

# Relationship between Morse and Murrell-Mottram potentials at long range

Teik-Cheng Lim

*Faculty of Engineering, Nanoscience and Nanotechnology Initiative, National University of Singapore, 9 Engineering Drive 1, S 117576, Republic of Singapore*

E-mail: alan.tc\_lim@yahoo.com

Received 3 November 2004; revised 15 March 2004

This paper develops a relationship between the Morse potential and the Murrell-Mottram's 2-body potential. By expressing both potentials in terms of a repulsive term and an attractive term, and approximating Maclaurin's expansion, comparison of coefficients and indices of the repulsive and attractive terms leads to parametric connections between these two potential functions. Non-dimensional curves of these potentials at long range show good agreement as compared to those obtained previously. A set of parametric relationships obtained recently, together with the presently proposed connections, are useful in paving a way for the development of a potential function converter.

**KEY WORDS:** covalent bonds, dissociation energy, interatomic potentials, Maclaurin's series, potential function, series approximation

**AMS subject classification:** 41A99, 70C20, 92E99

## 1. Introduction

Simulation in condensed matter either requires calculation of Schrödinger equation in the quantum mechanical approach or calculation using empirical potential energy function. Notwithstanding the exactness of the former, the latter is especially useful for calculation of very large dynamical system. The concept of model potentials is based on the Born-Oppenheimer approximation

$$U_{\text{Total}} = \sum_{n=1}^N U_{n\text{-body}} = U_{1\text{-body}} + U_{2\text{-body}} + \cdots + U_{N\text{-body}} \quad (1)$$

for  $N$  number of particles in the system, where  $U_{n\text{-body}}$  represents the sum of  $n$ -body interaction energies. Since  $U_{1\text{-body}}$  is the sum of non-interacting particles,

the total interaction energy of a system of  $N$  interacting particles is

$$U = U_{\text{Total}} - U_{1\text{-body}} = \sum_{n=2}^N U_{n\text{-body}}. \quad (2)$$

Many-body expansions as in BCC or FCC elements are normally truncated after the 3-body term [1]. For polymeric chains, expansion is truncated after the 4-body term. The 2-body, 3-body and 4-body terms are also known as the stretching, bending and twisting energy of bonds, respectively. With the variety of potential functions, there may exist a need to convert parameters of one potential function to another due to mismatch in available data corresponding to one potential function and the purchased software that adopts another set of potential function.

Recently, mathematical connections between bond-torsion potentials [2] and bond-bending potentials [3] have been established. For the case of bond-stretching potential, exact relationship between the harmonic [4], Morse [5] and Murrell-Mottram [6] potentials has been obtained for near equilibrium, or short range. As expected, the harmonic and the Morse potentials diverge at bond separation. On the other hand, the parametric relationships between Morse and Murrell-Mottram for 2-body – exact at equilibrium – gives a higher potential energy for the latter than the former by a factor of 2 [7]. As such, the available parametric relationship between Morse and Murrell-Mottram potential functions is valid only for short range. In this letter, a long range relationship between these two potentials is proposed.

## 2. Analysis

The Morse potential function

$$U_{\text{M}} = D_{\text{M}} [1 - \exp(-\alpha(r - r_0))]^2 \quad (3)$$

is a commonly used potential function for 2-body interactions in modeling chemicals [8], polymeric chains [9] and molecular machines [10, 11] whereby  $D_{\text{M}}$  and  $\alpha$  are the Morse parameters. The Murrell-Mottram potential function exists as a summation of a 2-body and a 3-body term, and has been proposed for elemental solids whereby its parameters for 2-body term ( $D_{\text{MM}}$  and  $a$ ) are determined by fitting phonon and elastic constant data, and the lattice energies and lattice constants of crystalline phase [6, 12–15]. The 2-body term of the Murrell-Mottram potential function is given as

$$U_{\text{MM}} = -D_{\text{MM}} \left( 1 + \frac{a}{r_0}(r - r_0) \right) \exp \left( -\frac{a}{r_0}(r - r_0) \right) \quad (4)$$

