

Significance of an infinite nested radical number and its application in van der Waals potential functions

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Abstract

This paper demonstrates the relations between a new mathematical constant and its relevance to the molecular potential energy function commonly adopted in computational chemistry softwares. This mathematical constant, 1.7767750401 (correct up to 12 decimal places), which fulfills the following infinite nested radical equation

$$n = \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \dots}}}} = \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \dots}}},$$

is shown to be applicable as the indices of a generalized Lennard-Jones potential energy function. This new potential function demonstrates very good agreement with the various versions of specific Lennard-Jones potential energy functions and the Buckingham potential function converted from the Lennard-Jones(12-6) function when the indices are positive integer multiples of the mathematical constant or when the indices are raised to the first four positive integer powers.

1. Introduction

Well-known mathematical constants such as π (3.141593...) and the golden ratio ϕ (1.618034...) were recently incorporated into a Lennard-Jones-type potential function to give [1]

$$U = D \left[\frac{\phi}{\pi - \phi} \left(\frac{R}{r} \right)^{m\pi} - \frac{\pi}{\pi - \phi} \left(\frac{R}{r} \right)^{m\phi} \right], \quad (1)$$

where D and r are the well-depth magnitude and the interatomic distance respectively, with $U = -D$ when $r = R$. The adjustable parameter m can be obtained as

$$m = R \sqrt{\frac{1}{\pi\phi D} \left(\frac{\partial^2 U}{\partial r^2} \right)_{r=R}} \tag{2}$$

from a set of potential energy experimental data whereby

$$\frac{\partial^2 U_i}{\partial r^2} = \frac{U_{i-1} - 2U_i + U_{i+1}}{0.25(r_{i+1} - r_{i-1})^2} \tag{3}$$

Based on the experimental data for Argon [2] and Eqs.(1) and (2), the adjustable parameter was obtained as $m = 4$. This value enables a good agreement between Eq.(1) and the experimental results over long range. This equation also gives good agreement with the Murrell-Sorbie potential function [3]

$$U = -D \left(1 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3 \right) e^{-a_1 \rho} \tag{4}$$

plot, based on the parameters given by Huxley and Murrell [4] for the covalent bond in the Al-Al diatomic molecule, within the range $0.9R < r < 1.3R$ by using the relation

$$m = R \sqrt{\frac{a_1^2 - 2a_2}{\pi\phi}} \tag{5}$$

In this paper a Lennard-Jones-type potential function incorporated with a new mathematical constant is tested by comparing it with commonly used van der Waals potential functions in computational softwares.

2. Analysis

A generalized infinite nested radical appears in the form

$$\chi = \sqrt[2]{x_1 + y_1 \times \sqrt[3]{x_2 + y_2 \times \sqrt[4]{x_3 + y_3 \times \sqrt[5]{x_4 + y_4 \times \dots}}} \tag{6}$$

An example of nested radical infinite product is shown below for describing pi [5-7]

$$\frac{1}{\pi} = \frac{1}{2} \left(\sqrt{\frac{1}{2}} \right) \left(\sqrt{\frac{1}{2} + \frac{1}{2} \sqrt{\frac{1}{2}}} \right) \left(\sqrt{\frac{1}{2} + \frac{1}{2} \sqrt{\frac{1}{2} + \frac{1}{2} \sqrt{\frac{1}{2}}}} \right) \dots \tag{7}$$

whereby $x_i = y_i = (1/2)$ and $z_i = 2$ for $i = 1, 2, 3, \dots$. The infinite nested radical of the form

$$f(n) = \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \dots}}} \tag{8}$$

whereby $x_i = y_i = 1$ and $z_i = n$ for $i = 1, 2, 3, \dots$ describes the golden ratio [8] and the plastic constant [9,10] when $n = 2$ and $n = 3$ respectively.

A new constant n is defined herein as the number that fulfills the equation

$$n = \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \dots}}}} = \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \dots}}} . \quad (9)$$

This equation can be obtained by writing

$$n = \sqrt[n]{n + (n^{n-1} - 1) \times n} . \quad (10)$$

By successive recursion, Eq.(10) becomes

$$n = \sqrt[n]{n + (n^{n-1} - 1) \times \sqrt[n]{n + (n^{n-1} - 1) \times \sqrt[n]{n + (n^{n-1} - 1) \times \sqrt[n]{n + \dots}}} . \quad (11)$$

Let

$$n^{n-1} - 1 = \frac{1}{n} \quad (12)$$

then Eq.(11) becomes

$$n = \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \sqrt[n]{n + \frac{1}{n} \times \dots}}} , \quad (13)$$

which is reflected on the right hand side of Eq.(9). It is of interest to note that interchanging the operations $+$ and \times in Eq.(13) while retaining the rest of the equation gives

$$n = \sqrt[n]{n \times \frac{1}{n} + \sqrt[n]{n \times \frac{1}{n} + \sqrt[n]{n \times \frac{1}{n} + \sqrt[n]{n \times \frac{1}{n} + \dots}}} . \quad (14)$$

