Alignment of Buckingham Parameters to Generalized Lennard-Jones Potential Functions

Teik-Cheng Lim

School of Science and Technology, SIM University, 535A Clementi Road, S 599490, Republic of Singapore

Reprint requests to T.-C. L.; E-mail: alan_tc_lim@yahoo.com

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The Lennard-Jones(12-6) and the Exponential-6 potential functions are commonly used in computational softwares for describing the van der Waals interaction energy. Some softwares allow switching between these two potentials under prescribed condition(s) that attempt to connect the parameter relationship between the two functions. Here we propose a technique by which the parameter relationship between both potentials is extracted by simultaneously imposing an equal force constant at the well depth's minimum and an equal mean interatomic energy from the point of equilibrium to the point of total separation. The former imposition induces good agreement for the interatomic compression and a small change in the interatomic distance near the equilibrium while the latter enables good agreement for large interatomic separation. The excellent agreement exhibited by the plots validates the technique of combined criteria proposed herein.

Key words: Parameter Conversion; Potential Function; van der Waals.
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1. Introduction

Arising from the introduction of the Lennard-Jones potential energy function [1 – 3]

$$U_{\mathrm{LJ}} = \frac{A}{r^m} - \frac{B}{r^n},\ (0 < n < m), \tag{1}$$

a number of molecular mechanics force fields apply the Lennard-Jones function for describing the interaction energy between non-bonded neutral atoms. A majority of these force fields adopt the Lennard-Jones(12-6) function (e. g. [4 – 12]), followed by the Lennard-Jones(9-6) function (e. g. [13, 14]). Less common are the Lennard-Jones(12-10), which is available in AMBER [11] as an option in addition to the usual Lennard-Jones(12-6) function, and the buffered Lennard-Jones(14-7) function [15]. Other force fields adopt the Exponential-6 potential function (e. g. [16 – 21]), which is a special case of the Buckingham potential function [22]

$$U_{\mathrm{B}} = a\exp(-br) - \frac{c}{r^\eta} \tag{2}$$

with $\eta = 6$. In DREIDING [8] and UFF [10] both the Lennard-Jones(12-6) and the Exponential-6 functions are available as options. It has been appreciated that the Exponential-6 function is more stable than the Lennard-Jones function [10]. As a result, a loose form of the Exponential-6 function was introduced as

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

where substitution by $\xi = 13.772$ and $\xi = 12$ fulfills the force constant

$$k = \left(\frac{\partial^2 U_{\mathrm{LJ(12\text{-}6)}}}{\partial r^2}\right)_{r=R} = \left(\frac{\partial^2 U_{\mathrm{X6}}}{\partial r^2}\right)_{r=R} \tag{4}$$

and the long range relationship

$$\lim_{r\to\infty} U_{\mathrm{LJ(12\text{-}6)}} = \lim_{r\to\infty} U_{\mathrm{X6}}, \tag{5}$$

respectively, with reference to the Lennard-Jones(12-6) function [8]. A drawback in the use of these two values is obvious during the switch of this factor in the intermediate range. Recently an intermediate scaling factor of $\xi = 12.6533$ was obtained by imposing the following equal energy integral from equilibrium to dissociation:

$$\int_R^\infty U_{\mathrm{LJ(12\text{-}6)}}\mathrm{d}r = \int_R^\infty U_{\mathrm{X6}}\mathrm{d}r. \tag{6}$$

With 3 scaling factors instead of 2, the Exponential-6 function is split into 3 parts with 2 switches in the scaling factor. An additional switch reduces the abruptness in the van der Waals energy description, hence resulting in a comparatively smoother Exponential-6 potential energy curve [23]. In the present paper, an attempt is made to propose the use of only one scaling factor to ensure a perfectly smooth potential energy curve, while maintaining an almost exact agreement not only with the commonly used Lennard-Jones(12-6) function, but also to any Lennard-Jones-type of function.

