Journal of Mathematical Chemistry Vol. 33, Nos. 3–4, May 2003 (© 2003)

Scaling function between the Exponential-6 and the generalized Lennard-Jones potential functions

Teik-Cheng Lim

Dean's Office, Faculty of Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Republic of Singapore

Received 17 January 2003

The van der Waals forces for non-bonded interaction can be expressed either by the Exponential-6 or by the Lennard-Jones(m-n) potential functions, whereby $m > n$. Hitherto a relationship exists between the Exponential-6 and the Lennard-Jones(12-6) potential functions, with a scaling factor $\xi = 13.772$ at or near the equilibrium and $\xi = 12.0$ for long range interaction. This paper attempts to develop relationships between Exponential-6 and a more generalized Lennard-Jones(m-n). Analysis reveals that the relationship exists only when $n = 6$ and that two sets of scaling factors (as functions of index m) applies for the relationship between Exponential-6 and the Lennard-Jones(m-6), whereby $m > 6$.

KEY WORDS: Exponential-6, force field, Lennard-Jones, molecular mechanics, non-bonded, potential function, van der Waals

AMS subject classification: 70C20, 70F05, 74B15, 74E40, 74G99

1. Introduction

In simulating molecular motion, two broad categories of interatomic interactions are considered: (i) bonded interactions and (ii) non-bonded interactions. Whilst bonded interactions involved interaction between neighboring atoms connected by strong covalent bonds (including stretching, bending and twisting), non-bonded interactions are associated with both intramolecular and intermolecular forces. These non-bonded interactions can be further classified under Coulombic interaction (due to charges), and van der Waals interaction. The van der Waals interaction energy can be expressed in the Exponential-6 form

$$U_{\mathrm{X6}} = A\exp(-Br) - \frac{C}{r^6}, \tag{1}$$

where A, B and C are the Exponential-6 parameters, whilst r is the distance between non-bonded atoms. The basis of the Exponential-6 form may well be seen from the repulsive force [1]

$$U_{\mathrm{rep}} = A\exp\left(-\frac{r}{\rho}\right), \tag{2}$$

0259-9791/03/0500-0279/0

where A and ρ are parameters describing the repulsive force; and the attractive force [1]

$$U_{\text{atr}} = \frac{-1}{\pi \varepsilon_0 r^6}\left[\frac{p^4}{6kT} + \frac{p^2\alpha}{2} + \frac{3}{16}\alpha^2 E_a\right], \tag{3}$$

where $\varepsilon_0 =$ vacuum permittivity, $k =$ Boltzmann's constant, $T =$ absolute temperature, $p =$ dipole moments, $\alpha =$ polarizability, and $E_a =$ characteristic of particles in their interaction as a function of the synchronous frequency of the electron shells for both particles. The Exponential-6 potential is widely used, as can be inferred from its adoption by various computational chemistry softwares such as EAS [2], MM2 [3], MM3 [4], DREIDING [5], EFF [6], MOMEC [7] and MM4 [8].

Alternative to the Exponential-6 is the Lennard-Jones potential functions. The most common of these are the Lennard-Jones(12-6) potential

$$U_{\text{LJ(12-6)}} = D\left[\left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^{6}\right], \tag{4}$$

where D is the well-depth of the minimum, which occurs at the van der Waals distance $r = R$. The Lennard-Jones function is widely adopted because it is simpler (two parameters instead of three) and faster to compute (elimination of an exponentiation). The Lennard-Jones(12-6) function has been employed in the following computational chemistry softwares: CVFF [9], CHARMM [10], GROMOS [11], TRIPOS [12], DREIDING [5], SHAPES [13], UFF [14], ECEPP [15], AMBER [16] and OPLS [17]. Other forms of the Lennard-Jones potential include the Lennard-Jones(9-6) function

$$U_{\text{LJ(9-6)}} = D\left[2\left(\frac{R}{r}\right)^{9} - 3\left(\frac{R}{r}\right)^{6}\right] \tag{5}$$

as adopted by CFF [18], QMFF [19] and ESFF [20]; the hydrogen-bonding

$$U_{\text{LJ(12-10)}} = D\left[5\left(\frac{R}{r}\right)^{12} - 6\left(\frac{R}{r}\right)^{10}\right] \tag{6}$$

adopted by ECEPP [15] and AMBER [16]; and the "Buffered(14-7)" potential

$$U_{\text{Buff(14-7)}} = D\left(\frac{1.07R}{r + 0.07R}\right)^7\left[\frac{1.12R^7}{r^7 + 0.12R^7} - 2\right] \tag{7a}$$

developed by Halgren [21] and adopted by the MMFF software [22] for rare gas interaction.

