

Application of Kihara parameters in conventional molecular force fields

Teik-Cheng Lim

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Abstract While the Lennard-Jones function has been widely adopted in molecular mechanics for describing neutral non-bonded interatomic interactions, the Kihara potential possesses the flexibility of describing intermolecular energy. Due to the pervasiveness of the former and the flexibility of the latter, a set of conversion formulas is described herein for enabling molecular mechanics software to describe intermolecular energy via slight alteration to the Lennard-Jones function. In this paper it is shown that the combined imposition of equal force constant and equal equilibrium-to-dissociation energy integral enables a pair of Lennard-Jones indices to be obtained. Plotted results exhibit impeccable agreement. Such relations allow quick adoption of Kihara parameters of molecules to be applied in conventional molecular mechanics software by imal re-coding of the latter—thereby saving time and cost.

Keywords Kihara · Lennard-Jones · Parameters

1 Introduction

Although the development of potential energy functions for gases has enabled good approximation to the intermolecular potential energy through the use of additional parameters and extended terms, most computational chemistry software adopt molecular force fields that employs simple potentials for non-bonded neutral interactions such as the conventional Lennard-Jones (12 – 6) function [1–9]. The use of simpler potential energy functions enable large-scale dynamical systems modeling to be performed within shorter timeframe and lower cost. On the other hand, potential functions

T.-C. Lim (✉)
School of Science and Technology, SIM University, 535A Clementi Road, Clementi 599490,
Republic of Singapore
e-mail: alan_tc_lim@yahoo.com

with higher complexities possess additional parameters that allow better curve-fitting to spectroscopic and/or ab initio data—hence superior accuracy. In the light of these competing factors, it is proposed that existing molecular force fields in computational chemistry software be amended to enable the simpler potential functions to approximate those that are functionally more flexible. In this way, a certain extent of accuracy can be improved without imposing excessive hardcoding to the algorithm. In this paper, we select the Kihara potential [10, 11] for conversion into Lennard-Jones form due to their functional similarities. The Kihara potential is of interest due to its applications gas hydrate [12–14], solid nitrogen [15] and even non-spherical fluids [16]. Recently, noble gases in Saturn’s largest Moon, Titan, were investigated [17] and parameterized [18, 19] for the Kihara potential. In view of the high applicability of the Kihara potential and the pervasive use of Lennard-Jones (12 – 6) potential in molecular force fields, this paper develops a class of Lennard-Jones function that can satisfactorily approximate the Kihara potential energy.

2 Analysis

The Kihara potential is written as

$$U_K = \begin{cases} \frac{M}{M-N} \left(\frac{M}{N}\right)^{\frac{N}{M-N}} D \left[\left(\frac{\sigma-2a}{r-2a}\right)^M - \left(\frac{\sigma-2a}{r-2a}\right)^N \right]; & r > 2a \\ \infty; & r \leq 2a \end{cases} \quad (1)$$

where D is the dissociation energy, σ is the collision diameter, a is the core radius, and r is the distance between the central cores. The non-dimensional parameters M and N are obtainable from curve-fitting. It is easily seen that when $M = 2N = 12$ and $a = 0$, Eq. (1) reduces to the conventional Lennard-Jones (12 – 6) function

$$U_{LJ(12-6)} = 4D \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (2a)$$

or

$$U_{LJ(12-6)} = D \left[\left(\frac{R}{r}\right)^{12} - 2 \left(\frac{R}{r}\right)^6 \right] \quad (2b)$$

where R is the equilibrium intermolecular distance. It is readily seen that the Kihara potential shown in Eq. (1) is in the same form with the conventional Lennard-Jones form in Eq. (2a). To obtain a modified Lennard-Jones function that approximates the Kihara potential, the latter is re-written in the same form as Eq. (2b). To do so, we impose