For both potentials, the coefficients  $D_M$  and  $D_{MM}$  refer to the energy required to completely separate the two bonded atoms,  $r$  refers to the bond length, and  $r_0$  corresponds to the equilibrium bond length. Since the Murrell-Mottram function for 2-body case gives a minimum well depth of  $U_{MM} = -D_{MM}$  at  $r = r_0$  and  $U_{MM} = 0$  as  $r \rightarrow \infty$ , we herein consider a modified Murrell-Mottram function

$$U_{MMM} = U_{MM} + D_{MM} = D_{MM} \left[ 1 - \left( 1 + \frac{a}{r_0}(r - r_0) \right) \exp \left( -\frac{a}{r_0}(r - r_0) \right) \right] \quad (5)$$

to give the minimum  $U_{MMM} = 0$  at  $r = r_0$  and  $U_{MMM} = D_{MM}$  as  $r \rightarrow \infty$  so as to pave a way for relating the Morse and the Murrell-Mottram parameters. In the present analysis, we recall that the van der Waals potential can be generally written as

$$U_{vdW} = U_{\text{repul}} - U_{\text{attr}} \quad (6)$$

in which the repulsive term ( $U_{\text{repul}}$ ) is dominant for  $r \leq r_0$  whilst the attractive term ( $U_{\text{attr}}$ ) becomes significant for  $r > r_0$  whereby a minimum well depth occurs at the equilibrium bond length while the energy diminishes to zero at infinite bond separation. For the case of 2-body bonded cases, we generally encounter the minimum of zero at equilibrium bond length with bond dissociation energy,  $D$ , at atomic separation. Hence

$$U_{2\text{-body}} = U_{\text{repul}} - U_{\text{attr}} + D \quad (7)$$

in order to conform to both the Morse and the 2-body modified Murrell-Mottram potentials, i.e. equations (3) and (5), at  $r = r_0$  and as  $r \rightarrow \infty$ . As such, comparison between equations (3) and (5) can be made by expressing them in the form given by equation (7), i.e.

$$U_M = D_M [\exp(-2\alpha(\delta r)) - 2 \exp(-\alpha(\delta r)) + 1] \quad (8)$$

and

$$U_{MMM} = D_{MM} \left[ (a - 1) \exp \left( -\frac{a}{r_0}(\delta r) \right) - a \frac{r}{r_0} \exp \left( -\frac{a}{r_0}(\delta r) \right) + 1 \right] \quad (9)$$

whereby  $\delta r = r - r_0$  denote the change on bond length. Both equations (8) and (9) exhibit the repulsive and attractive energies in the first and second terms on the RHS, and are thus analogous to equation (7). For long range relationship, we set

$$D_{MM} = D_M \quad (10)$$

in order to allow equal bond dissociation energy. We then recall the Maclaurin's expansion for the following terms:

$$\frac{1}{1-x} = \sum_{m=0}^{+\infty} x^m = 1 + x + x^2 + x^3 + \dots \approx 1 + x \quad (11)$$

and

$$\exp(-x) = \sum_{m=0}^{+\infty} \frac{(-x)^m}{m!} = 1 - \frac{x^1}{1!} + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots \approx 1 - x. \quad (12)$$

Based on equations (11) and (12), substituting

$$\frac{r}{r_0} = 1 + \frac{\delta r}{r_0} \approx \left(1 - \frac{\delta r}{r_0}\right)^{-1} \approx \left[\exp\left(-\frac{\delta r}{r_0}\right)\right]^{-1} = \exp\left(\frac{\delta r}{r_0}\right) \quad (13)$$

into the attractive term of equation (9) leads to

$$U_{\text{MMM}} = D_{\text{MM}} \left[ (a-1) \exp\left(-\frac{a}{r_0}(\delta r)\right) - a \exp\left(-\frac{a-1}{r_0}(\delta r)\right) + 1 \right]. \quad (14)$$

Comparing the coefficients of equations (8) and (14), we have

$$a = 2. \quad (15)$$

Substituting equation (15) into equation (14) and comparing the exponential indices, we note that

$$\frac{1}{r_0} = \alpha. \quad (16)$$

Substituting equations (10) and (15) into equation (9), and applying equation (16) only to the exponential indices, we arrive at

$$U_{\text{MMM}} = D_{\text{M}} \left[ \left(1 - 2\frac{r}{r_0}\right) \exp(-2\alpha(\delta r)) + 1 \right], \quad (17)$$

i.e. the modified Murrell-Mottram potential in terms of Morse parameters.