2. Analysis

The energy integral approach was found to be useful for obtaining the shape parameter of a potential function from a group of parameters in another potential function. Unlike the limit approach, e. g. (5), the use of an energy integral from equilibrium interatomic distance to dissociation provides a shape parameter that ensures minimal discrepancies [24 – 26]. Furthermore the limit approach is of little practical value as most computational softwares impose energy cut-off beyond certain range of interatomic distance. However, the energy integral approach does not ensure good agreement near the minimum well depth. The imposition of an equal second-order derivative or a related approach ensures good correlation near the minimum well depth, but not for a longer range [27 – 30].

To achieve good correlation over the whole range, i. e. both in the near range and the far range, there is need to implement both the imposition of an equal energy curvature and an equal energy integral. This will, of course, lead to two different values of the scaling factor. As such we herein consider the Buckingham function in its loose form

$$U_{\mathrm{B}} = D\left\{\frac{\eta}{\xi-\eta}\exp\left[\xi\left(1-\frac{r}{R}\right)\right]-\frac{\xi}{\xi-\eta}\left(\frac{R}{r}\right)^{\eta}\right\}, \tag{7}$$

which contains two shape parameters, ξ and η, instead of just one. The Lennard-Jones function considered herein is of the general form

$$U_{\mathrm{LJ}} = D\left[\frac{n}{m-n}\left(\frac{R}{r}\right)^{m}-\frac{m}{m-n}\left(\frac{R}{r}\right)^{n}\right] \tag{8}$$

with m and n as the two shape parameters. Here, the parameters ξ and m can be viewed as the repulsive indices while the parameters η and n are the attractive indices of the potential energy functions.

The imposition of an equal second-order derivative at the minimum well depth

$$\left(\frac{\partial^2 U_{\mathrm{LJ}}}{\partial r^2}\right)_{r=R} = \left(\frac{\partial^2 U_{\mathrm{B}}}{\partial r^2}\right)_{r=R} \tag{9}$$

gives the product of the Lennard-Jones indices as

$$mn = \frac{\xi\eta\,(\xi-\eta-1)}{\xi-\eta}, \tag{10}$$

while the imposition of an equal energy integral from the well depth's minimum to infinite interatomic distance

$$\int_R^\infty U_{\mathrm{LJ}}\mathrm{d}r = \int_R^\infty U_{\mathrm{B}}\mathrm{d}r \tag{11}$$

leads to

$$\frac{1-m-n}{(m-1)(n-1)} = \frac{1}{\xi-\eta}\left(\frac{\eta}{\xi}-\frac{\xi}{\eta-1}\right). \tag{12}$$

The two independent relations described by (10) and (12) are useful for obtaining the Lennard-Jones shape parameters (m,n) from those of the Buckingham potential (ξ,η) and vice versa. The corresponding Buckingham parameters to the conventional Lennard-Jones(12-6) can be obtained by substituting $m = 2n = 12$ into (10) and (12); solving these equations gives $\xi = 14.3863$ and $\eta = 5.6518$. In the same way, by substituting $2m = 3n = 18$ into (10) and (12) for the case of the Lennard-Jones(9-6) function enables one to solve the Buckingham parameters numerically as $\xi = 11.9507$ and $\eta = 5.3212$.

In order to provide a proper measure between the two potentials, we consider the Hilbert space for these functions. The distance between the two functions U_{B} and U_{LJ} in an inner product space is written as

$$d(U_{\mathrm{B}},U_{\mathrm{LJ}}) = \|U_{\mathrm{B}}-U_{\mathrm{LJ}}\|, \tag{13}$$

where the norm of the function $U_{\mathrm{B}}-U_{\mathrm{LJ}}$ is given in terms of the inner products as

$$\|U_{\mathrm{B}}-U_{\mathrm{LJ}}\| = \langle U_{\mathrm{B}}-U_{\mathrm{LJ}}\,,\,U_{\mathrm{B}}-U_{\mathrm{LJ}}\rangle^{\frac{1}{2}}. \tag{14}$$