Equation (14) can be proven by writing

$$n = \sqrt[n]{n \times (n^{n-1} - 1) + n} . \quad (15)$$

Successive recursion in Eq.(15) leads to

$$n = \sqrt[n]{n \times (n^{n-1} - 1) + \sqrt[n]{n \times (n^{n-1} - 1) + \sqrt[n]{n \times (n^{n-1} - 1) + \sqrt[n]{n \times \dots}}} . \quad (16)$$

Substituting Eq.(12) into Eq.(16) gives Eq.(14). The expression shown in Eq.(14) is, of course, redundant. It can be better expressed as

$$n = \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \sqrt[n]{1 + \dots}}}} , \quad (17)$$

which is reflected on the left hand side (LHS) of Eq.(9). From Eq.(12), the solution to n is obtained by solving

$$g(n) = n^{n-1} - n^{-1} - 1 \quad (18)$$

for $g(n) = 0$. The numerical solution is $n = 1.7767750401$, accurate up to ten decimal places. Based on criteria for acceptable potential function

$$\left\{ \begin{array}{l} U \\ (\partial U / \partial r) \end{array} \right\}_{r \rightarrow 0} = \left\{ \begin{array}{l} +\infty \\ -\infty \end{array} \right\} \quad (19)$$

$$U_{r=R} = -D \quad (20)$$

$$U_{r \rightarrow \infty} = \left(\frac{\partial U}{\partial r} \right)_{r=R} = \left(\frac{\partial U}{\partial r} \right)_{r \rightarrow \infty} = 0, \quad (21)$$

five Lennard-Jones-type potential functions that incorporate the defined mathematical constant are proposed. In the first proposed potential function, the indices are n raised to integer powers at the repulsive and attractive parts to give

$$\frac{U_{P4P3}}{D} = \frac{1}{n-1} \left(\frac{R}{r} \right)^{n^4} - \frac{n}{n-1} \left(\frac{R}{r} \right)^{n^3}, \quad (22)$$

while in the second proposed potential function the indices are integer multiples of n , i.e.

$$\frac{U_{M8M4}}{D} = \left(\frac{R}{r} \right)^{8n} - 2 \left(\frac{R}{r} \right)^{4n}. \quad (23)$$

The first two and last two subscripts on the LHS correspond to the indices of the repulsive and attractive parts respectively, whereby subscripts P and M refer to integer powers and multiples respectively. The other three proposed potential functions are hybrids of Eqs.(22) and (23), i.e. the repulsive and attractive indices are integer multiples of and integer powers of n respectively:

$$\frac{U_{M7P3}}{D} = \frac{n^2}{7-n^2} \left(\frac{R}{r} \right)^{7n} - \frac{7}{7-n^2} \left(\frac{R}{r} \right)^{n^3}, \quad (24)$$

$$\frac{U_{M7P4}}{D} = \frac{n^3}{7-n^3} \left(\frac{R}{r} \right)^{7n} - \frac{7}{7-n^3} \left(\frac{R}{r} \right)^{n^4}, \quad (25)$$

$$\frac{U_{M8P3}}{D} = \frac{n^2}{8-n^2} \left(\frac{R}{r} \right)^{8n} - \frac{8}{8-n^2} \left(\frac{R}{r} \right)^{n^3}. \quad (26)$$

The coefficients selected in Eqs.(22) to (26) ensure that the criteria for acceptable potential function as laid out in Eqs.(19) to (21) are fulfilled.

3. Results and discussion

To test the applicability of Eqs.(22) to (26) for describing van der Waals energy of interaction, we recall the corresponding potential functions applied in computational chemistry softwares such as the Lennard-Jones(12-6)

$$\frac{U_{LJ(12-6)}}{D} = \left(\frac{R}{r} \right)^{12} - 2 \left(\frac{R}{r} \right)^6 \quad (27)$$

used in OPLS (Optimized Potentials for Liquid Simulations) [11], UFF (Universal Force Field) [12], AMBER (Assisted Model Building and Energy Refinement) [13] and ECEPP (Empirical Conformational Energy Programs for Peptides) [14] softwares. AMBER and ECEPP also incorporate the Lennard-Jones(12-10)

$$\frac{U_{LJ(12-10)}}{D} = 5\left(\frac{R}{r}\right)^{12} - 6\left(\frac{R}{r}\right)^{10} \quad (28)$$

as an option. Other softwares such as ESFF (Extensible Systemic Force Field) [15] and CFF (Class II Force Field) [16] adopt the Lennard-Jones(9-6)

$$\frac{U_{LJ(9-6)}}{D} = 2\left(\frac{R}{r}\right)^9 - 3\left(\frac{R}{r}\right)^6 \quad (29)$$

while the Lennard-Jones(14-7)

$$\frac{U_{LJ(14-7)}}{D} = \left(\frac{R}{r}\right)^{14} - 2\left(\frac{R}{r}\right)^7 \quad (30)$$

is employed by MMFF (Merck Molecular Force Field) [17]. The Buckingham potential function used for van der Waals energy is normally of the form

$$\frac{U_{Buck}}{D} = \frac{6}{\xi - 6} e^{\xi\left(1 - \frac{r}{R}\right)} - \frac{\xi}{\xi - 6} \left(\frac{R}{r}\right)^6 \quad (31)$$

for conversion from Lennard-Jones(12-6), which is available in UFF [12], DREIDING [18], a modified version of DREIDING [19], and a force field by Karasawa *et al* [20].