$$\left(\frac{\partial U_K}{\partial r}\right)_{r=R} = 0 \quad (3)$$

and

$$(U_K)_{r=R} = -D \tag{4}$$

to give

$$M \left(\frac{\sigma - 2a}{R - 2a} \right)^M = N \left(\frac{\sigma - 2a}{R - 2a} \right)^N \tag{5}$$

and

$$\frac{\sigma - 2a}{R - 2a} = \left(\frac{N}{M} \right)^{\frac{1}{M-N}} \tag{6}$$

respectively, thereby leading to

$$\frac{U_K}{D} = \frac{N}{M - N} \left(\frac{R - 2a}{r - 2a} \right)^M - \frac{M}{M - N} \left(\frac{R - 2a}{r - 2a} \right)^N, \tag{7}$$

which is similar in form to that of Eq. (2b). The equilibrium interatomic distance may then be inferred from Eq. (5) to give

$$R = 2a + (\sigma - 2a) \left(\frac{M}{N} \right)^{\frac{1}{M-N}}. \tag{8}$$

The modified Lennard-Jones can be written in a general form

$$U_{LJ} = D \left[\frac{n}{m - n} \left(\frac{R}{r} \right)^m - \frac{m}{m - n} \left(\frac{R}{r} \right)^n \right] \tag{9}$$

whereby substitution of $m = 2n = 12$ simplifies it into Eq. (2b). Imposing equal force constant on both potentials, as defined by

$$\left(\frac{\partial^2 U_K}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_{LJ}}{\partial r^2} \right)_{r=R}, \tag{10}$$

we obtain

$$MN \left(1 - 2 \frac{a}{R} \right)^{-2} = mn \tag{11}$$

while imposition of equal stretching energy integral from equilibrium to dissociation

$$\int_R^\infty U_K dr = \int_R^\infty U_{LJ} dr \tag{12}$$

leads to

$$\left(1 - 2\frac{a}{R}\right) \frac{1 - M - N}{(M - 1)(N - 1)} = \frac{1 - m - n}{(m - 1)(n - 1)}. \quad (13)$$

The parameters of the modified Lennard-Jones function can thereby be extracted from Eqs. (11) and (13) to give

$$\begin{Bmatrix} m \\ n \end{Bmatrix} = \frac{1}{2} \begin{bmatrix} +1 & +1 \\ +1 & -1 \end{bmatrix} \left\{ \sqrt{\left[1 - \frac{IC}{1-I}\right]^2 - 4C} \right\} \quad (14)$$

where

$$C = MN \left(1 - 2\frac{a}{R}\right)^{-2} \quad (15)$$

and

$$I = \left(1 - 2\frac{a}{R}\right) \frac{1 - M - N}{(M - 1)(N - 1)}. \quad (16)$$

3 Results and discussion

To verify the validity of the modified Lennard-Jones functions for describing the Kihara potential energy, a recent set of Kihara parameters [20] is used. Table 1 shows the parameters of *n*-propanol according to the Kihara potential by Chapoy et al. [20] and the modified Lennard-Jones potential based on the present set of parameter conversion.

Figures 1 and 2 show the potential energy curves of the sII and sH structures of *n*-propanol, respectively, in comparison with the conventional and modified Lennard-Jones functions, respectively.

Table 1 The modified Lennard-Jones parameters from the Kihara parameters of *n*-propanol [20]

Structure	sII	sH
<i>D</i> (K)	248.61	336.86
σ (Å)	5.4058	5.6488
<i>a</i> (Å)	1.2664	1.2664
<i>R</i> (Å)	5.757633	6.030392
<i>C</i>	229.5123	214.0353
<i>I</i>	-0.17312	-0.17927
<i>m</i>	26.06413	24.96331
<i>n</i>	8.805677	8.573994
<i>a/R</i>	0.219951	0.210003

Fig. 1 Conventional and modified Lennard-Jones function in comparison to the Kihara potential energy for *n*-propanol (s-II structure)

