AN INTERATOMIC POTENTIAL FOR SATURATED HYDROCARBONS BASED ON THE MODIFIED EMBEDDED-ATOM METHOD

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Abstract

In this work, we developed an interatomic potential for saturated hydrocarbons using the modified embedded-atom method (MEAM), a semi-empirical many-body potential based on density functional theory and pair potentials. We parameterized the potential by fitting to a large experimental and first-principles (FP) database consisting of 1) bond distances, bond angles, and atomization energies at 0 K of a homologous series of alkanes and their select isomers from methane to \textit{n}-octane, 2) the potential energy curves of \textit{H}_2, \textit{CH}, and \textit{C}_2 diatomics, 3) the potential energy curves of hydrogen, methane, ethane, and propane dimers, i.e., \((\text{H}_2)_2\), \((\text{CH}_4)_2\), \((\text{C}_2\text{H}_6)_2\), and \((\text{C}_3\text{H}_8)_2\), respectively, and 5) pressure-volume-temperature \textit{(PVT)} data of a dense high-pressure methane system with the density of 0.5534 g/cc. We compared the atomization energies and geometries of a range of linear alkanes, cycloalkanes, and free radicals calculated from the MEAM potential to those calculated by other commonly used potentials for hydrocarbons, i.e., second-generation reactive empirical bond order (REBO) and reactive force field (ReaxFF). MEAM reproduced the experimental and/or FP data with great accuracy, comparable to or better than REBO or ReaxFF. The experimental \textit{PVT} data for a relatively large series of methane, ethane, propane, and butane systems with different densities were predicted reasonably well by MEAM. Although the MEAM formalism has been applied to atomic systems with predominantly metallic bonding in the past, the current work demonstrates the promising extension of the MEAM potential to covalently bonded molecular systems, specifically saturated hydrocarbons and saturated hydrocarbon-based polymers. The MEAM potential has already been parameterized for a large number of metallic unary, binary, ternary, carbide, nitride, and hydride systems, and extending it to saturated hydrocarbons provides a reliable and transferable potential for atomistic/molecular studies of complex material phenomena involving hydrocarbon-metal or polymer-metal interfaces, polymer-metal nanocomposites, fracture and failure in hydrocarbon-based polymers, etc. The latter is especially true since MEAM is a reactive potential that allows for dynamic bond formation and bond breaking during simulation. However, it is important to note that the current parameterization does not accurately reproduce the energetics and structures of unsaturated hydrocarbons and, therefore, should not be applied to such systems.
1 Introduction

The embedded-atom method (EAM), developed by Daw and Baskes [1, 2] in the early 1980s, is a semi-empirical N-body potential useful for the atomistic simulations of metal systems. It has successfully been utilized to calculate the energetics and structures of complex metallic systems involving free surfaces, defects, grain boundaries, etc [3]. The potential was later modified by Baskes [4, 5] to include the directionality of bonding in covalent materials such as silicon and germanium [6], leading to the modified embedded-atom method (MEAM) [5] introduced in 1992. It has undergone several modifications and enhancements since then to include, for example, second nearest-neighbor interactions [7, 8, 9] and, more recently, a multi-state formalism [10]. The unique feature of the MEAM formalism is its ability in reproducing the physical properties of a large number of fcc [9, 11], bcc [8, 12], hcp [13, 14], and diamond cubic [15] crystal structures in unary, binary, ternary, and higher order [16] metal systems with the same semi-empirical formalism. MEAM is also both reliable and transferable [17] in the sense that it accurately reproduces the physical properties of the element or alloy (reliability) and performs reasonably well under circumstances other than the ones used for its parameterization (transferability) [17]. Horstemeyer [18] has an excellent review of the MEAM potential in the context of a multi-scale modeling methodology (integrated computational materials engineering) for metals.

The MEAM formalism has traditionally been used for pure metals and impurities, binary and ternary alloys, and carbide, nitride, and hydride metal systems with great success [19]. In addition, complex nanostructured systems have been studied using various MEAM-based potentials. For example, Xiao et al. [20] calculated the interaction of carbon nanotubes with nickel (Ni) nanoparticles, and Uddin et al. [21] recently studied the mechanical properties of carbon nanotube-Ni composites using the MEAM potential. We extend the MEAM formalism in the current paper to saturated hydrocarbons with the ultimate aim of capturing the energetics and geometries of commercially important hydrocarbon-based polymers (polyolefins), such as polyethylene and polypropylene. Currently, potentials such as MM3 [22, 23, 24], MM4 [25], DREIDING [26], first- [27] and second-generation reactive empirical bond order (REBO) [28], reactive force field (ReaxFF) [29], and condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) [30] are used for hydrocarbon simulations, but they are often either not suitable for hydrocarbon-metal systems or are not parameterized for such multi-component systems. In addition, of this list only REBO and ReaxFF allow for bond breaking. In this paper, we developed a new set of parameters within the MEAM framework to describe the interactions and equilibrium geometries of saturated hydrocarbons, specifically bond distances, bond angles, and atomization energies at 0 K. We show that MEAM gives a comparable or more accurate reproduction of these properties relative to experimental and first-principles (FP) data in comparison with REBO and ReaxFF. We also reproduce the potential energy curves of H2, CH, and C2 diatomics and (H2)2, (CH4)2, (C2H6)2, and (C3H8)2 dimer configurations and predict the pressure-volume-temperature (PVT) relationships of a series of select methane, ethane, propane, and butane systems in a reasonable agreement with the experimental data. The development of the first MEAM-based interatomic potential for saturated hydrocarbons and hydrocarbon-based polymers is a step towards reliably simulating systems and phenomena that have hitherto been difficult to study, such as reactive multicomponent (organics/metal) systems, polymer-metal interfaces and nanocomposites, fracture and crack growth in polymers, etc.

