ORIGINAL PAPER

Split series potential energy function

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Abstract A split series potential energy function is developed herein such that it can be primarily reduced into generalized forms of Lennard-Jones, Morse, Buckingham, Linnett, and anything in between them by altering the type-parameters. Unlike the previous approach whereby the type-parameters act as weighting parameter between the inverse power and the exponential decay terms, the current approach attaches the type-parameters as indices to the denominator of every summation term. A change of the index shifts the series summation to mimic a curve that is representative of an inverse power, an exponential index, or a weighted proportion between the two. Comparison with the Lennard-Jones (12–6) and Exponential-6 (both $\xi = 13.772$ and $\xi = 12$) in the case of uncharged non-bonded interactions by using type-parameters $(p, q) = (0, 0)$ and $(p, q) = (1, 0)$ respectively in the model gives very good correlation. Comparison with the Morse potential in the case of bonded interaction by using $(p, q) = (1, 1)$ gives excellent agreement. All results show that the use of only five expansion terms is sufficient for providing good agreement with the classical potentials. Better fit to experimental data and ab initio results are expected with the incorporation of coefficients in every term of the series expansion. The proposed model is useful for modeling the transition state from solid to fluid and vice versa.

Keywords Generalized potential function · Series expansion · Type-parameters

1 Introduction

There exists a class of potential energy functions in which substitution of numerical values into one or two of the parameters reduce the potential function into specific

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potentials. The former is generalized in two ways: (i) they possess additional parameters, and (ii) the specific potential energy functions reduced from each generalized potential are distinct. An example of such a general potential function is

$$U = C_0 \lambda^2 \left(1 + \sum_{i=1}^{\infty} C_i \lambda^i \right) \tag{1}$$

in which the function λ has been given by Thakkar [1] and Molski [2] as

$$\lambda = sign(p) \left[1 - \left(\frac{R}{r} \right)^p \right] \tag{2}$$

and

$$\lambda = \frac{r - R}{ar + (1 - a)R} \tag{3}$$

respectively. Substitution of $p = -1$ and $p = 1$ into Eq. (2) reduces Eq. (1) into the Dunham [3,4] and the Simons–Parr–Finlan (SPF) [5] potentials respectively, while substitution of $a = 0$, $a = 1$ and $a = 0.5$ into Eq. (3) reduces Eq. (1) into the Dunham [3,4], SPF [5] and Ogilvie [6] potentials respectively. Here, the type-parameters p and a, corresponding to Eqs. (2) and (3) respectively, shift the weighting of Eq. (1) in a one-dimensional manner. A generalized potential energy function that possesses two type-parameters, for enabling two-dimensional weight shifting, was proposed by Lim [7] as

$$\frac{U_F}{D} = \frac{n^x \xi_2^{1-x}}{m^y \xi_1^{1-y} - n^x \xi_2^{1-x}} \left(\frac{R}{r} \right)^{my} \exp \left[\xi_1 \left(1 - \frac{r}{R} \right) (1 - y) \right]$$
$$- \frac{m^y \xi_1^{1-y}}{m^y \xi_1^{1-y} - n^x \xi_2^{1-x}} \left(\frac{R}{r} \right)^{nx} \exp \left[\xi_2 \left(1 - \frac{r}{R} \right) (1 - x) \right] \tag{4}$$

such that substitution of $(x, y) = (0,0)$, $(1,1)$, $(1,0)$ and $(0,1)$ reduce Eq. (4) into generalized forms of Lennard-Jones [8], Morse [9], Buckingham [10] and Linnett [11,12] functions respectively. Recently it has been shown that Eq. (4), even with simplifying assumptions of $\xi_1 = m$, $\xi_2 = n$ and $x = y = 0.5$, can be parameterized to fit both interatomic bond energy and intermolecular interaction energy [13]. Empirical functions reduced from Eq. (4) are easily executed but the assumption of a single functional form produces important deviation of the "true" potential-energy function, unlike the power-series expansions [14]. The latter gives very accurate potential-energy curve close to the minimum zone. In order to reap the benefit of both systems of potential energy functions, Huffaker [15–17] proposed a potential of the form shown in Eq. (1) with

$$\lambda = 1 - e^{-\alpha(r-R)}. \tag{5}$$

This function reduces Eq. (1) to the Morse potential when $C_i = 0$ for $i > 0$. In this paper, the potential function given in Eq. (4) is converted into a series expansion such that series coefficients can be incorporated to allow greater flexibility in curve-fitting to spectroscopic data and/or *ab initio* results.