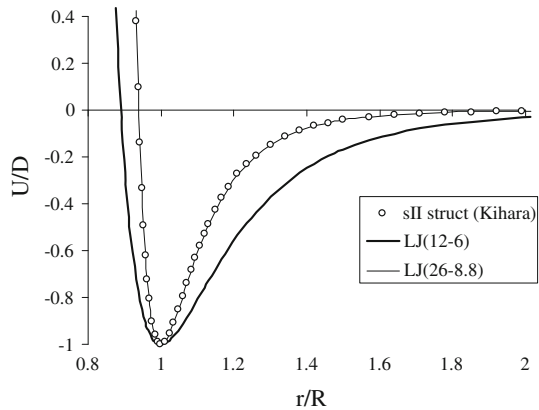
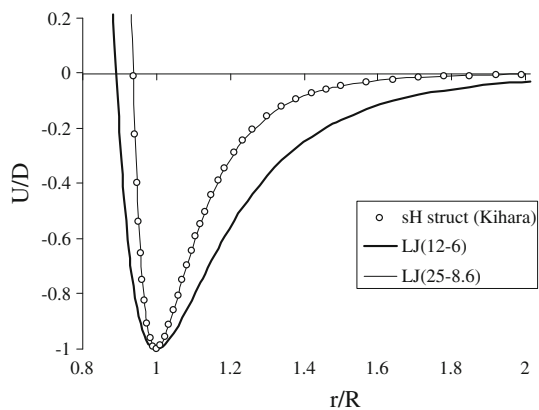


Fig. 2 Conventional and modified Lennard-Jones function in comparison to the Kihara potential energy for *n*-propanol (s-H structure)



It is evident that the conventional Lennard-Jones (with $m = 12$ and $n = 6$) gives very large underestimation of the *n*-propanol interaction energy, as expected. However, the modified Lennard-Jones function gives a very satisfactory agreement with the Kihara potential energy.

Modification to the Lennard-Jones function enables the potential energy functions between two molecules to be conveniently computed. For two molecules with x number of atoms each, the total number of Lennard-Jones terms required would be x^2 . As such for the case of *n*-propanol, a total of 144 Lennard-Jones terms are required to give the potential energy between two of these molecules. Where a partial Unified Atom Model (UAM) is applied on groups of atoms based on proximity, the number of Lennard-Jones terms is reduced. In the case of *n*-propanol, if the CH_3 , CH_2 and OH groups are each lumped into a unified atom, there are 16 Lennard-Jones terms to grapple with. For a fully UAM approach where the entire molecule is lumped as an entity, only one Lennard-Jones function would be required, although the parameters would need to be modified. In this paper it has been shown that the modified Lennard-Jones function agrees well with the Kihara potential when $m = 25.5 \pm 0.5$ and $n = 8.7 \pm 0.1$ for *n*-propanol.

Why does the parameter conversion give such good agreement? In early approach [21–23], the imposition of equal force constant, i.e. Eq. (10), alone enables good agreement near the minimum well depth $r \cong R$ and for intermolecular compression $r < R$. However, discrepancies appear for $1.2R < r < 2.4R$. The compared potentials appear to agree for $r > 2.4R$, but this observation is due to the independently converging functions. In later approach the imposition of equal force constant was replaced with equal stretching energy integral [24–26], as described in Eq. (12). In that approach, the accuracy of the converted parameters appear to be slightly compromised near the minimum well depth but good agreement was observed for $R < r < \infty$. However, it was observed that the accuracy is severely unreliable for intermolecular compression. The imposition of both approaches, as shown in this paper, ensures that the potential energy accuracy is maintained when converting the Kihara parameters into those of the modified Lennard-Jones potential.

4 Conclusions

It has been shown that equating the force constants and energy integrals of the Kihara and the general Lennard-Jones functions enable parameters of the latter to be extracted to give good agreement to the former. In this way, the conventional Lennard-Jones functions in molecular force fields can be easily modified to accurately describe intermolecular potential energy on the principle of UAM. As such, very quick computation can be performed on the intermolecular energy of molecules with minimal amendment to the existing computational chemistry packages that adopt the Lennard-Jones function.

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