This paper is organized in the following manner. In Section 2 the theory of the MEAM formalism is reviewed. In Section 3 the potential development and parameterization is described. The results are given in Section 4.
2 Modified Embedded-Atom Method Formulation

In the EAM and MEAM formalisms \[1, 2, 5\] the total energy of a system of like atoms \((E_{tot})\) is given by

\[
E_{tot} = \sum_i F_{\tau_i}(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} S_{ij} \varphi_{\tau_i\tau_j}(R_{ij}) ,
\]

(1)

where \(F_{\tau_i}\) is the embedding energy function for element type \(\tau_i\), which is defined as the energy required to embed an atom of element type \(\tau_i\) in the background electron density \(\bar{\rho}_i\) at site \(i\). \(S_{ij}\) is the screening factor between atoms at sites \(i\) and \(j\) (defined in Eqs. \[25\] and \[28\]), and \(\varphi_{\tau_i\tau_j}\) is the pair interaction between atoms of element types \(\tau_i\) and \(\tau_j\) at sites \(i\) and \(j\) at the separation distance of \(R_{ij}\). To emphasize the multi-component nature of the model, the element type of the atom at site \(i\) is denoted as \(\tau_i\) in this manuscript to distinguish it from site designation \(i\), and the screening factor is explicitly separated from the pair potential. The embedding function is given by the specific simple form

\[
F_{\tau_i}(\bar{\rho}_i) = \begin{cases} 
A_{\tau_i} E_{\tau_i}^0 \left( \frac{\sqrt{\bar{\rho}_i^{0\tau_i}}}{\bar{\rho}_i^{0\tau_i}} \ln \frac{\bar{\rho}_i^{0\tau_i}}{\bar{\rho}_i^{0\tau_i}} \right) & \text{if } \bar{\rho}_i^{0\tau_i} \geq 0 \\
-A_{\tau_i} E_{\tau_i}^0 \left( \frac{\sqrt{\bar{\rho}_i^{0\tau_i}}}{\bar{\rho}_i^{0\tau_i}} \right) & \text{if } \bar{\rho}_i^{0\tau_i} < 0
\end{cases}
\]

(2)

where \(A_{\tau_i}\) is a scaling factor, \(E_{\tau_i}^0\) is the sublimation (cohesive) energy, and \(\bar{\rho}_i^{0\tau_i}\) is the background electron density for the reference structure of the atom of element type \(\tau_i\) at site \(i\). For most cases, the reference structure is the equilibrium structure of the element in its reference state. However, the reference structure of carbon is taken as diamond. We will denote the properties of the equilibrium reference state with a superscript zero. The analytic continuation of the embedding function for negative electron densities was considered as a computational convenience to prevent systems from entering this unphysical regime. The origin of negative electron densities arises below in Eq. \[8\]. The MEAM formalism introduces directionality in bonding between atoms through decomposing \(\bar{\rho}_i\) into spherically symmetric \((\rho_i^{(0)})\) and angular \((\rho_i^{(1)}, \rho_i^{(2)}, \text{and } \rho_i^{(3)})\) partial electron densities \[5, 19, 31\] as given by

\[
\rho_i^{(0)} = \sum_{j \neq i} S_{ij} \rho_i^{a(0)}(R_{ij}) ,
\]

(3)

\[
\left( \rho_i^{(1)} \right)^2 = \sum_{j \neq i} \left[ \frac{R_{ij} \sum_{\alpha} \rho_i^{a(1)}(R_{ij})}{S_{ij} \left( \tau_j^{(1)} \right)^2 \rho_{\tau_j}(R_{ij})} \right] \rho_i^{(0)} ,
\]

(4)

\[
\left( \rho_i^{(2)} \right)^2 = \sum_{j \neq i} \left[ \frac{R_{ij} \sum_{\alpha,\beta} \rho_i^{a(2)}(R_{ij})}{S_{ij} \left( \tau_j^{(2)} \right)^2 \rho_{\tau_j}(R_{ij})} \right] \rho_i^{(0)} ,
\]

(5)

\[
\left( \rho_i^{(3)} \right)^2 = \sum_{j \neq i} \left[ \frac{R_{ij} \sum_{\alpha,\beta,\gamma} \rho_i^{a(3)}(R_{ij})}{S_{ij} \left( \tau_j^{(3)} \right)^2 \rho_{\tau_j}(R_{ij})} \right] \rho_i^{(0)} .
\]

(6)
The atomic electron densities for element type \( \tau \) is calculated from

\[
\bar{\rho}_i = \rho_i^{(0)} G(\Gamma_i) ,
\]

\[
G(\Gamma_i) = \begin{cases} 
\sqrt{1 + \Gamma_i} & \text{if } \Gamma_i \geq -1 \\
-\sqrt{1 + \Gamma_i} & \text{if } \Gamma_i < -1
\end{cases} ,
\]

\[
\Gamma_i = \sum_{h=1}^{3} \tilde{t}_i^{(h)} \left[ \frac{\rho_i^{(h)}}{\rho_i^{(0)}} \right]^2 ,
\]

\[
\tilde{t}_i^{(h)} = \frac{1}{\rho_i^{(0)}} \sum_{j \neq i} \tilde{t}_j^{(h)} \rho_{\tau_j}^{(0)} S_{ij} .
\]

In the absence of angular contributions to the density, \( \Gamma_i = 0 \), \( G(\Gamma_i) = 1 \), and the model reduces to the EAM formalism. For systems with negative \( \tilde{t}_i^{(h)} \) values in certain geometries, \( \Gamma_i < -1 \), and for computational convenience we perform an analytic continuation of \( G(\Gamma_i) \). We choose to do this by allowing \( G(\Gamma_i) \) and hence \( \bar{\rho}_i \) to become less than zero.

If we apply Eqs. 7 and 9 to the equilibrium reference structure, we obtain

\[
\bar{\rho}_\tau^0 = Z_\tau^0 \rho_\tau^0 G(\Gamma_\tau^0) ,
\]

\[
\Gamma_\tau^0 = \sum_{h=1}^{3} \tilde{t}_\tau^{(h)} s_\tau^{(h)} \left( \frac{1}{Z_\tau^0} \right)^2 .
\]

where we have assumed that the reference structure has only first nearest-neighbor interactions. In Eq. 11 \( \rho_\tau^0 \) is an element-dependent electron density scaling factor, and \( Z_\tau^0 \) is the first nearest-neighbor coordination number of the reference structure. \( s_\tau^{(h)} (h = \{1, 2, 3\}) \) are “shape factors” that depend on the reference structure for element type \( \tau \). The shape factors are given in the original MEAM paper by Baskes [5]. The atomic electron density for element type \( \tau \) is calculated from

\[
\rho_\tau^{(h)}(R) = \rho_\tau^0 e^{-\beta_\tau^{(h)} \left( \frac{R}{R_\tau^0} - 1 \right)} ,
\]

where \( \beta_\tau^{(h)} (h = \{0, 1, 2, 3\}) \) are adjustable element-dependent parameters, and \( R_\tau^0 \) is the nearest-neighbor distance in the equilibrium reference structure for the element type \( \tau \).
The pair interaction for like atoms of element type $\tau$ can be calculated using a first nearest-neighbor (1NN) or second nearest-neighbor (2NN) formalism. In this work, the former is used and is given by

$$
\phi_{\tau\tau} (R) = \frac{2}{Z_{\tau}^0} \left\{ E_{\tau}^u (R) - F_{\tau} \left[ \tilde{\rho}_{\tau}^{ref} (R) \right] \right\} .
$$