To reduce the Buffered(14-7) potential function to the Lennard-Jones function, we rewrite equation (7a) as

$$U_{\text{Buff(14-7)}} = D\left(\frac{R + 0.07R}{r + 0.07R}\right)^7\left[\frac{R^7 + 0.012R^7}{r^7 + 0.12R^7} - 2\right]. \tag{7b}$$

Neglecting the buffered terms ($0.07R$ and $0.12R^7$), equation (7b) reduces to

$$U_{\text{LJ(14-7)}} = D\left[\left(\frac{R}{r}\right)^{14} - 2\left(\frac{R}{r}\right)^{7}\right]. \tag{8}$$

In order to apply Exponential-6 parameters into computational softwares that adopt Lennard-Jones function or vice versa, there exists a need to relate these two van der Waals functions. Presently the relationship that exists is that between Exponential-6 and Lennard-Jones(12-6) function, which is written in a loose form of the Exponential-6:

$$U_{\text{X6}} = D\left[\left(\frac{6}{\xi - 6}\right)\exp\left(\xi\left(1 - \frac{r}{R}\right)\right) - \left(\frac{\xi}{\xi - 6}\right)\left(\frac{R}{r}\right)^{6}\right], \tag{9}$$

whereupon substitution of the scaling factor $\xi = 13.772$ gives equal result to the Lennard-Jones(12-6) near equilibrium, and substituting $\xi = 12.0$ leads to the Lennard-Jones(12-6) function at long range. However, no relationship between other Lennard-Jones forms, such as (9-6), (12-10) and (14-7), was made with the Exponential-6 form. To do so, we write down the generalized Lennard-Jones potential function,

$$U_{\text{LJ}} = D\left[E\left(\frac{R}{r}\right)^{m} - F\left(\frac{R}{r}\right)^{n}\right], \tag{10}$$

where the indices m and n are positive integers such that $m > n$. The following analysis relates the generalized Lennard-Jones function with the Exponential-6 function, in such a manner that the generalized relationship can be reduced to other Lennard-Jones function, including that of (12-6). Both the applicability and limitation of the generalized relationship is herein discussed.

2. Analysis

In order to compare the Exponential function and the generalized Lennard-Jones(m-n) potential functions, we note that both curves should have equal well depth at the van der Waals distance,

$$(U_{\text{X6}})_{r=R} = (U_{\text{LJ}})_{r=R}. \tag{11}$$

To relate both potential functions at near the equilibrium, the slopes and curvatures are equated:

$$\left(\frac{\partial U_{\text{X6}}}{\partial r}\right)_{r=R} = \left(\frac{\partial U_{\text{LJ}}}{\partial r}\right)_{r=R} \tag{12}$$

and

$$\left(\frac{\partial^2 U_{\text{X6}}}{\partial r^2}\right)_{r=R} = \left(\frac{\partial^2 U_{\text{LJ}}}{\partial r^2}\right)_{r=R}. \tag{13}$$

Hence substituting equations (1) and (10) into equations (11)–(13) gives

$$A\exp(-BR) - \left(\frac{C}{R^6}\right) = D(E-F), \tag{14}$$

$$(BR)A\exp(-BR) - 6\left(\frac{C}{R^6}\right) = D(mE-nF) \tag{15}$$

and

$$(BR)^2 A\exp(-BR) - 42\left(\frac{C}{R^6}\right) = D\big[m(m+1)E - n(n+1)F\big], \tag{16}$$

respectively. At the van der Waals distance, both potential functions should be equal to the well-depth, D:

$$(U_{\mathrm{vdW}})_{r=R} = -D. \tag{17}$$

By definition, the slopes of both van der Waals potential functions are zero at $r = R$, i.e.,

$$\left(\frac{\partial U_{\mathrm{vdW}}}{\partial r}\right)_{r=R} = 0. \tag{18}$$

Comparing equations (17) and (18) with equations (14) and (15), respectively, we have

$$E - F = -1 \tag{19}$$

and

$$mE - nF = 0. \tag{20}$$

Solving equations (19) and (20) simultaneously, the generalized Lennard-Jones' coefficients (E and F) can be expressed in terms of its indices (m and n) as

$$\begin{Bmatrix} E \\ F \end{Bmatrix} = \frac{1}{m-n}\begin{Bmatrix} n \\ m \end{Bmatrix}. \tag{21}$$

