

The Relationship between Lennard-Jones (12-6) and Morse Potential Functions

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The most commonly used potentials for van der Waals interactions are the Exponential-6 and the Lennard-Jones (12-6) potential. In this paper a correlation between them is described. The Morse function, which is normally applied for quantifying 2-body interactions, has been adopted in one software. This paper deals with the validity of the Morse function for non-bonded interactions by means of obtaining a relationship between the Morse and the Lennard-Jones (12-6) potential functions. An approximate and an exact mathematical relationship is demonstrated to exist between these two potentials.

Key words: Lennard-Jones; Mathematical Relationship; Morse; Potential Functions; van der Waals.

1. Introduction

The interaction between two non-bonded and uncharged atoms, known as the van der Waals interaction, has been expressed in terms of the potential energy. A commonly adopted potential energy for the van der Waals interaction is the Exponential-6 function

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

where r is the distance between the nuclei of the two atoms, whilst A , B , and C are parameters. Another commonly adopted potential for van der Waals interaction is the Lennard-Jones (12-6) function

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

where the van der Waals distance R characterizes the minimum energy of interaction between the two atoms, with D_{LJ} representing the magnitude of the minimum well-depth. Due to its simplicity, the Lennard-Jones function is widely used, as can be inferred from its adoption by various molecular modeling softwares, such as CVFF [1], CHARMM [2], GROMOS [3], TRIPOS [4], DREIDING [5], SHAPES [6], UFF [7], ECEPP [8], AMBER [9] and OPLS [10].

The relationship between the Exponential-6 and Lennard-Jones (12-6) potential has been given through

a loose form of the Exponential-6 potential [11], i. e.

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

with

$$D_{LJ} \left(\frac{6}{\xi - 6} \right) e^{\xi} = A \quad (4)$$

and

$$D_{LJ} \left(\frac{\xi}{\xi - 6} \right) R^6 = C, \quad (5)$$

where $\xi = BR$ is a dimensionless scaling factor. Putting $\xi = 13.772$ gives the same curvature as the Lennard-Jones (12-6) function at $r = R$, while putting $\xi = 12.0$ leads to the long range approximation of the Lennard-Jones (12-6) function. To a limited extent, the Morse potential function

$$U_M = D_M \left[1 - e^{-\alpha(r-R)} \right]^2 \quad (6)$$

can be extended for quantifying the van der Waals potential energy. It must be borne in mind that the Morse potential was developed for describing 2-body interactions. As such, the Morse potential has been adopted in representing stretching and compression of covalent bonds connecting two atoms. Nevertheless, the Morse

potential has been employed for describing the van der Waals interaction in the COSMIC [12] molecular modeling software. We note that the Morse function (6) has a minimum and is zero at the equilibrium bond length R . At infinite atomic separation, the Morse potential tends to the separation energy D_M . Hence, subtracting D_M from U_M , we have

$$U_M^* = U_M - D_M = D_M \left[e^{-2\alpha(r-R)} - 2e^{-\alpha(r-R)} \right], \quad (7)$$

U_M^* having a minimum well depth of $U_M^* = -D_M$ at $r = R$ and $U_M^* \rightarrow 0$ as $r \rightarrow \infty$. In this manner, the modified Morse potential U_M^* can be made analogous to the Exponential-6 and the Lennard-Jones (12-6) potential functions. In this paper, the parametric relationship between the Lennard-Jones (12-6) and Morse functions is given for both near the equilibrium and long range. The connections between the parameters of these two potential functions for non-bonded interactions complement the recently established relationships among the potential functions for bond-torsion [13], bond-bending [14], bond-stretching [15], and non-bonded interactions [16, 17].