2 Analysis

The terms (R/r) and $\exp(1 - (r/R))$ can be expressed in power-series by invoking the Maclaurin series expansion as

$$\frac{R}{r} = \frac{1}{1 - [1 - (r/R)]} = \sum_{h=0}^{\infty} (1 - (r/R))^h \tag{6}$$

and

$$e^{1-\frac{r}{R}} = \sum_{h=0}^{\infty} \frac{(1 - (r/R))^h}{h!} \tag{7}$$

respectively. Both series can be generalized as

$$S = \sum_{h=0}^{\infty} \frac{(1 - (r/R))^h}{(h!)^t} \tag{8}$$

whereby substituting $t = 0$ and $t = 1$ reduce Eq. (8) into Eqs. (6) and (7) respectively. Having demonstrated that the assumption

$$\begin{Bmatrix} \xi_1 \\ \xi_2 \end{Bmatrix} = \begin{Bmatrix} m \\ n \end{Bmatrix} \tag{9}$$

is valid [13], we herein consider the simplified version of Eq. (4)

$$\frac{U}{D} = \frac{n}{m-n} \left(\frac{R}{r}\right)^{my} e^{m(1-\frac{r}{R})(1-y)} - \frac{m}{m-n} \left(\frac{R}{r}\right)^{nx} e^{n(1-\frac{r}{R})(1-x)}. \tag{10}$$

Since

$$\left(\frac{R}{r}\right)^Z = \left(\sum_{h=0}^{\infty} (1 - (r/R))^h\right)^Z \tag{11}$$

and

$$e^{Z(1-\frac{r}{R})} = \left(\sum_{h=0}^{\infty} \frac{(1 - (r/R))^h}{h!}\right)^Z \tag{12}$$

	x	y	p	q
Lennard-Jones	1	1	0	0
Morse	0	0	1	1
Buckingham	1	0	1	0
Linnett	0	1	0	1

Table 1 Comparison between the type-parameters of Lim [7] and the present paper

then

$$\frac{U}{D} = \frac{n}{m-n} \left(\sum_{i=0}^{\infty} \frac{(1-(r/R))^i}{(i\,!)^p} \right)^m - \frac{m}{m-n} \left(\sum_{j=0}^{\infty} \frac{(1-(r/R))^j}{(j\,!)^q} \right)^n \quad (13)$$

whereby $m > n$ such that substitution of $p = q = 0$, $p = q = 1$, $p = q + 1 = 1$ and $p + 1 = q = 1$ reduce Eq. (13) to the generalized power-series forms of the Lennard-Jones, Morse, Buckingham and Linnett potential energy functions respectively. A comparison between the previous general model, Eqs. (4) or (10), with the present model, Eq. (13), is shown in Table 1. It should be cautioned that the relation between the type-parameters (x, y) of Eqs. (4) or (10) with the type-parameters (p, q) of Eq. (13) is neither the switching between "0" and "1" as shown in the first two rows of Table 1, nor the direct transpose of (x, y) to (p, q) as shown in the last two rows of the same table. See Fig. 1a, b. Rather, the relations are

$$p + y = 1 \quad (14)$$

and

$$q + x = 1 \quad (15)$$

or as schematically depicted in Fig. 1c, whereby the Morse and LJ potentials coincide with the origins of the (x, y) and (p, q) axes respectively.

Equation (13) can be made more versatile for curve-fitting all neutral interatomic and intermolecular interaction energy by introducing coefficients c_i and c_j to give

$$\frac{U}{D} = \frac{n}{m-n} \left(\sum_{i=0}^{\infty} c_i \frac{(1-(r/R))^i}{(i\,!)^p} \right)^m - \frac{m}{m-n} \left(\sum_{j=0}^{\infty} c_j \frac{(1-(r/R))^j}{(j\,!)^q} \right)^n . \quad (16)$$

The coefficients are ideally 1 if Eq. (16) were to be reduced to any of the 4 classical empirical functions. Hence any deviation of c_i and c_j from 1 provide a set of numerical values upon which the classical potential function deviates from true potential energy function. In the following sections, we let $c_i = c_j = 1$ in order to assess the required number of summation terms for Eq. (13) to realistically align with the empirical functions.