In this equation $\tilde{\rho}_{\tau}^{ref} (R)$ is the background electron density in the reference structure evaluated from Eqs. 7-10 at a nearest-neighbor distance of $R$ and is given by

$$
\tilde{\rho}_{\tau}^{ref} (R) = Z_{\tau}^0 \rho_{a} (0) G \left( \Gamma_{\tau}^{ref} \right) ,
$$

and $E_{\tau}^u$ is the universal equation of state (UEOS) of Rose et al. for element type $\tau$ given by

$$
E_{\tau}^u (R) = -E_{\tau}^0 \left[ 1 + a^* + \delta \frac{R_{\tau}^0}{R} (a^*)^3 \right] e^{-a^*} ,
$$

$$
a^* = \alpha_{\tau}^0 \left( \frac{R}{R_{\tau}^0} - 1 \right) ,
$$

$$
\delta = \left\{ \begin{array}{ll}
\delta_{\tau}^a & \text{if } a^* \geq 0 \\
\delta_{\tau}^r & \text{if } a^* < 0
\end{array} \right. ,
$$

$$
\alpha_{\tau}^0 = \sqrt{\frac{9K_{\tau}^0 \Omega_{\tau}^0}{E_{\tau}^0}} ,
$$

or

$$
\alpha_{\tau}^0 = \sqrt{\frac{k_{\tau}^0 \Omega_{\tau}^0}{E_{\tau}^0}} .
$$

In the above equations $K_{\tau}^0$ ($k_{\tau}^0$) and $\Omega_{\tau}^0$ are the bulk modulus (spring constant) and the atomic volume of the reference structure, respectively, and $\delta$ is an adjustable, element-dependent parameter that has two components, attractive $\delta_{\tau}^a$ and repulsive $\delta_{\tau}^r$. Eq. 20 is used when the reference structure is a three-dimensional (3D) crystal and Eq. 21 is used when the reference structure is a diatomic.

The pair interaction for unlike atoms of element types $\tau$ and $\upsilon$ is similarly obtained from the reference structure of the unlike atoms. For this work, the reference structure is taken as a diatomic, which gives

$$
\phi_{\tau\upsilon} (R) = \frac{1}{Z_{\tau\upsilon}^0} \left\{ 2E_{\tau\upsilon}^u (R) - F_{\tau} \left[ \tilde{\rho}_{\tau}^{d} (R) \right] - F_{\upsilon} \left[ \tilde{\rho}_{\upsilon}^{d} (R) \right] \right\} ,
$$

where $Z_{\tau\upsilon}^0 = 1$ is the coordination number for the diatomic and

$$
\tilde{\rho}_{\tau}^{d} (R) = \rho_{\tau}^{a(0)} G \left( \Gamma_{\tau}^{d} \right) ,
$$

$$
\Gamma_{\tau}^{d} = \sum_{h=1}^{3} t_{\tau}^{(h)} s_{\tau}^{(h)} \left( \frac{\rho_{\tau}^{a(h)}}{\rho_{\tau}^{a(0)}} \right)^2 ,
$$

or
where the shape factors $s^{(h)}_{d}$ are those for a diatomic. The UEOS $E_{\tau'v'}$ is given by Eqs. [17]-[21] using parameters $E_{\tau'v'}^{0}, R_{\tau'v'}^{0}, k_{\tau'v'}^{0}, \delta_{\tau'v'}^{0},$ and $\delta_{\tau'v'}$.

The screening factor $S_{ij}$ is defined as the product of all screening factors $S_{ikj}$, where the interaction between atoms at sites $i$ and $j$ are screened by neighboring atoms at site $k$ as given by

$$S_{ij} = \sum_{k \neq i,j} S_{ikj}. \quad (25)$$

If it is assumed that all three sites $i$, $j$, and $k$ lie on an ellipse on the $xy$-plane with sites $i$ and $j$ on the $x$-axis, the following equation can be derived:

$$x^2 + \frac{1}{C} y^2 = \left(\frac{1}{2} R_{ij}\right)^2, \quad (26)$$

where

$$C_{ikj} = \frac{2(X_{ik} + X_{kj}) - (X_{ik} - X_{kj})^2 - 1}{1 - (X_{ik} - X_{kj})^2}, \quad (27)$$

In the above equation $X_{ik} = (R_{ik}/R_{ij})^2$ and $X_{kj} = (R_{kj}/R_{ij})^2$. The screening factor $S_{ikj}$ for like atoms is defined as

$$S_{ikj} = f_c \left( \frac{C_{ikj} - C_{min}(\tau_i, \tau_k, \tau_j)}{C_{max}(\tau_i, \tau_k, \tau_j) - C_{min}(\tau_i, \tau_k, \tau_j)} \right), \quad (28)$$

where $C_{min}(\tau_i, \tau_k, \tau_j)$ and $C_{max}(\tau_i, \tau_k, \tau_j)$ determine the extent of screening of atoms of element type $\tau$ at sites $i$ and $j$ by an atom at site $k$. Similar expressions can be written for the screening of unlike atoms. The smooth cutoff function $f_c$ is defined as

$$f_c(x) = \begin{cases} 
1 & \text{if } x \geq 1 \\
\left[ 1 - (1 - x)^4 \right]^2 & \text{if } 0 < x < 1 \\
0 & \text{if } x \leq 0 
\end{cases}. \quad (29)$$

$S_{ij} = 1$ means that the interaction between atoms at sites $i$ and $j$ is not screened, while $S_{ij} = 0$ means it is completely screened.

