASIC=0: FBASIC=1:LANGUAGE=0:
1080 FOR L=1 TO 0:LANGUAGE=
LANGUAGE+L:NEXT
1090 R0=1! : R1=1.5 : R2=2! :R3=2.5 : V0=-1
:V3=0
1100 DEF FNV(R,V1,V2)=-(R <r001)*10< td=""></r001)*10<>
+(R>=R001)*(R <r1)*((v1-v0) (r1-r0)*(r-<="" td=""></r1)*((v1-v0)>
R0)+V0)
+(R>=R1)*(R <r2)*((v2-v1) (r2-r1)*(r-<="" td=""></r2)*((v2-v1)>
R1)+V1)
+(R>=R2)*(R <r3)*((v3-v2) (r3-r2)*(r-<="" td=""></r3)*((v3-v2)>
R2)+V2)
1110 'R0 IS CHANGED INTO (R0-0.01) TO
COUNTER ROUNDOFF ERRORS
1120 DIM SP(200,6),PHASE(50)
1130 CLS
1140 SS=.01
1150 GOSUB *FILENAME
1160 '====STARTING COLOR
1170 C0=3
1180' READ DATA OF PHASES
1190 KT=0: READ HEADER\$
1200 KT=KT+1: READ SP\$
1210 IF SP\$="\$" THEN 1270
1220 FOR A=1 TO 3
1230 SP(KT,A)=VAL(LEFT\$(SP\$,INSTR(SP\$,";")-
1))
1240 SP\$=RIGHT\$(SP\$,LEN(SP\$)-
INSTR(SP\$,";"))
1250 NEXT
1260 GOTO 1200
1270 CLS
1280 PRINT "THIS FILE IS";OD\$;
1290 PRINT " PARENT PROGRAM
IS";PROGRAM\$

```
1300 PRINT "STARTING COLOR IS";C0
1310 IT=1 :PHASE(IT)=0
1320 IF LANGUAGE=N88BASIC THEN X0=300
  :Y0=110 ELSE X0=400 :Y0=220
1330 IF LANGUAGE=N88BASIC THEN XB=100
  :YB=-50 ELSE XB=200 :YB=-200
1340 IF LANGUAGE=N88BASIC THEN OPEN
  OD$ FOR OUTPUT AS #1 ELSE OPEN OD$
  FOR APPEND AS #1
1350 PRINT #1,"OUTLINE OF ";OBJECT$
1360 PRINT #1,"PARENT PROGRAM IS
  ";PROGRAM$;" ";
1370 IF LANGUAGE=N88BASIC THEN PRINT
  #1.
" N88BASIC" ELSE PRINT #1," F-BASIC"
1380 STARTTIME$=DATE$+" "+TIME$+"
  STARTED"
1390 PRINT #1,STARTTIME$
1400 '_____
                 =MAIN
1410 FOR V1=-1 TO 1 STEP SS : FOR V2=-1 TO
  1 STEP SS
1420 GOSUB *FINDMIN
1430 GOSUB *NEWPHASE
1440 VK=VK+C0
1450 IF LANGUAGE=N88BASIC THEN
 C=(VK MOD 8)+1 ELSE C=(VK MOD 16)+1
1460 PSET (V1*XB+X0,V2*YB+Y0),C
1470 NEXT : NEXT
1480 PRINT #1,"ENDED ON ";DATE$;" ";TIME$
1490 CLOSE
1500 INPUT "END ";A$
1510 PRINT "SYSTEM"
1520 END
1530 '_____
1540 *FINDMIN
1550 VMINT=100 : VK=1
1560 FOR K=1 TO KT
1570 X=SP(K,2):Y=SP(K,3)
1580 VMIN=V0
1590 P=SQR(X*X+Y*Y) : GOSUB *VSUM
1600 P=SQR((X+R0)^2+Y^2) : GOSUB *VSUM
1610 P=SQR((X-R0)^2+Y^2) : GOSUB *VSUM
1620 P=SQR((2*X)^2 +(2*Y)^2) : GOSUB
  *VSUM
1630 P=SQR((X+2*R0)^2 +Y^2) : GOSUB
```

```
*VSUM
1640 P=SQR((2*X+R0)^2 +(2*Y)^2) : GOSUB
  *VSUM
1650 P=SQR((2*X-R0)^2 +(2*Y)^2) : GOSUB
  *VSUM
1660 P=SQR((X-2*R0)^{2}+Y^{2}) : GOSUB
  *VSUM
1670 P=SQR((2*X+2*R0)^2+(2*Y)^2) : GOSUB
  *VSUM
1680 P=SQR((2*X-2*R0)^2+(2*Y)^2): GOSUB
  *VSUM
1690 IF VMIN<VMINT THEN VMINT=VMIN :
  VK=K
1700 NEXT
1710 RETURN
1720 '_____
1730 *NEWPHASE
1740 NP=1
1750 FOR I=1 TO IT
1760 IF VK=PHASE(I) THEN NP=0: I=IT
1770 NEXT
1780 IF NP=0 THEN 1820
1790 IT=IT+1: PHASE(IT)=VK
1800 PRINT "VK=";PHASE(IT)
1810 PRINT #1,VK;";";V1;";";V2;";";VMIN
1820 RETURN
1830 '_____
1840 *VSUM
1850 VMIN=VMIN + FNV(P,V1,V2)
1860 RETURN
1870 '====
1880 *FILENAME
1890 DT$=RIGHT$(DATE$,8)
1900 DY$=LEFT$(DT$,2)
1910 DM$=HEX$(VAL(MID$(DT$,4,2)))
1920 DD=VAL(RIGHT$(DT$,2)):IF DD<10
  THEN DD$=CHR$(DD+48) ELSE
  DD$=CHR$(DD+55)
1930 TM$=RIGHT$(TIME$,8)
1940 TT=VAL(LEFT$(TM$,2))*3600
 +VAL(MID$(TM$,4,2))*60
 +VAL(RIGHT$(TM$,2))
1950 TT=TT*12*4096/86400!
1960 TT$=RIGHT$("000"+HEX$(TT),4)
1970 OBJECT$=DY$+DM$+DD$+TT$
```