2. Analysis

The first and second derivatives for both the Lennard-Jones (12-6) and Morse potential functions with respect to r are

$$\frac{\partial U_{LJ}}{\partial r} = -12D_{LJ} \left[\frac{R^{12}}{r^{13}} - \frac{R^6}{r^7} \right], \quad (8)$$

$$\frac{\partial U_M^*}{\partial r} = -2D_M \alpha \left[e^{-2\alpha(r-R)} - e^{-\alpha(r-R)} \right], \quad (9)$$

$$\frac{\partial^2 U_{LJ}}{\partial r^2} = D_{LJ} \left[156 \frac{R^{12}}{r^{14}} - 84 \frac{R^6}{r^8} \right], \quad (10)$$

$$\frac{\partial^2 U_M^*}{\partial r^2} = 2D_M \alpha^2 \left[2e^{-2\alpha(r-R)} - e^{-\alpha(r-R)} \right]. \quad (11)$$

To obtain the relationship between the Lennard-Jones (12-6) and Morse functions at or near equilibrium ($r \approx R$), we consider

$$(U_{LJ})_{r=R} = (U_M^*)_{r=R}, \quad (12)$$

which gives

$$D_{LJ} = D_M \equiv D. \quad (13)$$

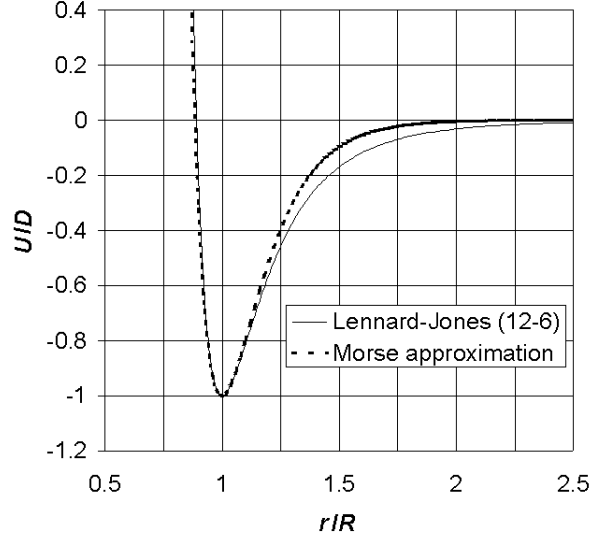


Fig. 1. Comparison between the Lennard-Jones (12-6) and the Morse approximation.

As expected,

$$\left(\frac{\partial U_{LJ}}{\partial r} \right)_{r=R} = \left(\frac{\partial U_M^*}{\partial r} \right)_{r=R} = 0. \quad (14)$$

Equating the curvatures at $r = R$

$$\left(\frac{\partial^2 U_{LJ}}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_M^*}{\partial r^2} \right)_{r=R}, \quad (15)$$

and considering (13) we have

$$\alpha R = 6. \quad (16)$$

To obtain the long range relationship between the Lennard-Jones (12-6) and Morse functions, (2) and (7) are written in the dimensionless form

$$\frac{U_{LJ}}{D_{LJ}} = \left(\frac{R}{r} \right)^6 \left[\left(\frac{R}{r} \right)^6 - 2 \right], \quad (17)$$

$$\frac{U_M^*}{D_M} = e^{-\alpha R \left(\frac{r}{R} - 1 \right)} \left[e^{-\alpha R \left(\frac{r}{R} - 1 \right)} - 2 \right]. \quad (18)$$

Comparing (17) and (18), the relationship shown in (13) remains valid for long range. In addition

$$\alpha R = \frac{\ln \left(\frac{r}{R} \right)^6}{\left(\frac{r}{R} - 1 \right)}. \quad (19)$$

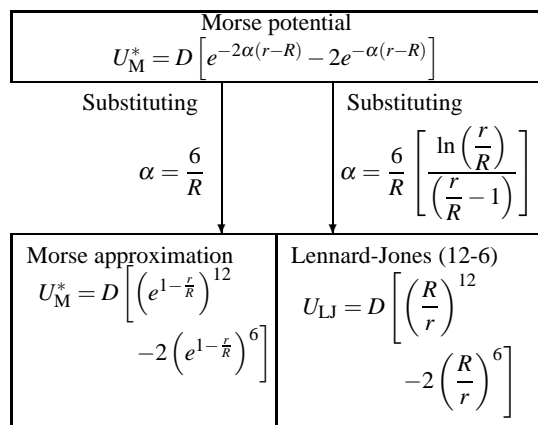


Fig. 2. Relationships between the Morse and Lennard-Jones (12-6) potential functions.