### 3. Results

For verification, we plot the non-dimensionalized 2-body potential ( $U/D_{\text{M}}$ ) versus the non-dimensionalized interatomic distance ( $r/r_0$ ) for C-H bond and C-C bond in a polymeric chain, based on data by Noid et al. [16], as furnished in table 1. Figure 1 shows the Morse potential curves, and the Murrell-Mottram 2-body potential using Morse parameters on the basis of short range relationship

Table 1  
Potential energy parameters for polyethylene.

Bond type	$\alpha$ (nm <sup>-1</sup> )	$r_0$ (nm)
C-H	17.5	0.109
C-C	19.4	0.153

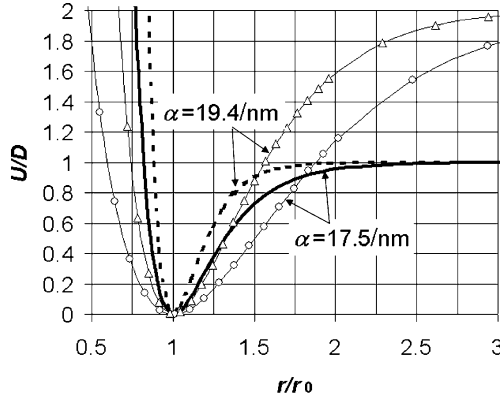


Figure 1. Murrell-Mottram's 2-body approximation to Morse potential short range relationship developed by Lim [7] (bold curves indicate Morse potential, thin curves indicate Murrell-Mottram's 2-body potential).

$$D_{MM} = 2D_M \quad (18)$$

and

$$\alpha = \frac{a}{r_0} \quad (19)$$

as previously obtained [7]. In this short range relationship, we have

$$\begin{aligned} U_M &= U_{MMM} = 0, \\ \frac{\partial U_M}{\partial r} &= \frac{\partial U_{MMM}}{\partial r} = 0, \quad r = r_0, \\ \frac{\partial^2 U_M}{\partial r^2} &= \frac{\partial^2 U_{MMM}}{\partial r^2} \end{aligned} \quad (20)$$

at equilibrium bond length but

$$U_{MMM} = 2U_M, \quad r \rightarrow \infty \quad (21)$$

for bond dissociation [7]. Exact agreement between both potentials at equilibrium bond length enables the overall repulsion and attraction to be observed for

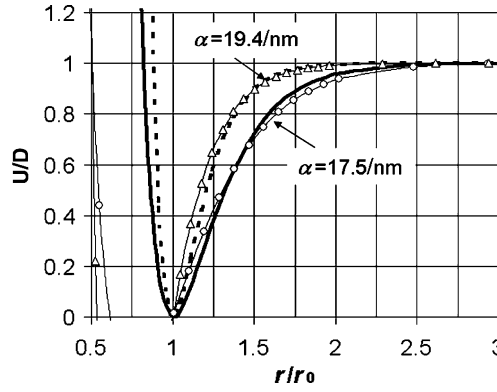


Figure 2. Murrell-Mottram's 2-body approximation to Morse potential long range relationship developed herein. (bold curves indicate Morse potential, thin curves indicate Murrell-Mottram's 2-body potential).

$r < r_0$  and  $r > r_0$ , respectively, as shown in figure 1. The only drawback for the short range relationship lies in cases where the bond length is far from equilibrium, thereby leading to doubling of required energy for bond rupture according to Murrell-Mottram's 2-body potential.