3 Modified Embedded-Atom Method Parameterization

The MEAM formalism presented in Eqs. [1]-[29] requires 16 independent model parameters for each element type $\tau$, i.e., $E_{\tau'}^{0}, R_{\tau'}^{0}, \alpha_{\tau'}^{0}, \delta_{\tau'}^{0},$ and $\delta_{\tau'}^{c}$ for the universal equation of state (Eq. [17]); $\beta_{\tau'}^{(0)}, \beta_{\tau'}^{(1)}, \beta_{\tau'}^{(2)}, \beta_{\tau'}^{(3)}, \delta_{\tau'}^{(1)}, \delta_{\tau'}^{(2)}, \delta_{\tau'}^{(3)},$ and $\rho_{\tau'}^{0}$ for the electron densities (Eqs. [3]-[13]); $A_{\tau}$ for the embedding function $F_{\tau}$ (Eq. [2]); and $C_{\min}$ and $C_{\max}$ for the screening factor (Eqs. [25]-[29]). In the current MEAM formalism for a single element, model is independent of $\rho_{\tau'}^{0}$, hence, $\rho_{\tau'}^{0} = 1$ is taken for one of the elements. For a diatomic composed of elements $\tau$ and $\nu$, 13 additional independent parameters are required, i.e., $E_{\tau'\nu'}^{0}, R_{\tau'\nu'}^{0}, \alpha_{\tau'\nu'}^{0}, \delta_{\tau'\nu'}^{0},$ and $\delta_{\tau'\nu'}^{c}$, four $C_{\min}$, and four $C_{\max}$ values.

In this work, we have parameterized elements carbon and hydrogen and the diatomic CH with the reference structures of diamond for carbon ($Z_{C_d}^{0} = 4$), diatomic H$_2$ for hydrogen ($Z_{H_d}^{0} = 1$), and diatomic CH for hydrocarbons ($Z_{CH_d}^{0} = 1$). As initial starting parameters for this potential, we utilized the MEAM parameters for carbon from the work of Xiao et al. [20] and the parameters for hydrogen from the work of Baskes [5]. The fitting procedure for the pure element parameters is described in detail by Baskes [5]. For the potential parameterization, we utilized a parameter fitting database consisting of
1) experimental bond distances, bond angles, and atomization energies at 0 K of a homologous series of alkanes and their isomers from methane to n-octane. 2) potential energy curves of H₂, C₂, and CH diatomics, generated in this work from FP calculations, 3) FP interaction energy curves of (H₂)₂ (H₂ dimer), (CH₄)₂ (methane dimer), (C₂H₆)₂ (ethane dimer), and (C₃H₈)₂ (propane dimer) in select molecular orientations, and 4) the pressure-volume-temperature (PVT) experimental data for a dense methane system. The FP data for H₂, C₂, and CH diatomics were generated with the CCSD(2) ab initio method and the aug-cc-pVTZ basis set using Q-Chem quantum chemistry physics software (V3.2) and restricted core orbitals. CCSD(2) is a high-accuracy FP method designed to calculate bond breaking with great precision. The MEAM fitting procedure involved a stepwise and iterative effort to first capture the energy versus distance characteristics of the H₂, CH, and C₂ diatomics. Next, we fit the atomization energies of the linear alkanes to the experimental data that were first corrected for the zero-point energy (ZPE). The bond distances and bond angles of the first four alkanes and one butane isomer were then fit to the experimental data. To enable a reliable prediction of the van der Waals forces, we further fit the MEAM parameters to the interaction energy curves of (H₂)₂, (CH₄)₂, (C₂H₆)₂, and (C₃H₈)₂ dimers, which we validated in subsequent molecular dynamics (MD) simulations of lower alkane systems to establish PVT relationships. This collective fitting to the FP dimer interactions was made in conjunction with the prediction of the experimental PVT behavior of a dense high-pressure methane system (density of 0.5534 g/cc). The FP data for the dimer interactions were taken from literature values, some of which are quite dated. However, since these dimer interactions were merely used as guidance to tune in the actual pressure values of the methane system at a given density and temperature, the comparisons of MEAM predictions with the FP data (see Section 4) should only be construed as qualitative. The PVT validations with the experimental data, together with the MEAM predictions for the bond distances, bond angles, dihedral (torsion) angles, and atomization energies of a series of alkanes and free radicals, are given in Section 4. The final sets of MEAM parameters for carbon, hydrogen, and CH is given in Tables 1 and 2.

During the parameterization process, we found the value of the α₀ parameter in the work of Baskes to be incorrect due to an error in the implementation of the equation for the diatomic force constant of the H-H bond. The value of this parameter was corrected in the present work, and the corrected value appears in Table 1.

4 Results

4.1 Single Molecules

The MEAM atomization energies of select alkanes, free radicals, and unsaturated compounds (for illustration purposes) are given in Table 3. In the same table, the experimental atomization energies at 0 K are also given, along with the values calculated using the REBO and ReaxFF potentials. The starting molecular structures were created in the Avogadro open-source molecular builder and visualization tool and initially optimized using Avogadros built-in Molecular Merck Force Field (MMFF94). The energies of the resulting structures were then minimized using MEAM, REBO, and ReaxFF potentials and the Polak-Ribiere conjugate gradient method. We utilized the parameters for carbon and hydrogen in the second-generation REBO and ReaxFF from the work of Brenner et al. and Chenoweth et al., respectively. The REBO and ReaxFF calculations were performed on the open-source large-scale atomic/molecular massively parallel simulator (LAMMPS) software package developed at Sandia National Laboratories (version April 20, 2012). All MEAM calculations and simulations were performed on DYNAMO software (V8.7), developed by Foiles, Daw, and Baskes at Sandia National Laboratories. The MEAM potential was fit to the experimental data corrected for ZPE. Hence, the corrected value in Table III should be compared with the ex-
Table 1: Single element MEAM parameters for carbon and hydrogen with diamond and diatomic H\(_2\) reference structures, respectively. \(E^0_\tau\) (eV) is the cohesive energy, \(R^0_\tau\) (Å) is the nearest neighbor distance in the equilibrium reference structure, \(\alpha^0_\tau\) is the exponential decay factor for the universal energy of Rose et al. [33], \(A_\tau\) is the electron density scaling factor for the embedding function, \(\rho^0_\tau\) is the electron density scaling factor, \(\delta^a_\tau\) and \(\delta^r_\tau\) are the attraction (\(a^* > 0\)) and repulsion (\(a^* \leq 0\)) cubic terms for the universal equation of state, \(\beta^{(0-3)}_\tau\) are the exponential decay factors for the atomic electron densities, \(t^{(1-3)}_\tau\) are the weighting parameters for the atomic electron densities, and \(C_{\min}\) and \(C_{\max}\) are the screening parameters for three like atoms of the element \(\tau\).