Substituting (16) into (18) we have the Morse approximation

$$\frac{U_M^*}{D_M} \approx e^{-6\left(\frac{r}{R}-1\right)} \left[e^{-6\left(\frac{r}{R}-1\right)} - 2 \right], \quad (20)$$

while the Lennard-Jones (12-6) function is exactly recovered substituting (19) into (18).

3. Results and Discussion

We note that, both for near equilibrium and long range, the Lennard-Jones' and Morse's minimum well depths are equal. This is expected since, physically, curve fitting using either potential functions should give equal minimum well depths. However, the rela-

tionship between α and R is constant for near equilibrium but non-linear for the case of long range. While the validity of (19) – for long range – is easily proven, that of (16) can be justified by comparing plots of the Lennard-Jones (12-6) and the Morse potential, incorporating $\alpha = (6/R)$. The non-dimensionalized potential energy, U/D , plotted with respect to the non-bonded atomic distance, r/R , is shown Figure 1. The Morse approximation, as described in (20), gives an insignificant under-estimation of the repulsive energy, whereby $r < R$, but an over-estimation of the attractive energy, whereby $r > R$. The so-called “bond hardness” is therefore overly manifested using the Morse approximation, whereby α is a constant, and should be limited to the case of near equilibrium within $(r/R) = 1 \pm 0.2$. Another case, whereby the $\alpha = (6/R)$ approximation is valid, is that in which $(r/R) > 2.5$, although the van der Waals potential energy is normally truncated at such distances in practice.

4. Conclusion

Two relationships between the Lennard-Jones (12-6) and the Morse potential functions have been obtained and summarized in Figure 2. The simpler of the two relationships, given by (16), is only valid for the near equilibrium case. Nevertheless it complies with the original Morse potential, whereby α is a constant. The more detailed relationship – described by (19) – is exact throughout but less convenient for execution since the corresponding Morse parameter α varies with respect to the non-bonded interatomic distance, r .

- [1] S. Lifson, A. T. Hagglar, and P. Dauber, *J. Amer. Chem. Soc.* **101**, 5111 (1979).
- [2] R. Brooks, R. E. Bruccoleri, B. D. Olafson, D. J. States, S. Swaminathan, and M. Karplus, *J. Comput. Chem.* **4**, 187 (1983).
- [3] W. F. van Gunsteren and H. J. C. Berendsen, *Groningen Molecular Simulation (GROMOS) library manual*, 1987.
- [4] M. Clark, R. D. Cramer III, and N. van Opdenbosch, *J. Comput. Chem.* **10**, 982 (1989).
- [5] S. L. Mayo, B. D. Olafson, and W. A. Goddard III, *J. Phys. Chem.* **94**, 8897 (1990).
- [6] V. S. Allured, C. M. Kelly, and C. R. Landis, *J. Amer. Chem. Soc.* **113**, 1 (1991).
- [7] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III, and W. M. Skiff, *J. Amer. Chem. Soc.* **114**, 10024 (1992).
- [8] 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**, 6472 (1992).
- [9] 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. Amer. Chem. Soc.* **117**, 5179 (1995).
- [10] W. Damm, A. Frontera, J. Tirado-Rives, and W. L. Jorgensen, *J. Comput. Chem.* **18**, 1955 (1997).
- [11] S. L. Mayo, B. D. Olafson, and W. A. Goddard, *J. Phys. Chem.* **94**, 8897 (1990).
- [12] S. D. Morley, R. J. Abraham, I. S. Haworth, D. E. Jackson, M. R. Saunders, and J. G. Vinter, *J. Comput.-Aided Mol. Des.* **5**, 475 (1991).
- [13] T. C. Lim, *J. Math. Chem.* **31**, 421 (2002).
- [14] T. C. Lim, *J. Math. Chem.* **32**, 249 (2002).
- [15] T. C. Lim, *J. Math. Chem.* **33**, 29 (2003).
- [16] T. C. Lim, *J. Math. Chem.* **33**, 229 (2003).
- [17] T. C. Lim, *J. Math. Chem.* **34**, 221 (2003).