Bull. Inst. Chem. Res., Kyoto Univ., Vol. 69, No. 4, 1991.

COMMUNICATION

New Potential Energy Functions Suitable for Computer Simulation

Soichi HAYASHI*

Received September 12, 1991

KEY WORDS: Potential energy/ Morse function/ Computer simulation

Various kinds of formula have been proposed to approximate potential energy as a function of inter-atomic distance. The most commonly used formulae are Morse function[1] for diatomic molecules, and Lenard-Jones[2] and Buckingham[3] types for non-bonded atom-atom or inter-molecular interaction. Recently, computer simulations using these functions of various systems at molecular level are developing, because they give non-experimental information on dynamical and average structures and physical properties. In the interest of computing efficiency, however, these functions are forced to be truncated at a cutoff distance r_c. Because they are not zero at finite distances, some deviation in calculation may be caused by the discontinuity at r_c. To reduce the deviation, the shifted force[4] or switching functions[5] have often been used. In this paper, a series of power formulae, which have no discontinuity at r_c. and an exponential form are proposed to be used as a potential energy function in computer simulation.

Potential energy function and its first derivative are schematically drown in Figure 1. Potential energy is $-D$ at equilibrium distance r_e, and is zero at σ. The potential function proposed is in the form,

$$V=-A_0S_0(1-B\ S_0)^n \qquad S_0\leqq 1/B, \tag{1}$$

and

$$V=0 \qquad S_0>1/B, \tag{2}$$

where $S_0=r-\sigma$, and A_0 and $B(=1/(r_c-\sigma))$ are parameters, and n is an integer. The function and its derivatives up to $(n-1)$th order are also zero at r_c. We describe hereafter the equation in the limit of $S_0\leqq 1/B$, because the function and their derivatives are assumed to be zero over the limit. The first derivative with respect to distance r is given by,

* 林 宗市: Laboratory of Surface Chemistry, Institute for Chemical Research, Kyoto Univ., Uji, Kyoto 611, Japan

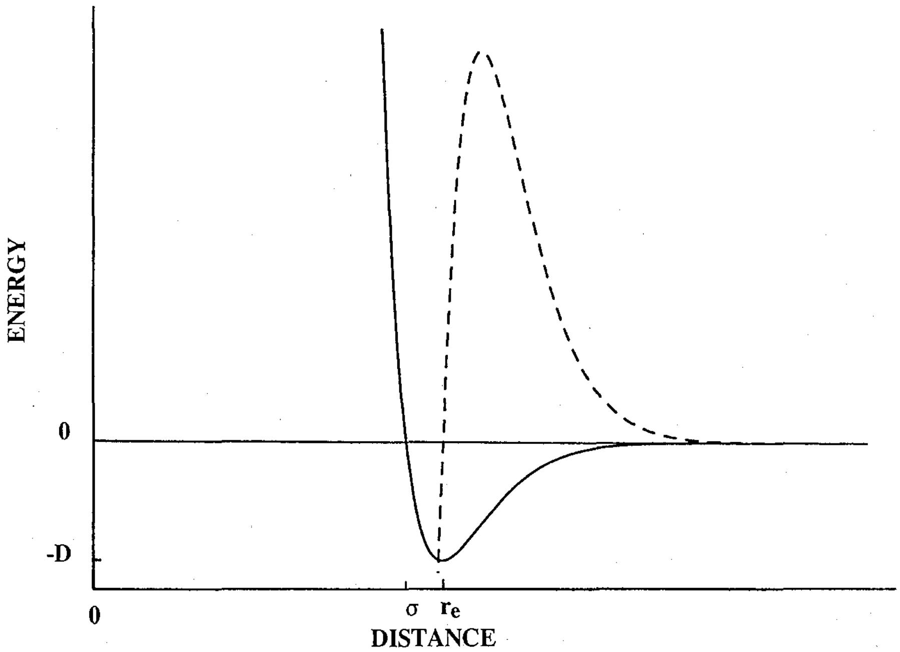

Fig. 1. An example ($r_e=1.12\sigma$, $n=20$) of potential energy functions (solid line) and its first derivative (broken line).

$$\frac{dV}{dr} = A_1 S_1 (1 - B\ S_0)^{n-1}, \tag{3}$$

where

$$A_1 = (n+1)\ A_0\ B, \tag{4}$$

and

$$S_1 = S_0 - \frac{1}{(n+1)B.} \tag{5}$$

From the condition that the function is $-D$ at r_e and its first derivative at r_e and r_c are zero, there is obtained

$$A_0 = D\left(\frac{n+1}{n}\right)^n \frac{1}{r_e - \sigma,} \tag{6}$$

$$B = \frac{1}{(n+1)(r_e - \sigma)}, \tag{7}$$

and

$$r_c = (n+1)(r_e - \sigma) + \sigma. \tag{8}$$

Finally, the general formula of a series of power forms is expressed as,

$$V = -D\left(\frac{n+1}{n}\right)^n \frac{r-\sigma}{r_e-\sigma}\left(1 - \frac{r-\sigma}{(n+1)(r_e-\sigma)}\right)^n \tag{9}$$