| Element | \(E^0_\tau\) | \(R^0_\tau\) | \(\alpha^0_\tau\) | \(A_\tau\) | \(\rho^0_\tau\) | \(\delta^a_\tau\) | \(\delta^r_\tau\) | \(\beta^{(1)}_\tau\) | \(\beta^{(2)}_\tau\) | \(\beta^{(3)}_\tau\) | \(t^{(1)}_\tau\) | \(t^{(2)}_\tau\) | \(t^{(3)}_\tau\) | \(C_{\min}\) | \(C_{\max}\) |
|---------|----------------|----------------|-----------------|---------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|-------------|
| C       | 7.370          | 1.44           | 3.60            | 0.64    | 1.00           | 0.00           | 0.00           | 4.20           | 4.50           | 4.30           | 4.18           | 0.50           | 0.45           | -3.80       | 2.00        | 2.80        |
| H       | 2.363          | 0.74           | 2.0388          | 2.50    | 1.80           | 0.00           | 0.05           | 2.72           | 2.045          | 2.25           | –             | 0.20           | -0.40          | 0.00         | 0.75        | 2.80        |
Table 2: MEAM interaction and screening parameters for the diatomic C-H. $R_{CH}^0$ (Å) is the first
nearest neighbor distance, $\alpha_{CH}^0$ is the exponential decay factor for the universal
equation of state (UEOS) of Rose et al. [33], $E_{CH}^0$ (eV) is the cohesive energy, $\delta_{CH}^a$ and $\delta_{CH}^r$ are the attraction ($a^* > 0$)
and repulsion ($a^* \leq 0$) cubic terms for the UEOS, respectively, and $C_{min}$ and $C_{max}$ are the parameters
for the screening factor. The middle atom screens the other two atoms (see Section 2).

| Parameter | Value  |
|-----------|--------|
| $R_{CH}^0$ | 1.02   |
| $\alpha_{CH}^0$ | 3.20   |
| $E_{CH}^0$ | 2.12   |
| $\delta_{CH}^a$ | 0.05   |
| $\delta_{CH}^r$ | 0.05   |
| $C_{min}$ (C, C, H) | 0.445  |
| $C_{max}$ (C, C, H) | 2.80   |
| $C_{min}$ (C, H, C) | 2.00   |
| $C_{max}$ (C, H, C) | 2.80   |
| $C_{min}$ (C, H, H) | 1.50   |
| $C_{max}$ (C, H, H) | 2.00   |
| $C_{min}$ (H, C, H) | 0.52   |
| $C_{max}$ (H, C, H) | 2.20   |

Experimental data. Similarly, in the second generation REBO, a ZPE correction needs to be applied
to the LAMMPS calculated energies of hydrocarbon structures [28]. The reported atomization energies
in Table III reflect these corrections based on the ZPE data reported by Brenner et al. [28] and
B3LYP/6-31G** density functional theory (DFT) ZPE calculations performed as part of this work.
Furthermore, since ReaxFF was fit to the heats of formation of hydrocarbons [29], it is necessary to
correct the LAMMPS calculated energies by the empirical “heat increments” discussed in the work
of van Duin et al. [29]. The root-mean-square (RMS) error associated with the MEAM-reproduced
atomization energies of the alkanes in Table 3 (0.19 eV) compares well with that of REBO (0.11 eV)
and is far better than that of ReaxFF (0.99 eV). The systems with the largest errors for MEAM
contain double and triple bonds, and MEAM is not parameterized for these systems. A comparison
between the atomization energies relative to the experimental data for the three potentials is given in
Fig. 1. Of course, REBO and ReaxFF have been parameterized to a larger database of both saturated
and unsaturated hydrocarbons, and therefore, they can be applied to a much larger range of systems.
Hence, the comparisons in Table 3 serve only as a guide.

The average equilibrium bond distances and bond angles for the first three molecules in the alkane
series and both isomers of butane are given in Tables 4 and 5, respectively, where the MEAM, REBO,
and ReaxFF values are compared to the experimental data [34]. The MEAM results give lower RMS
errors for both bond distances and bond angles than REBO or ReaxFF. In Figs. 2 and 3, the bond
distances and bond angles relative to the experimental data are depicted for the three potentials.

In Table 6, the MEAM-predicted dihedral (torsion) angle for the gauche conformer of isobutane
is compared to the predictions by REBO and ReaxFF as well as the experimental data. MEAM
reproduces the angle within 20% of the experimental value, while REBO and ReaxFF reproduce it
within 5% and 3%, respectively.