Equation (21) must be fulfilled if the bottom of the well-depth occurs at $r = R$. Applying equation (21), equations (14)–(16) simplify to

$$A\exp(-BR) - \left(\frac{C}{R^6}\right) = -D, \tag{22}$$

$$\left(\frac{C}{R^6}\right) = \frac{BR}{6}A\exp(-BR) \tag{23}$$

and

$$(BR)^2 A\exp(-BR) - 42\left(\frac{C}{R^6}\right) = mnD, \tag{24}$$

respectively. Equation (24) implies that a similar van der Waals interaction, expressed in different forms of Lennard-Jones functions, will give equal curvature near the equilibrium point as long as (i) the coefficients (E and F) are expressed in terms of the indices (m and n) as described in equation (21), and that (b) the product of the LJ indices, mn, are equal. Now, substituting equation (23) into equations (22) and (24) leads to

$$\left(\frac{BR-6}{6}\right)A\exp(-BR) = D \tag{25}$$

and

$$BR(BR-7)A\exp(-BR) = mnD. \tag{26}$$

By eliminating the exponential term $A\exp(-BR)$, the term BR can be solved from equations (25) and (26) to give

$$12\xi = (42+\psi) \pm \sqrt{1764 - 60\psi + \psi^2}, \tag{27}$$

where $\xi = BR$ is the scaling factor, and $\psi = mn$ is the product of the generalized Lennard-Jones indices. To incorporate the scaling factor into one of the van der Waals potential function, we rewrite equation (1) as

$$U_{\mathrm{X6}} = A\exp\left[-\frac{\xi r}{R}\right] - \frac{C}{R^6}\left(\frac{R}{r}\right)^6 \tag{28}$$

and equation (25) as

$$A = D\left(\frac{6}{\xi-6}\right)\exp(\xi). \tag{29}$$

Substituting equation (29) into (23), we have

$$\frac{C}{R^6} = D\left(\frac{\xi}{\xi-6}\right). \tag{30}$$

Therefore, substituting equations (29) and (30) into (28) leads back to equation (9). As such, the relationship between the Exponential-6 and the generalized Lennard-Jones(m-n) is defined by the scaling factor ξ.

3. Discussion

Perusal to the second term of equation (28) reveals that the only Lennard-Jones(m-n) functions which can be related to the Exponential-6 form are those where $n = 6$. As such, the van der Waals potential function given in equation (9) applies in relating the Lennard-Jones(m-6) forms,

$$U_{\mathrm{LJ}(m\text{-}6)} = D\left[\left(\frac{6}{m-6}\right)\left(\frac{R}{r}\right)^m - \left(\frac{m}{m-6}\right)\left(\frac{R}{r}\right)^6\right], \tag{31}$$

with the Exponential-6 form given in equation (1), whereby the scaling factor is simplified to

$$\xi = \frac{1}{2}(m+7) \pm \sqrt{m^2 - 10m + 49}, \tag{32}$$

where m is an integer greater than 6. Mathematically, two solutions exist for equation (32), and that both sets of solutions increase with m. To select the actual solution for the scaling factor, we note that, for any integer m, the lower solution is less than 6 while the upper solution is greater than 6. With reference to equations (29) and (30), for a given positive value of well-depth D, both the Exponential-6 parameters (A and D) will only be positive if and only if $\xi > 6$. Therefore the upper value,

$$\xi = \frac{1}{2}(m+7) + \frac{1}{2}\sqrt{m^2 - 10m + 49} \tag{33}$$

is selected as the actual solution to the scaling factor in relating the Exponential-6 and the Lennard-Jones(m-6) potential functions. Substituting $m = 12$ and $m = 9$ into equation (33) gives the short range scaling factor for relating the Exponential-6 potential with LJ(12-6) and LJ(9-6) as $\xi = 13.722$ and $\xi = 11.162$, respectively. Substituting $\xi = m$ into the Exponential-6 form of equation (9), we recover the Lennard-Jones(m-6) form. Hence substituting $\xi = 12$ and $\xi = 9$ into equation (9) leads to equations (4) and (5), respectively, for long range.

4. Conclusions and recommendation

A relationship between the parameters of the Exponential-6 function and a generalized Lennard-Jones(m-n) function has been attempted, and shown to be achievable only when $n = 6$. The previously known relationship given in equation (9), for relating Exponential-6 with Lennard-Jones(12-6), remains applicable for relating Exponential-6 with Lennard-Jones(m-6) whereby $m > 6$. However, it can be seen that the scaling factor (ξ) is a function of the index m, and that the previously known $\xi = 13.772$ (short range) for Lennard-Jones(12-6) is a subset that can be obtained from the generalized function given in equation (33). Furthermore, the previously known $\xi = 12.0$ (long range) is a subset of the relation $\xi = m$. In view of the more generalized scaling factor, being a function of index m, we hereby term the generalized scaling factor described in equation (33) as the scaling function.