Fig. 1 Interconnections between the Lennard-Jones, Morse, Buckingham and Linnett potentials within the framework of (**a**) Eqs. (4) or (10), (**b**) Eq. (13), and (**c**) the type-parameter relationship between the (x, y) and (p, q) systems
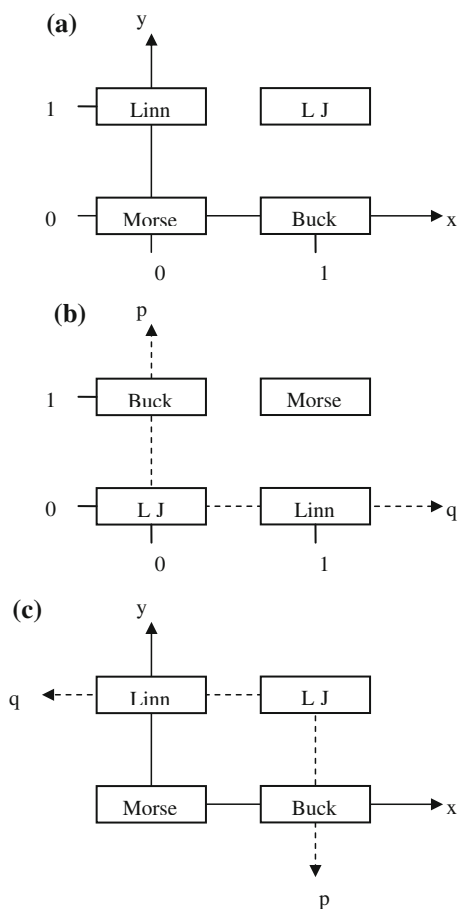

3 Non-bonded interactions

In this section an assessment on the required number of summation terms is made for the case of van der Waals interaction using the conventional Lennard-Jones potential

$$\frac{U_{LJ}}{D} = \left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^{6}, \tag{17}$$

which is commonly used for molecular mechanics computation [18–26]. Equation (13) was computed using $m = 2n = 12$ and $p = q = 0$, i.e.

$$\frac{U}{D} = \left(\sum_{i=0}^{k}\left(1 - \frac{r}{R}\right)^{i}\right)^{12} - 2\left(\sum_{j=0}^{k}\left(1 - \frac{r}{R}\right)^{j}\right)^{6}. \tag{18}$$

Fig. 2 Deviation of the split series potential from the conventional Lennard-Jones function
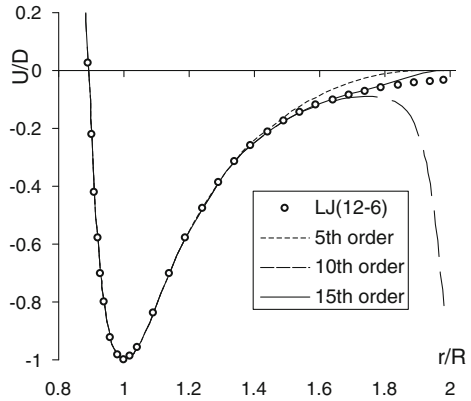
for $i = j$ terminating in multiples of 5. Figure 2 shows the plot of the conventional Lennard-Jones potential and that of Eq. (18) with order number $k = 5, 10, 15$. Deviation of the latter from the former is observed from r/R=1.4, 1.6 and 1.8 for k=5, 10 and 15 respectively.

An alternative form for quantifying van der Waals interaction is the Exponential-6 function [26–32]

$$U_{X6} = Ae^{-Br} - \frac{C}{r^6},\tag{19}$$

which is a specific case of the Buckingham potential. In addition to the form shown in Eq. (19), the Exponential-6 function has also been used in its loose form [26]

$$\frac{U_{X6}}{D} = \frac{6}{\xi - 6}e^{\xi(1-\frac{r}{R})} - \frac{\xi}{\xi - 6}\left(\frac{R}{r}\right)^6.\tag{20}$$

For comparison, Eq. (13) was computed with $n = 6$, $m = \xi$, $p = 1$ and $q = 0$, i.e.

