

Exact non-linear relationship between Exponential-6 and Lennard-Jones (12-6) potential functions

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The relationship between two of the most frequently adopted van der Waals potential functions – Exponential-6 and Lennard-Jones (12-6) – is shown to be faulty upon comparison of the repulsive terms. By using the Maclaurin's series expansions, an exact relationship between both the potential functions is obtained by means of a non-linear correction factor. A purely Exponential-6 form is recovered when the correction factor is taken at zeroth order, while a purely Lennard-Jones (12-6) form is attained as the order of the correction factor tends to infinity. For real van der Waals systems that are bounded by the Exponential-6 and Lennard-Jones (12-6) potential functions, a positive integer order of the correction factor may possibly provide good curve-fitting to experimental data.

KEY WORDS: correction factor, Exponential-6, Lennard-Jones, potential function, van der Waals

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1. Introduction

In computational simulation of molecular systems, two of the most frequently adopted potentials for describing the interaction energy between non-bonded, uncharged atoms are the Exponential-6 and the Lennard-Jones (12-6) functions. The Exponential-6 potential function is given as

$$U_{X6} = Ae^{-Br} - \frac{C}{r^6}, \quad (1)$$

where A , B and C are the Exponential-6 parameters, while r is the distance between the two unbonded and uncharged atoms. This potential function is incorporated in the following softwares for describing van der Waals interaction: EAS [1], MM2 [2], DREIDING [3], MM3 [4], EFF [5], MOMEK [6] and MM4 [7]. The Lennard-Jones (12-6) potential function is written as

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

where D is the magnitude of the minimum well-depth, while R is the van der Waals distance whereby non-bonded interaction energy between two uncharged atoms are at the minimum. The Lennard-Jones (12-6) potential function has been adopted in the following softwares for quantifying van der Waals interaction: CVFF [8], CHARMM [9], GROMOS [10], TRIPOS [11], DREIDING [3], SHAPES [12], ECEPP [13], UFF [14], AMBER [15] and OPLS [16]. For both potential functions mentioned, the first and second terms on the RHS are the energy terms corresponding to the repulsive and attractive forces, respectively. Previously, the relationship between both the van der Waals potential functions has been given as

$$U_{X6} = D \left[\left(\frac{6}{\xi - 6} \right) e^{\xi(1-r/R)} - \left(\frac{\xi}{\xi - 6} \right) \left(\frac{R}{r} \right)^6 \right], \quad (3)$$

where ξ , a non-dimensional scaling factor, is equal to 13.772 for near equilibrium ($r \cong R$) and 12.0 for long range [3,14,17,18]. While double differential with respect to the separation distance for both potential functions reveals equal curvature at $r = R$, comparison of terms between equations (2) and (3) shows discrepancy for long range. The long-range comparison ($\xi = 12.0$), on the other hand, bears no exact relationship between these two potential functions. An exact relationship between both potential functions is proposed herein with the inclusion of a non-linear correction factor. The present paper is an extension of mathematical relations among frequently adopted potential functions in bond-torsion [19], bond-bending [20] and bond-stretching [21]. Whilst a previous paper on non-bonded interactions [22] attempts to form a generalized relationship between the Exponential- n and the Lennard-Jones (m - n), the present paper focuses on an exact relationship between both the Exponential-6 and the Lennard-Jones (12-6) functions via inclusion of a non-linear correction factor.

2. Analysis

Substitution of $\xi = 12.0$ into equation (3) gives

$$U_{X6} = D \left[(e^{1-r/R})^{12} - 2 \left(\frac{R}{r} \right)^6 \right]. \quad (4)$$

Perusal to equations (2) and (4) reveals equal attractive terms. However, comparison of the repulsive terms incorrectly implies that

$$\frac{R}{r} = e^{1-r/R}, \quad (5)$$

which is only valid (i) at equilibrium ($r = R$), and (ii) at infinite separation ($r \rightarrow \infty$).

To obtain an exact relationship between the Lennard-Jones (12-6) and the Exponential-6 potential functions, we introduce a correction factor k , raised to the power of ξ , into the repulsive term of equation (3) so that

$$U_{X6}^{(n)} = D \left[(k^{(n)})^\xi \left(\frac{6}{\xi - 6} \right) e^{\xi(1-r/R)} - \left(\frac{\xi}{\xi - 6} \right) \left(\frac{R}{r} \right)^6 \right], \quad (6)$$

where n refers to the order of accuracy. Thus at $\xi = 12.0$, we have

$$U_{X6}^{(n)} = D \left[(k^{(n)} e^{1-r/R})^{12} - 2 \left(\frac{R}{r} \right)^6 \right] \quad (7)$$

such that, upon comparing equations (2) and (7),

$$\frac{R}{r} = k^{(n)} e^{1-r/R}. \quad (8)$$

Writing the change of atomic nuclei distance as $\delta r = r - R$ and applying Maclaurin's series expansion, we have

$$e^{1-r/R} = e^{-\delta r/R} \equiv \sum_{n=0}^{+\infty} \frac{1}{n!} \left(-\frac{\delta r}{R} \right)^n \quad (9)$$

and

$$\frac{R}{r} = \frac{1}{1 - (-\delta r/R)} \equiv \sum_{n=0}^{+\infty} \left(-\frac{\delta r}{R} \right)^n. \quad (10)$$

Substitution of equations (9) and (10) into equation (8) gives the correction factor of order n as

$$k^{(n)} = \frac{\sum_{i=0}^n (-1)^i (\delta r/R)^i}{\sum_{i=0}^n [(-1)^i / i!] (\delta r/R)^i}. \quad (11)$$

Previous relationship as described by equation (3) [3,14,17,18] corresponds to the case $k = 1$ (or $n = 0$).