The mth derivatives are written as,

$$\frac{d^m V}{dr^m} = (-1)^{m+1} A_m S_m\ (1 - B\ S_0)^{n-m}, \tag{10}$$

where

$$A_m = \frac{(n+1)!}{(n+1-m)!} A_0\ B^m, \tag{11}$$

and

$$S_m = S_0 - \frac{m}{(n+1)B}. \tag{12}$$

The force constant k, the second derivative of the function at r_e, is

$$k = \frac{n+1}{n} D \frac{1}{(r_e-\sigma)^2}. \tag{13}$$

The function vary with n as some examples shown in Fig. 2. The limit approaching infinity of n becomes to the following exponential form,

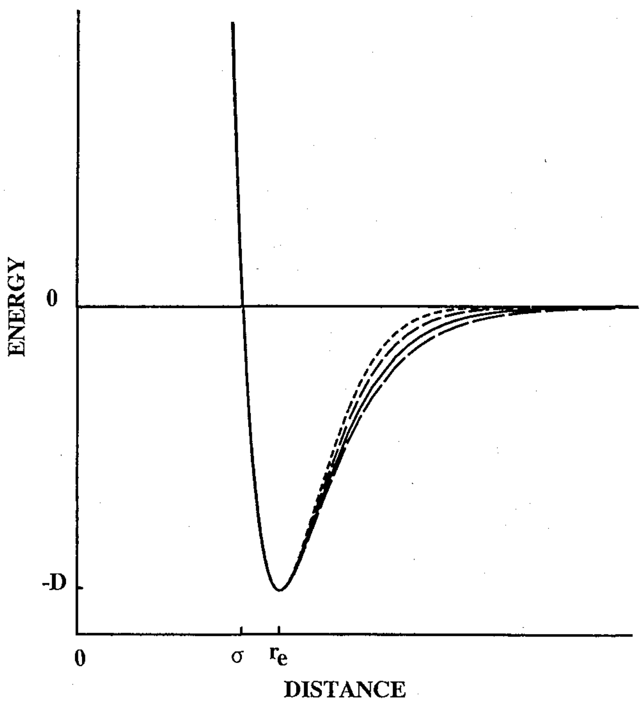

Fig. 2. Comparison among potential energy functions. From the top, a power form ($n=10$), another power form ($n=20$), exponential form, and Morse function.

$$V = -D\ C\ S_0 \exp(1 - C\ S_0). \tag{14}$$

The first derivative is

$$\frac{dV}{dr} = D\ C^2\ S_1 \exp(1 - C\ S_0), \tag{15}$$

in which

$$S_1 = S_0 - \frac{1}{C}. \tag{16}$$

The mth derivative is simply

$$\frac{d^m V}{dr^m} = (-C)^{m+1}\ D\ S_m \exp(1 - C\ S_0), \tag{17}$$

where

$$S_m = S_0 - \frac{m}{C}, \tag{18}$$

and

$$C = \frac{1}{r_e - \sigma}. \tag{19}$$

The force constant k become

$$k = D\ C^2. \tag{20}$$

The exponential form can also be expressed as,

$$V = -D \frac{r - \sigma}{r_e - \sigma} \exp\left(\frac{r_e - r}{r_e - \sigma}\right). \tag{21}$$

The proposed formulae are simple, and their derivatives have the similar form. The function of power form, as well as its derivatives, converges quite sommthly to zero at r_c, and then dose not show discontinuity. The proposed function of exponential form and its derivatives approach more quickly to zero than commonly used functions. The functions, especially the exponential form, resemble Morse function, and then may be used to approximate potential energy for a stretching coordinate. Although the exponential form is not zero at a finite distance, this functions and its derivative approach more quickly to zero than Morse functions.

The attractive part of non bonded potential is usually expressed by a term of minus sixth power of distance. The proposed potential functions are more close to that having larger number in inverse power of distance. Comparison in merit between proposed potential functions and truncated form of popular formula may depend on kind of system and property to be obtained.

Thanks are due to Professor K. Machida, Faculty of Pharmaceutical Science, Kyoto University and Dr. Y. Kataoka, Faculty of Science, Kyoto University for valuable discussions.

REFERENCES

(1) P. Morse, *Phys. Rev.*, **34**, 57 (1929).

(2) J. E. Lenard-Jones, *Proc. Roy. Soc.* (London), **A106**, 463(1924).

(3) R. A. Buckingham, *Proc. Roy. Soc.* (London), **A168**, 264(1938).

(4) W. B. Street, D. J. Tildesley, and G. Saville, "Computer Modeling of Matter" edited by P. Lykos, ACS Symposium series,(1978), p. 144.

(5) A. Ben-Naim, and F. H. Stillinger, "Structure and Transport Processes in Water Aqueous Solution" edited by R. A. Horne, Wiley-Interscience, New York, (1972), p. 144.