To validate whether the MEAM potential correctly predicts the formation of molecular species with
expected geometries after energy minimization, two atomic configurations were selected and energy-
minimized: 1) CH$_3$ in non-planar configuration with an initial $\angle$H-C-H of 109.5$^\circ$ (to validate the
formation of planar structure after energy minimization and a final $\angle$H-C-H of 120$^\circ$), and 2) CH$_4$+2H
with the two extra hydrogen atoms on either side of the methane molecule and very close to it (to
validate the repulsion of the two extra hydrogen atoms and formation of a hydrogen molecule away
| Molecule       | Atomization energy at 0 K (eV) |
|----------------|--------------------------------|
|                | Expt. | ZPE | DYNAMO | Corr. | REBO | LAMMPS | Corr. | LAMMPS | Corr. |
| H₂             | 4.478 | 0.263 | 4.726 | 4.463 | 4.506 | 4.243 | 4.804 | 4.845 |
| C₂             | 6.219 | 0.111 | 5.804 | 5.693 | 6.21  | 6.099 | 10.902| 6.697 |
| Alkanes        |       |      |       |       |       |       |       |       |       |
| methane        | 17.018| 1.135 | 18.319| 17.184| 18.185| 17.05 | 19.202| 17.181|
| ethane         | 28.885| 1.921 | 30.991| 29.07 | 30.846| 28.925| 33.279| 29.196|
| propane        | 40.88 | 2.706 | 43.658| 40.952| 43.589| 40.883| 47.64 | 41.495|
| n-butane       | 52.896| 3.492 | 56.322| 52.83 | 56.332| 52.84 | 61.921| 53.714|
| isobutane      | 52.977| 3.492 | 56.377| 52.885| 56.331| 52.839| 62.063| 53.856|
| n-pentane      | 64.915| 4.278 | 68.985| 64.707| 69.076| 64.798| 76.022| 65.753|
| isopentane     | 64.964| 4.278 | 69.107| 64.829| 69.073| 64.795| 76.26  | 65.991|
| neopentane     | 65.123| 4.278 | 69.177| 64.899| 69.061| 64.783| 76.614| 66.345|
| n-hexane       | 76.922| 4.892 | 81.648| 76.756| 81.819| 76.929| 90.204| 77.873|
| isohexane      | 76.975| 4.896 | 81.68 | 76.784| 81.817| 76.921| 90.259| 77.928|
| 3-methylpentane| 76.946| 4.885 | 81.712| 76.827| 81.817| 76.932| 90.312| 77.981|
| 2,3-dimethylbutane| 76.97 | 4.867 | 81.73 | 76.863| 81.815| 76.948| 90.467| 78.136|
| neohexane      | 77.06 | 4.876 | 81.772| 76.896| 81.804| 76.928| 90.721| 78.39 |
| n-heptane      | 88.957| 5.623 | 94.31 | 88.688| 94.502| 88.939| 104.489| 90.096|
| isooctane      | 89.008| 5.628 | 94.346| 88.724| 94.56  | 88.938| 104.652| 90.259|
| n-octane       | 100.971| 6.359 | 106.975| 100.616| 107.306| 100.947| 118.692| 102.237|
| RMS Errora, b  | -     | -    | -     | 0.19  | -    | 0.11  | -     | 0.99  |
| Alkenes        |       |      |       |       |       |       |       |       |       |
| ethene (ethylene) | 23.066| 1.303 | 22.955| 21.652| 24.528| 23.225| 27.183| 23.059|
| Alkynes        |       |      |       |       |       |       |       |       |       |
| ethyne (acetylene) | 16.857| 0.686 | 14.552| 13.866| 17.565| 16.879| 19.952| 15.7874|
| Cycloalkanes   |       |      |       |       |       |       |       |       |       |
| cyclopentane   | 34.818| 2.089 | 37.636| 35.547| 36.889| 34.8  | 41.27 | 35.084|
| cyclobutane    | 46.848| 2.875 | 50.441| 47.566| 49.898| 47.023| 54.402| 46.154|
| cyclohexane    | 59.707| 3.66  | 63.252| 59.592| 63.643| 59.983| 70.197| 59.887|
| cyclopentane   | 71.963| 4.446 | 76.059| 71.613| 76.46 | 72.014| 84.901| 72.529|
| RMS Errora, b  | -     | -    | -     | 0.54  | -    | 0.17  | -     | 0.48  |
| Aromatics      |       |      |       |       |       |       |       |       |       |
| benzene        | 56.62 | 2.594 | 52.308| 49.714| 60.231| 57.637| 68.236| 55.742|
| Radicals       |       |      |       |       |       |       |       |       |       |
| CH             | 3.469 | 0.165 | 5.493 | 5.328 | 4.526 | 4.361 | 5.029 | 2.947 |
| CH₂            | 7.41  | 0.517 | 10.027| 9.51  | 8.469 | 7.952 | 9.766 | 7.704 |
| CH₃            | 12.534| 0.826 | 14.265| 13.439| 13.375| 12.549| 14.806| 12.764|
| C₂H₃          | 11.125| 0.377 | 10.149| 9.772 | 11.572| 11.195| 14.897| 10.712|
| H₂C₂H₂        | 24.572| 1.612 | 26.597| 25.355| 26.588| 24.976| 29.012| 24.908|

a Root-Mean-Square Error.
b From the NIST Computational Chemistry Comparison and Benchmark Database.  
In Table 3, atomization energies of a homologous series of alkanes from methane to n-octane and their select isomers, cycloalkanes, free radicals, hydrogen, and carbon diatomic reproduced by MEAM, REBO, and ReaxFF potentials versus experimental data.
from the methane molecule). Correct prediction of the resulting molecular species and their geometries is crucial for reliably simulating reactions involving free radicals. MEAM and REBO both predicted a planar CH$_3$ structure with a final $\angle$H-C-H of 120° after energy minimization, while ReaxFF gave a slightly non-planar structure with a final $\angle$H-C-H of 117.4°. Furthermore, for the CH$_4$+2H structure, both MEAM and REBO predicted the formation of a hydrogen molecule away from an equilibrated methane molecule, while ReaxFF minimized the structure to a non-equilibrium configuration. The initial and final structures for the CH$_4$+2H atomic configuration calculated by MEAM, REBO, and ReaxFF are given in Fig. 4.

Figure 1: Errors associated with the corrected MEAM, REBO, and ReaxFF atomization energies of a) hydrogen and linear alkanes and b) cycloalkanes and free radicals relative to the experimental data. The actual data are given in Table 3.
Table 4: Average equilibrium C-H and C-C bond distances for select alkanes after energy minimization of the molecular structures using the MEAM, REBO, and ReaxFF potentials. The results are compared to the experimental data [34].

| Molecule  | C-H Bond distance (Å) | C-C Bond distance (Å) |
|-----------|------------------------|------------------------|
|           | Expt.\textsuperscript{a} | MEAM | REBO | ReaxFF | Expt.\textsuperscript{a} | MEAM | REBO | ReaxFF |
| methane   | 1.087                   | 1.089 | 1.089 | 1.118 | - | - | - | - |
| ethane    | 1.094                   | 1.092 | 1.090 | 1.090 | 1.535 | 1.534 | 1.543 | 1.534 |
| propane   | 1.107                   | 1.093 | 1.090 | 1.110 | 1.532 | 1.533 | 1.542 | 1.542 |
| n-butane  | 1.117                   | 1.094 | 1.090 | 1.110 | 1.531 | 1.533 | 1.542 | 1.556 |
| isobutane | 1.113                   | 1.094 | 1.090 | 1.112 | 1.535 | 1.525 | 1.543 | 1.545 |

\textsuperscript{a} From Lide [34].