3. Results and discussion

To observe the extent of attainable accuracy with respect to n , a set of master curves of non-dimensional repulsion energy is plotted against the non-dimensional non-bonded atomic distance (r/R), i.e.,

$$\left(\frac{U_{X6}^{(n)}}{D} \right)_{\text{repul}} = (k^{(n)} e^{1-r/R})^{12} \quad (12)$$

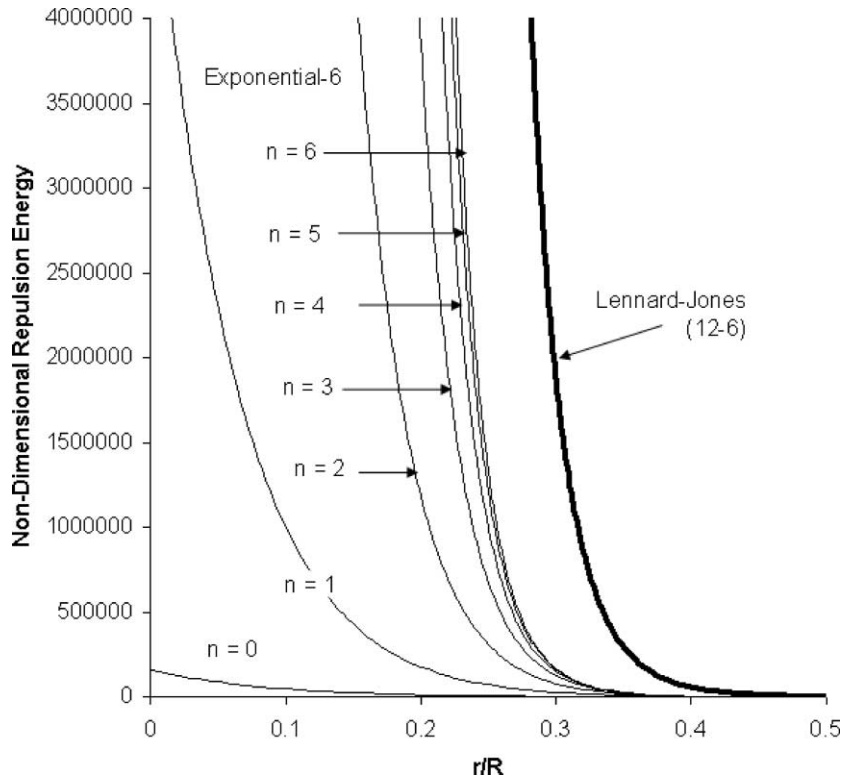


Figure 1. Comparison of the loose form of Exponential-6 (thin curves), at various orders of n , with the Lennard-Jones (12-6) (thick curve).

for $n = 0, 1, 2, 3, 4, 5, 6$ and

$$\left(\frac{U_{LJ}}{D}\right)_{\text{repul}} = \left(\frac{r}{R}\right)^{-12}, \quad (13)$$

as shown in figure 1. We note that:

- At $n = 0$, equation (7) gives a purely Exponential-6 form such that the repulsion term is finite as $r \rightarrow 0$;
- As $n \rightarrow \infty$, equation (7) gives a purely Lennard-Jones (12-6) form such that the repulsion term is infinite as $r \rightarrow 0$;
- For $n \in [0, \infty]$, equation (7) allows one to describe an interlace of Exponential-6 and Lennard-Jones (12-6), with n quantifying the extent of each potential function;
- The repulsion term increases with the order n , as evident from figure 1;
- For van der Waals repulsion that are bounded between the purely Exponential-6 and the purely Lennard-Jones (12-6), a positive integer of n that gives the best fit may possibly exist.

4. Conclusions and suggestion

A discrepancy in the relationship between Exponential-6 and Lennard-Jones (12-6) has been considered in this paper, and a correction factor proposed herein. Using the Maclaurin's series expansion for the terms e^x and $(1-x)^{-1}$, a non-linear correction factor of order n (a non-negative integer) was extracted. The correction factor, introduced into the repulsive term, gives a purely Exponential-6 form at $n = 0$ and a purely Lennard-Jones (12-6) form as $n \rightarrow \infty$.

It is hereby suggested that curve-fitting of experimental data be made at various n for interaction between different van der Waals systems. The values of n in real systems that give the most appropriate fit await experimental results. It also remains to be ascertained if a constant value of n exists in all, or most, van der Waals interactions.

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