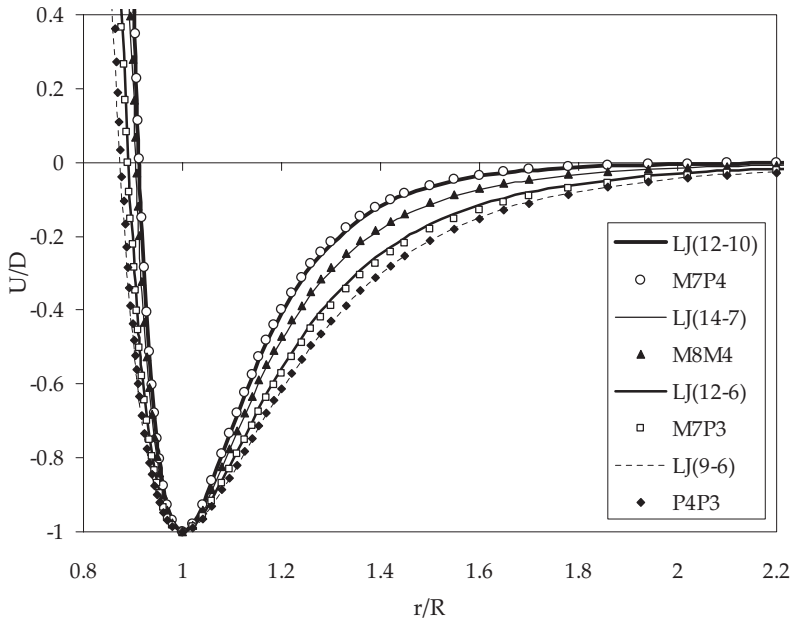


Fig. 1. Comparison of Eqs.(22) to (25) with common used Lennard-Jones potential function in molecular force fields.

The short and long range conversions are attained when $\xi = 13.772$ and $\xi = 12$ respectively. Comparison of the commonly used Lennard-Jones potentials used in computational chemistry softwares and those that incorporate the new mathematical constant reveals that Eqs.(22), (23), (24) and (25) provide very good agreement with the Lennard-Jones (9-6), (14-7), (12-6) and (12-10) respectively, as evident from Fig.1.

Figure 2 shows the correlation of Eqs.(24) and (26) with the Buckingham potential, Eq.(31), whereby $\xi = 12$ and $\xi = 13.772$ respectively. The closeness of these four potential energy curves may well be attributed to the fact that Eq.(31) is based on the Lennard-Jones(12-6) potential function.

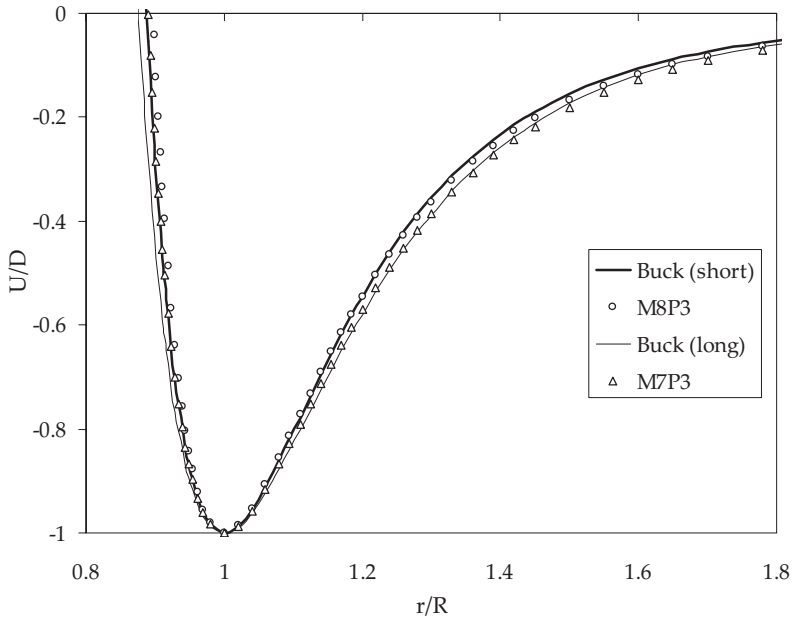


Fig. 2. Comparison of Eq.(24) and (26) with the short and long range forms of Buckingham potential function converted from Lennard-Jones(12-6).

4. Conclusions

A mathematical constant, $n = 1.7767750401$, has been conceptualized and incorporated into Lennard-Jones-type potential function. Five types of these potential functions that adopt n^1 , n^2 , n^3 and n^4 in the coefficients and indices

have been shown to agree well with the type of van der Waals potential energy functions used in typical molecular force fields. Arising from the mathematical significance and its chemical application, it is herein suggested that this new mathematical constant be examined for its relevance to other phenomenon of chemical relevance.

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