\textsuperscript{b} Root-Mean-Square Error.
Table 5: Average equilibrium $\angle$H-C-H, $\angle$H-C-C, and $\angle$C-C-C bond angles for select alkanes after energy minimization of the molecular structures using the MEAM, REBO, and ReaxFF potentials. The results are compared to the experimental data [34].

| Molecule  | $\angle$H-C-H | $\angle$H-C-C | $\angle$C-C-C |
|-----------|---------------|---------------|---------------|
|           | Expt.$^a$     | MEAM          | REBO          | ReaxFF        |
| methane   | 109.47        | 109.47        | 109.47        | -             |
| ethane    | 107.70        | 107.70        | 108.54        | 111.17        |
| propane   | 107.00        | 107.40        | 108.35        | -             |
| n-butane  | N/A           | 107.50        | 108.22        | 111.00        |
| isobutane | N/A           | 107.40        | 108.54        | 111.40        |
| RMS Error$^b$ | 0.23 | 0.92 | 0.23 | - |

$^a$ From Lide [34].
$^b$ Root-Mean-Square Error.
Figure 2: Errors associated with the MEAM-, REBO-, and ReaxFF-reproduced bond distances for the a) C-H and b) C-C bonds of select alkanes relative to the experimental data. The actual data are given in Table 4.

Table 6: Equilibrium dihedral angle for the gauche conformer of isobutane after energy minimization of the molecular structure using the MEAM, REBO, and ReaxFF potentials. The results are compared to the experimental data.

| Dihedral angle (°) | Expt. | MEAM | REBO | ReaxFF |
|--------------------|-------|------|------|--------|
| 65                 | 78    | 68   | 67   |

*From Lide [34].*
Figure 3: Errors associated with the MEAM-, REBO-, and ReaxFF-reproduced bond angles for the a) $\angle$H-C-H, b) $\angle$H-C-C, and c) $\angle$C-C-C angles relative to the experimental data. The actual data are given in Table 5.
Figure 4: Initial and final structures of CH$_4$+2H atomic configuration resulting from the energy minimization of the structure using the MEAM, REBO, and ReaxFF potentials.
4.2 Diatomic molecules

The potential energy curves for H₂, CH, and C₂ diatomics generated by the MEAM, REBO, and ReaxFF potentials are presented in Fig. 5. As stated in Section 3, the FP data were generated in this work using CCSD(2) and the aug-cc-pVTZ basis set, and MEAM was fitted to these potential energy curves. The ReaxFF potential implementation in LAMMPS [50] gives a non-zero energy value for a single carbon atom, \( E = -0.075568 \) eV. The ReaxFF interaction curves for CH and C₂ were corrected for this non-zero energy associated with the isolated carbon atom at infinite interatomic distances.

![Potential energy curves](image)

Figure 5: Potential energy curves of a) H₂, b) CH, and c) C₂ diatomics. The MEAM results are compared to those of REBO, ReaxFF, and the CCSD(2)/aug-cc-pVTZ FP data generated in this work.

4.3 Dimer molecules

To reproduce the van der Waals interactions between the molecules, we used the FP interaction energy curves of hydrogen, methane, ethane, and propane dimers in the fitting database (see Section 3). The MEAM-reproduced interaction curves are plotted for the five dimers in select molecular orientations versus the FP data in Figs. 6-9. All atoms were constrained at each distance increment, and the energy was calculated by subtracting the total energy of the structure at infinite atomic distance from the actual energy at each distance increment. The FP data for the hydrogen dimer were taken from the work of Burton et al. [37], where their four different molecular configurations denoted as collinear
coplanar (T), linear (L), parallel or rectangular (P), and crossed or elongated tetrahedron (C) were considered. The configurations are also depicted in Fig. 6. The FP data for methane and ethane dimers were taken from the work of Szczesniak et al. [38] and Rowley and Yang [39], respectively. In the former, four molecular configurations designated in their work as A, B, D, and F were considered ($R_{CH} = 1.091$ Å). These configurations are depicted in Fig. 7. In the latter, only the first four configurations out of 22 reported in the work of Rowley and Yang, designated as routes 1-4, were used for fitting purposes [39] ($R_{CH} = 1.102$ Å, $R_{CC} = 1.523$ Å). These routes are given as insets in Fig. 8. The FP data for propane dimer were taken from the work of Jalkanen et al. [40] with three molecular orientations, designated as bb-ccc90, bb-bb 90, and ccs-cs 90, used for fitting purposes ($R_{CH} = 1.102$ Å, $R_{CC} = 1.529$ Å). For details on these orientations and the relevant coding of them, refer to Jalkanen et al. [40]. MEAM reproduces the general trends of the van der Waals bonding. Note that no additional van der Waals term is added to the MEAM formalism presented in Section 2. The van der Waals interactions result directly from the tails of the electron density and pair potentials.

Figure 6: First-principles (FP) [37] versus MEAM-calculated interaction energy curves for (H$_2$)$_2$ (hydrogen dimer). The molecular configurations are a) collinear coplanar (T), b) linear (L), c) parallel or rectangular (P), and d) crossed (C) as reported in the work of Burton et al. [37]. The atoms are constrained during energy calculation at each distance increment.
Figure 7: First-principles (FP) versus MEAM-calculated interaction energy curves for (CH$_4$)$_2$ (methane dimer). The molecular configurations A, B, D, and F are reported in the work of Szczesniak et al. [38]. The atoms are constrained during energy calculation at each distance increment.

4.4 Bond dissociation and rotational barrier

The MEAM-reproduced C-H and C-C bond dissociation energy curves in methane and ethane and the associated FP data are shown in Figs. 10a and 10b, respectively. The FP curve for the C-H dissociation in methane was generated in this work, while the FP data for the C-C bond dissociation in ethane was taken from the work of Lorant et al. [52]. The separating carbon and hydrogen atoms in methane and the two carbon atoms in ethane were constrained, while the structure was minimized at each distance increment. For the FP data of the C-H dissociation, the constrained geometries were minimized with CCSD(T)/aug-cc-pVTZ, basis set and single point energies were calculated with CCSD(2)/aug-cc-pVTZ basis set. The MEAM-generated data show reasonable agreement with the FP results, especially at longer bond distances. To further validate the dissociating geometry of the ethane molecule, the intermediate MEAM-calculated $\angle$H-C-C bond angles are compared to the FP data [52] in Fig. 11. The general trend of the FP dissociation curves (Fig. 10) is qualitatively captured by MEAM, while the angles at intermediate distances deviates some from FP calculations. However, the beginning and end states of the dissociated molecule have the correct $\angle$H-C-C bond angles at similar C-C dissociation distances.