$$\frac{U}{D} = \frac{6}{\xi - 6}\left(\sum_{i=0}^{k}\frac{(1 - (r/R))^i}{i!}\right)^\xi - \frac{\xi}{\xi - 6}\left(\sum_{j=0}^{k}\left(1 - \frac{r}{R}\right)^j\right)^6\tag{21}$$

with order number $k = 5, 10, 15$. Figure 3 shows the plot of Eqs. (20) and (21) with $\xi = 12$ for coinciding with the conventional Lennard-Jones function at long range, while Fig. 4 corresponds to the case of $\xi = 13.772$ for coinciding with the conventional Lennard-Jones potential near the minimum well-depth. Deviation of Eq. (21) from the Exponential-6 function is observed from $r/R = 1.4$, 1.6 and 1.8 onwards for $k = 5$, 10 and 15 respectively.

Plots of conventional van der Waals potential functions with the split series potential reveal three observations, the most obvious being the fact that deviation of the split-series potential from the classical potential is delayed for higher order. The second observation, which is glaringly evident in Figs. 2, 3, 4, is that lower order split-series

Fig. 3 Deviation of the split series potential from the Exponential-6 function with $\xi = 12$
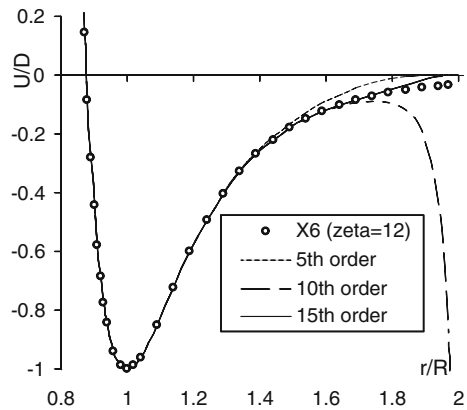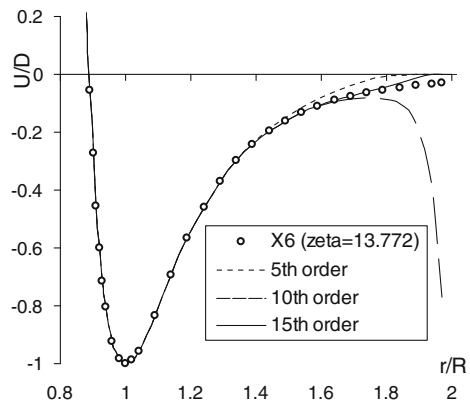

Fig. 4 Deviation of the split series potential from the Exponential-6 function with $\xi = 13.772$


potentials do not necessarily give bad correlation. This can be seen upon comparing plots where $k = 5$ and $k = 10$. Although plots with $k = 5$ deviate earlier, they are better than those with $k = 10$ as the latter give highly divergent result from $r/R = 1.7$ onwards. The third observation is that the higher orders do not necessarily provide convergence. This can be seen by comparing split-series potential plots with $k = 5$ and $k = 15$, whereby the former converges while the latter diverges. Hence the use of fifth order would be sufficiently accurate provided that the coefficients c_i and c_j are incorporated to minimize any error from the actual potential energy.

4 Bonded interactions

In this section, an assessment on the required number of summation terms is made for the category of covalent bonds using the conventional Morse potential [9,18,26,23,33]

$$U_{\text{Morse}} = D \left(1 - e^{-\alpha(r-R)}\right)^2. \tag{22}$$

Fig. 5 No observable deviation of the split-series potential from the Morse function within short range
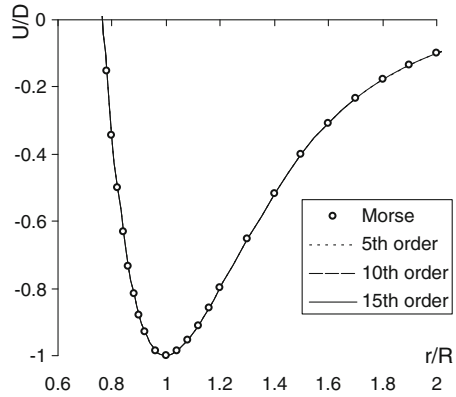
An alternate form is given as

$$U_M = U_{\text{Morse}} - D = D\left(e^{-2\alpha(r-R)} - 2e^{-\alpha(r-R)}\right) \tag{23}$$

or, in dimensionless groups,

$$\frac{U_M}{D} = e^{2\alpha R\left(1-\frac{r}{R}\right)} - 2e^{\alpha R\left(1-\frac{r}{R}\right)}. \tag{24}$$