1980 OD\$=OBJECT\$+".DAT"

1990 RETURN 2000 '_____ 2010 DATA K; X ; Y ; 2020 DATA 1; 0 ; 1 ; 2030 DATA 2; 0 ; 1.11803; 2040 DATA 3; 0 ; 1.14564; 2050 DATA 4; 0 ; 1.25 ; 2060 DATA 5; 0 ; 1.5 ; 2070 DATA 6; 0 ; 1.73205; 2080 DATA 7; 0 ; 2 ; 2090 DATA 8; 0 ; 2.29129; 2100 DATA 9; 0 ; 2.5 ; 2110 DATA 10; .5 ; .866025; 2120 DATA 11; .5 ; 1 ; 2130 DATA 12; .5 ; 1.14564; 2140 DATA 13; .5 ; 1.25 ; 2150 DATA 14; .5 ; 1.32288; 2160 DATA 15; .5 ; 1.41421; 2170 DATA 16; .5 ; 1.93649; 2180 DATA 17; .5 ; 2 ; 2190 DATA 18; .5 ; 2.44949; 2200 DATA 19; .125; .992157; 2210 DATA 20; .21875; .975781; 2220 DATA 21; .25 ; .968246; 2230 DATA 22; .3125; .949918; 2240 DATA 23; .28125; .975781; 2250 DATA 24; .2625; .990502; 2260 DATA 25; .25; 1; 2270 DATA 26; .3 ; .979796; 2280 DATA 27; .28125; 1.02269; 2290 DATA 28; .020833; 1.13632; 2300 DATA 29; .0625; 1.17094; 2310 DATA 30; .390625; 1.1874; 2320 DATA 31; .4375; 1.24844; 2330 DATA 32; .1875; 1.21031; 2340 DATA 33; .25 ; 1.22474; 2350 DATA 34; .15625; 1.2402; 2360 DATA 35; .166667; 1.24722; 2370 DATA 36; .171875; 1.23813; 2380 DATA 37; .4375; 1.39054; 2390 DATA 38; .375; 1.45237; 2400 DATA 39; .125 ; 1.65359; 2410 DATA 40; .375; 1.89984; 2420 DATA 41; .4375; 1.95156;

2430 DATA \$