A set of relationships between both the van der Waals potential functions are useful as this allows a fitted Exponential-6 curve to be directly converted into the Lennard-Jones function, and vice versa. Moreover, available parametric data from Exponential-6 function can be quickly converted into Lennard-Jones(m-6) parameters, and vice versa, for immediate computational application.

The present parametric connection for van der Waals potential functions would complement recent parametric relations amongst force fields for bond-torsion [23], bond-bending [24] and bond-stretching [25], and therefore may pave a way for a software that is capable for relating and converting computational chemistry softwares that adopt different combinations of molecular potential functions.

In order to obtain an exponential form of the Lennard-Jones(m-n) whereby n can be any integer not necessarily confined to $n = 6$, it is hereby suggested that the exponential form can be expressed as an Exponential-n function

$$U_{\mathrm{X}n} = A\exp(-Br) - \frac{C}{r^n}. \tag{34}$$

The more generalized form given in equation (34), as compared to equation (1), would free up the constraint in extracting the exponential form from the Lennard-Jones functions pertaining to the hydrogen bonding ($n = 10$), rare gas interaction ($n = 7$), or any other Lennard-Jones forms whereby n is not necessarily equals to 6.

References

[1] L. Sodomka, *Structure and Properties of Solids* (Iliffe Books, London, 1967).
[2] E.M. Engler, J.D. Andose and P.v.R. Schleyer, J. Am. Chem. Soc. 95 (1973) 8005.
[3] N.L. Allinger, J. Am. Chem. Soc. 99 (1977) 8127.
[4] N.L. Allinger, Y.H. Yuh and J.H. Lii, J. Am. Chem. Soc. 111 (1989) 8551.
[5] S.L. Mayo, B.D. Olafson and W.A. Goddard III, J. Phys. Chem. 94 (1990) 8897.
[6] J.L.M. Dillen, J. Comput. Chem. 16 (1995) 595.
[7] P. Comba and T.W. Hambley, *Molecular Modeling of Inorganic Compounds* (VCH, Veinheim/New York, 1995).
[8] N.L. Allinger, K. Chen and J.H. Lii, J. Comput. Chem. 17 (1996) 642.
[9] S. Lifson, A.T. Haggler and P. Dauber, J. Am. Chem. Soc. 101 (1979) 5111.
[10] R. Brooks, R.E. Bruccoleri, B.D. Olafson, D.J. States, S. Swaminathan and M. Karplus, J. Comput. Chem. 4 (1983) 187.
[11] W.F. van Gunsterenm and H.J.C. Berendsen, Groningen Molecular Simulation (GROMOS) library manual (1987).
[12] M. Clark, R.D. Cramer III and N. van Opdenbosch, J. Comput. Chem. 10 (1989) 982.
[13] V.S. Allured, C.M. Kelly and C.R. Landis, J. Am. Chem. Soc. 113 (1991) 1.
[14] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard III and W.M. Skiff, J. Am. Chem. Soc. 114 (1992) 10024.
[15] G. Nemethy, K.D. Gibsen, K.A. Palmer, C.N. Yoon, G. Paterlini, A. Zagari, S. Rumsey and H.A. Sheraga, J. Phys. Chem. 96 (1992) 6472.
[16] W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz, Jr., D.M. Ferguson, D.C. Spellmeyer, T. Fox, J.W. Caldwell and P.A. Kollman, J. Am. Chem. Soc. 117 (1995) 5179.
[17] W. Damm, A. Frontera, J. Tirado-Rives and W.L. Jorgensen, J. Comput. Chem. 18 (1997) 1955.
[18] M.J. Hwang, T.P. Stockfisch and A.T. Hagler, J. Am. Chem. Soc. 116 (1994) 2515.
[19] J.R. Maple, M.J. Hwang, T.P. Stockfisch, U. Dinur, M. Waldman, C.S. Ewig and A.T. Haggler, J. Comput. Chem. 15 (1994) 162.
[20] S. Barlow, A.L. Rohl, S. Shi, C.M. Freeman and D. O'Hare, J. Am. Chem. Soc. 118 (1996) 7579.
[21] T.A. Halgren, J. Am. Chem. Soc. 114 (1992) 7827.
[22] T.A. Halgren, J. Comput. Chem. 17 (1996) 490.
[23] T.C. Lim, J. Math. Chem. 31 (2002) 421.
[24] T.C. Lim, J. Math. Chem. 32 (2002) 249.
[25] T.C. Lim, J. Math. Chem. 33 (2003) 29.