Figure 2 shows the Morse potential curves as before, but with the Murrell-Mottram potential using Morse parameters on the basis of long range relationship proposed herein, as described in equation (17). In this long range relationship, we have

$$\begin{aligned}
 U_M &= U_{MMM} = 0, \\
 \frac{\partial U_M}{\partial r} &\neq \frac{\partial U_{MMM}}{\partial r}, \quad r = r_0 \\
 \frac{\partial^2 U_M}{\partial r^2} &\neq \frac{\partial^2 U_{MMM}}{\partial r^2}
 \end{aligned} \tag{22}$$

at equilibrium bond length, but

$$U_{MMM} = U_M = D_M, \quad r \rightarrow \infty \tag{23}$$

for bond rupture. Gross underestimation of the potential energy occurs for  $r < r_0$  in the Murrell-Mottram's long range approximation to the Morse potential. However, reasonable correlation between both potentials are observed for  $r > r_0$ , and especially so with the increase of interatomic distance, as evident from figure 2.

#### 4. Conclusions

Previous relationship between Murrell-Mottram's 2-body potential and the Morse potential was obtained by equating the potential energy, the slope and the curvature at the bond equilibrium length that leads to valid relationship only at short range interatomic displacement [7]. The present approach of extracting and identifying the repulsive and attractive terms enable long range relationship between these two potentials to be obtained. The long range relationship developed herein between these two potentials gives superior approximation for  $r > r_0$  but inferior correlation for  $r < r_0$ . The presently obtained relationship, together with previously formulated relationship between  $n$ -body ( $n = 2, 3, 4$ ) and non-bonded potential functions [2,3,7,17–21] will be used for refining an existing potential function converter [22,23] to convert parameters from one set of potential function to another set of potentials adopted in computational condensed matter software.

#### References

- [1] J.N. Murrell, S. Carter, S.C. Farantos, P. Huxley and A.J.C. Varandas, *Molecular Potential Energy Functions* (Wiley, New York, 1984).
- [2] T.C. Lim, J. Math. Chem. 31 (2002) 421.
- [3] T.C. Lim, J. Math. Chem. 32 (2002) 249.
- [4] N. Bjerrum, Verhandl. Deut. Physik. Ges. 16 (1914) 737.
- [5] P.M. Morse, Phys. Rev. 34 (1929) 57.
- [6] J.N. Murrell and R.E. Mottram, Mol. Phys. 69 (1990) 571.
- [7] T.C. Lim, J. Math. Chem. 33 (2003) 29.
- [8] I. Dostrovsky, E.D. Hughes and C.K. Ingold, J. Chem. Soc. (1946) 173.
- [9] B.G. Sumpter, D.W. Noid and B. Wunderlich, J. Chem. Phys. 93 (1990) 6875.
- [10] R.E. Tuzun, D.W. Noid and B.G. Sumpter, Nanotechnology 6 (1995) 52.
- [11] R.E. Tuzun, D.W. Noid and B.G. Sumpter, Nanotechnology 6 (1995) 64.
- [12] J.N. Murrell and J.A. Rodriguez-Ruiz, Mol. Phys. 71 (1990) 823.
- [13] A.R. Al-Derzi, R.L. Johnston, J.N. Murrell and J.A. Rodriguez-Ruiz, Mol. Phys. 73 (1991) 265.
- [14] B.R. Eggen, R.L. Johnston, S. Li and J.N. Murrell, Mol. Phys. 76 (1992) 619.
- [15] S. Li, R.L. Johnston and J.N. Murrell, J. Chem. Soc. Faraday Trans. 88 (1992) 1229.
- [16] D.W. Noid, R.E. Tuzun and B.G. Sumpter, Nanotechnology 8 (1997) 119.
- [17] T.C. Lim, J. Math. Chem. 33 (2003) 279.
- [18] T.C. Lim, J. Math. Chem. 34 (2003) 221.
- [19] T.C. Lim, Z. Naturforsch. A 58 (2003) 615.
- [20] T.C. Lim, Z. Naturforsch. A 59 (2004) 116.
- [21] T.C. Lim, Czech. J. Phys. 54 (2004) 553.
- [22] T.C. Lim, MATCH Commun. Math. Comput. Chem. 49 (2003) 155.
- [23] T.C. Lim, MATCH Commun. Math. Comput. Chem. 50 (2004) 185.