To cater for the Morse potential, Eq. (1) was computed with $m = 2n = 2\alpha R$ and $p = q = 1$, i.e.

$$\frac{U}{D} = \left(\sum_{i=0}^{k}\frac{(1-(r/R))^i}{i!}\right)^{2\alpha R} - 2\left(\sum_{j=0}^{k}\frac{(1-(r/R))^j}{j!}\right)^{\alpha R} \tag{25}$$

for $k = 5, 10, 15$. Based on the parameters $\alpha = 1.94/\overset{\text{O}}{\text{A}}$ and $R = 1.53\,\overset{\text{O}}{\text{A}}$ used by Noid et al. [34] for C-C covalent bond in polymeric chains, we have the dimensionless parameter $\alpha R = 2.9682$. The C-C bond energy according to the Morse potential, Eq. (24), and the split-series potential with $k = 5, 10, 15$ are plotted in Fig. 5. All three curves adhere to the Morse potential based on the short range to intermediate range shown. To observe the convergence of the three split-series plots, the bond length range is widened up to $r/R = 6$, as shown in Fig. 6. Here, the plot with $k = 10$ reveals divergence while convergence is seen for $k = 5$ and $k = 15$. Further observation by zooming into the energy range of $-0.006 \le (U/D) \le 0$, as shown in Fig. 7, reveals that the lowest order in comparison ($k = 5$) exhibits discrepancies well before the next comparative order ($k = 10$) does.

As with the case of non-bonded interaction, three major observations can be obtained for the case of bonded interaction. An obvious observation is that convergence is not dependent on the magnitude of the order. A less obvious observation is that deviation from the empirical potential is delayed for higher orders. It follows that for

Fig. 6 No observable deviation
of the split-series potential from
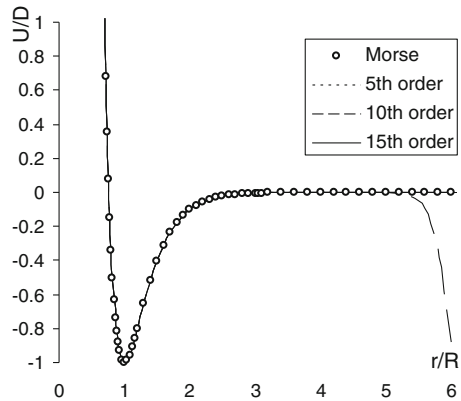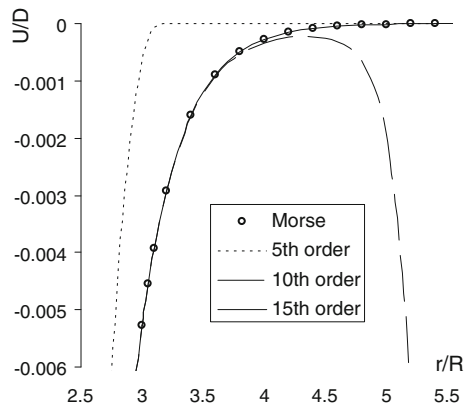the Morse function at long range

Fig. 7 Zoom in view for
observable deviation of the
split-series potential from the
Morse function

divergent split-series potentials with sufficiently high order (i.e. $k = 10$ in this case), implementation of a cut-off point would suffice for practical applications.