The inner product $\langle U_{\mathrm{B}}-U_{\mathrm{LJ}}\,,\,U_{\mathrm{B}}-U_{\mathrm{LJ}}\rangle$ is defined in the space of real-valued functions with domain to the real line $\Re$ as

$$\begin{aligned}&\langle U_{\mathrm{B}}-U_{\mathrm{LJ}}\,,\,U_{\mathrm{B}}-U_{\mathrm{LJ}}\rangle\\ &= \textstyle\int_{\Re}(U_{\mathrm{B}}-U_{\mathrm{LJ}})\,\left(\overline{U_{\mathrm{B}}-U_{\mathrm{LJ}}},\right)\,\mathrm{d}r,\end{aligned} \tag{15}$$

m	n	ξ	η	α	β	γ	$d(U_{\rm B},U_{\rm LJ})$	Ref.
12	6	13.772	6	0.168715	−0.33962	0.171821	$0.030210\,D\sqrt{R}$	[8]
12	6	12	6	0.183081	−0.35309	0.171821	$0.042563\,D\sqrt{R}$	[8]
12	6	14.3863	5.6518	0.171468	−0.34277	0.171821	$0.022717\,D\sqrt{R}$	This paper

Table 1. The distance $d(U_{\rm B},U_{\rm LJ})$ between the Buckingham and the Lennard-Jones(12-6) functions based on the Hilbert space.

where the bar denotes the conjugate. In this analysis, both potential functions do not consist of imaginary parts, hence

$$(U_{\rm B}-U_{\rm LJ})\,\left(\overline{U_{\rm B}-U_{\rm LJ}}\right)=(U_{\rm B}-U_{\rm LJ})^2\,. \qquad (16)$$

Substituting (16) into (15) and taking the integral leads to the distance between both potential functions as

$$d(U_{\rm B},U_{\rm LJ})=D\sqrt{R\,(\alpha+\beta+\gamma)}, \qquad (17)$$

where

$$\alpha=\frac{\xi\eta}{(\xi-\eta)^2}\left[\frac{\eta}{2\xi^2}-\frac{2}{\xi+\eta}+\frac{\xi}{\eta(2\eta-1)}\right], \qquad (18)$$

$$\beta=-\frac{2}{(\xi-\eta)(m-n)}\left[\frac{\eta n}{\xi+m}-\frac{\eta m}{\xi+n}-\frac{\xi n}{\eta+m-1}+\frac{\xi m}{\eta+n-1}\right], \qquad (19)$$

$$\gamma=\frac{mn}{(m-n)^2}\left[\frac{n}{m(2m-1)}-\frac{2}{m+n-1}+\frac{m}{n(2n-1)}\right]. \qquad (20)$$

Table 1 compares the distance between both potential functions in the inner product space. It can be seen that the use of a combined equal force constant and an equal energy integral gives the lowest distance compared to a previous approach [8]. The present approach gives the distance between the two potentials as three quarter and half of the distances based on DREIDING's [8] near range indices $\xi=13.772$ and $\eta=6$, and far ranges indices $\xi=12$ and $\eta=6$, respectively.

3. Results and Discussion

To test the validity of the relations described in (10) and (12) in a practical sense, the dimensionless interaction energy (U/D) versus the dimensionless interatomic distance (r/R) is plotted for the Lennard-Jones (12-6) potential

$$\frac{U_{\rm LJ(12\text{-}6)}}{D}=\left(\frac{R}{r}\right)^{12}-2\left(\frac{R}{r}\right)^{6} \qquad (21)$$

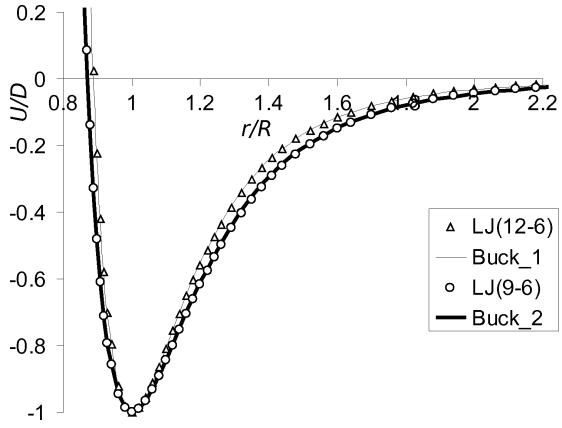

Fig. 1. Normalized Lennard-Jones(12-6) and Lennard-Jones(9-6) potentials compared with the Buckingham forms described by (21) – (24).

and the Lennard-Jones(9-6) potential

$$\frac{U_{\rm LJ(9\text{-}6)}}{D}=2\left(\frac{R}{r}\right)^{9}-3\left(\frac{R}{r}\right)^{6} \qquad (22)$$

with their corresponding counterparts in the Buckingham forms

$$\frac{U_{\rm B_1}}{D}=0.6471\mathrm{e}^{14.3863\left(1-\frac{r}{R}\right)}-1.6471\left(\frac{R}{r}\right)^{5.6518} \qquad (23)$$

and

$$\frac{U_{\rm B_2}}{D}=0.8027\mathrm{e}^{11.9507\left(1-\frac{r}{R}\right)}-1.8027\left(\frac{R}{r}\right)^{5.3212}, \qquad (24)$$

respectively, in Figure 1. This figure shows the plots of the Lennard-Jones(12-6) and Lennard-Jones(9-6) potentials in triangles and circles, respectively, while the Buckingham potentials with $(\xi,\eta)=(14.3863,\ 5.6518)$ and $(11.9507, 5.3212)$ are denoted by thin and bold lines, respectively.

Since the interatomic force is defined as

$$F=-\frac{\partial U}{\partial r}, \qquad (25)$$

we introduce the normalized interatomic force defined herein as

$$F^*=\frac{R}{D}\left(\frac{\partial U}{\partial r}\right) \qquad (26)$$

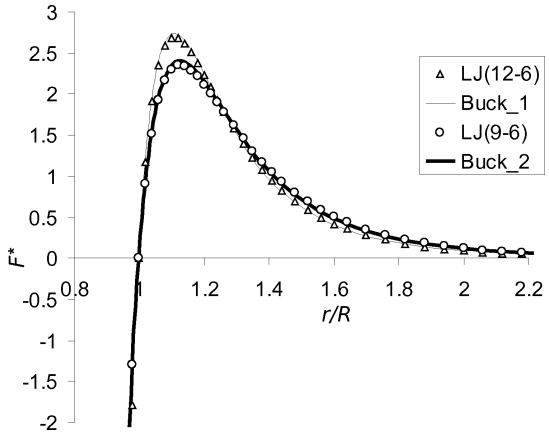

Fig. 2. Normalized interatomic force of the Lennard-Jones(12-6) and Lennard-Jones(9-6) potentials compared with the Buckingham forms.

to give

$$F_{\mathrm{B}}{}^{*} = \frac{\xi\eta}{\xi-\eta}\left\{\left(\frac{R}{r}\right)^{\eta+1} - \exp\left[\xi\left(1-\frac{r}{R}\right)\right]\right\} \quad (27)$$

and

$$F_{\mathrm{LJ}}{}^{*} = \frac{mn}{m-n}\left[\left(\frac{R}{r}\right)^{n+1} - \left(\frac{R}{r}\right)^{m+1}\right] \quad (28)$$

corresponding to the Buckingham and the Lennard-Jones potentials, respectively. See Fig. 2 for the corresponding normalized plots of the interatomic force. The excellent agreement of the interatomic force observed between both pairs of corresponding potential functions attest the validity of the parameter relationships of (10) and (12).

4. Conclusions

It was shown that any Lennard-Jones-type potential energy function can be expressed in terms of an Exponential-6-type function by modifying the latter's repulsive and attractive indices. The adjusted repulsive and attractive indices can be obtained by equating the force constant and the energy integral. The existence of the attractive index, η, removes the requirement for the scaling factor, ξ, to be adjustable. The fixed value of the scaling factor ensures that the Exponential-6-type potential function is perfectly smooth. The two sets of parameter relationships of (10) and (12) also allow any given Exponential-6-type parameters to be converted into those of the Lennard-Jones-type potential for application in computational softwares adopting the latter function for quantifying the van der Waals interaction energy.

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