Notwithstanding its low popularity in comparison with the Lennard-Jones, Morse and Buckingham potentials, the Linnett potential is nevertheless suitable for accurate representation for limited cases of interatomic potential energy. For completeness' sake, Eq. (13) can be reduced to the Linnett potential via substitution of $p = 0$ and $q = 1$ to give

$$\frac{U}{D} = \frac{n}{m-n}\left(\sum_{i=0}^{k}\left(1-\frac{r}{R}\right)^i\right)^m - \frac{m}{m-n}\left(\sum_{j=0}^{k}\frac{(1-(r/R))^j}{(j\,!)^q}\right)^n \tag{26}$$
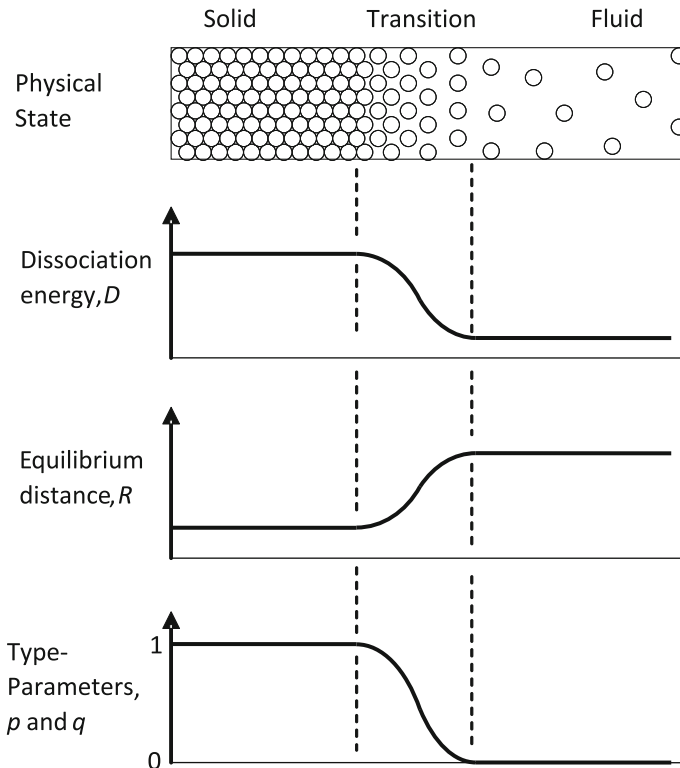
where $m > n > 0$.

Fig. 8 Schematic for the importance of type-parameter transition

5 Applications

The type-parameters enable the switching from one group of potentials that are normally used for describing bonded interactions to another group of potentials that is normally used for describing non-bonded interactions. An example is illustrated in Fig. 8 whereby a solid undergoes transition into a fluid. It is well known that the dissociation energy is high for bonded interaction but low for non-bonded interaction between two particles, while the equilibrium distance (the distance at which the potential energy is at the well-depth's minimum) is shorter for bonded interaction but longer for non-bonded interaction. In addition, there is a preferential switch from a potential that is normally used for quantifying bonded interactions, such as Morse potential function, to a potential that is normally used for quantifying non-bonded interactions, such as Lennard-Jones potential function, during a solid-to-fluid transition. It follows that gradual shifts in the dissociation energy, equilibrium distance and type-parameters occur during transition. While gradual shifting of dissociation energy and equilibrium length can be implemented in other potentials, the advantage of the proposed potential is its flexibility of allowing more parameters to be gradually altered, including the shift from a "bonded potential" to a "non-bonded potential". With reference to the example shown in Fig. 8, the transition from solid to fluid can

be implemented, in addition to shift in dissociation energy and equilibrium distance, by a gradual shift of $p = q = 1$ (Morse) to $p = q = 0$ (Lennard-Jones).

In addition to the above-mentioned transition that occurs throughout the entire material, the implementation of gradual shift in potential function parameters can also be used for solids that gradually undergo atomization from the surface toward the core, or in the case of saturated liquid that undergoes nucleation and subsequent crystal growth.

6 Conclusions

A split-series potential energy function has been developed herein to mimic the empirical potential energy functions of Lennard-Jones, Morse, Buckingham and Linnett, and at the same time possesses the flexibility of the Dunham, SPF, Ogilvie and other power-series expansions. Based on the present results, the use of 5th order series would suffice for both bonded and non-bonded interactions provided that suitable coefficients are implemented. It is of interest to note that the split-series potential function resembles the Dunham potential when the repulsive index is zero. This implies that the split-series coefficients are hinged at $c_i = c_j = 1$ when the split-series potential is to be related to the four classical empirical potentials considered herein, but no such pattern exists for the coefficients of Dunham or any other power-series potential. As such, the magnitudes $|c_i - 1|$ and $|c_j - 1|$ offer a glimpse on the deviation of the empirical potentials from the "true" potential energy function.

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