The MEAM-calculated rotational barrier for ethane, ethylene and the associated FP data are given in Fig. 12. The FP data calculations are described above. We have calculated the rotational barrier in
Figure 8: First-principles (FP) \cite{39} versus MEAM-calculated interaction energy curves for \((\text{C}_2\text{H}_6)_2\) (ethane dimer). The molecular configurations (Routes 1-4) are reported in the work of Rowley and Yang \cite{39}. The atoms are constrained during energy calculation at each distance increment.

ethylene in this work, but obtained a barrier of essentially zero. Modification of the model to properly reproduce rotation around double bonds is a subject of future research.
Figure 9: First-principles (FP) [40] versus MEAM-calculated interaction energy curves for \((C_3H_8)_2\) (propane dimer). The molecular configurations (bb-ccce 90, bb-bb 90, and ccs-ccs 90) are reported in the work of Jalkanen et al. [40]. The atoms are constrained during energy calculation at each distance increment.
Figure 10: The potential energy curves for the C-H bond dissociation in methane (a) and the C-C bond dissociation in ethane predicted by MEAM versus the FP data. The FP data for a) were generated in this work, while they were taken from the work of Lorant et al. [52] for b). The C and H atoms in CH₄ and both C atoms in C₂H₆ were constrained, while the energy was minimized at each distance increment.
Figure 11: MEAM-reproduced intermediate H-C-C bond angles during the C-C bond dissociation in ethane compared to the FP data reported in the work of Lorant et al. [52]. Both carbon atoms in ethane were constrained, while the energy was minimized at each distance increment.
Figure 12: The rotational barrier for a) ethane and b) ethylene calculated by MEAM versus the FP data calculated using a) CCSD(2)/aug-cc-pVTZ and b) CCSD(T)/aug-cc-pVTZ FP.
4.5 Molecular dynamics simulations

We further validated our MEAM potential for saturated hydrocarbons with experimental pressure-volume-temperature (PVT) data for select alkane systems. The MEAM-calculated pressure for a high-pressure methane system with the density of 0.5534 g/cc was used for fitting purposes. A series of MD simulations were run with NVT (constant number of atoms $N$, constant volume $V$, and constant temperature $T$) on a series of 3D periodic methane, ethane, propane, and butane systems with different densities and at different temperatures (Table VII). The total number of atoms in these systems and the cut-off distance (5 Å) were kept at a minimum due to the large computation times required for running these simulations on the serial DYNAMO [51] code. To ensure the reliability of the results with a cut-off distance of 5 Å, a representative MD simulation was run on a methane system (density of 0.2021 g/cc) with a larger cut-off distance of 9 Å. The results of both simulations (using a cut-off distance of 5 Å versus 9 Å) agree to within 1%. Hence, all the rest of simulations were run using the lower 5 Å cut-off distance. We built the starting periodic structures in Accelrys® Materials Studio® software (V5.5) and relaxed them using the COMPASS [30] force field and Polak-Ribiere conjugate gradient method [48] for 1000 iterations. Then we imported the relaxed periodic structures into DYNAMO and ran the MD simulations on this platform for a total simulation time of 200 ps with a time step of 0.5 fs. The small time step was chosen to ensure energy conservation in these systems containing the light element hydrogen. A typical run took from 6-95 hr on a single processor depending on the size and density of the system. Temperature was controlled by a Nosé-Hoover thermostat [53, 54]. All systems equilibrated after 50 ps. The calculated pressures for each time step were time-averaged over the last 150 ps of the simulation, and an average pressure was calculated. The details of dynamics simulations and the final MEAM-predicted average pressures along with the experimental data are given in Table 7. In spite of typical uncertainties in experimental data and the fact that a small system was used for the MD simulations, MEAM-reproduced average pressures agree well with the experimental data.

Table 7: Details on the molecular dynamics simulations of a series of periodic methane, ethane, propane, and butane systems under the $NVT$ ensemble for a total simulation time of 200 ps. The final MEAM-calculated time-averaged pressure is compared to the experimental data. The data are reported in the ascending order of density for each molecular species.

| System  | No. of atoms | Cell Size ($Å^3$) | Density (g/cc) | Temp. (K) | Expt. Pressure (MPa) | MEAM Pressure (MPa) | Difference (MPa) |
|---------|--------------|------------------|----------------|-----------|----------------------|---------------------|------------------|
| methane-1 | 500          | 47.65x47.65x47.65 | 0.0246         | 400       | 5.005$^a$            | 5.09                | 0.09             |
| methane-2 | 500          | 42.71x42.71x42.71 | 0.0342         | 305       | 5.001$^a$            | 4.98                | -0.02            |
| methane-3 | 500          | 28.22x28.22x28.22 | 0.1185         | 298       | 14.994$^a$           | 12.75               | -2.24            |
| methane-4 | 500          | 23.62x23.62x23.62 | 0.2021         | 450       | 59.975$^a$           | 58.65               | -1.33            |
| methane-5 | 500          | 19.17x19.17x19.17 | 0.3782         | 338       | 179.829$^a$          | 162.44              | -17.39           |
| methane-6 | 500          | 18.80x18.80x18.80 | 0.4008         | 298       | 188.059$^a$          | 173.59              | -14.47           |
| methane-7 | 500          | 16.88x16.88x16.88 | 0.5534         | 373       | 1000$^b$             | 1002.41             | 2.41             |
| ethane-1 | 800          | 51.25x51.25x51.25 | 0.0371         | 308       | 2.550$^c$            | 1.09                | -1.46            |
| ethane-2 | 800          | 26.36x26.36x26.36 | 0.2726         | 308       | 5.387$^c$            | 5.57                | 0.18             |
| ethane-3 | 800          | 21.68x21.68x21.68 | 0.4901         | 260       | 31.294$^c$           | 29.22               | -2.07            |
| propane-1 | 880          | 28.62x28.62x28.62 | 0.2497         | 325       | 26.891$^d$           | 4.28                | -22.61           |
| propane-2 | 880          | 22.40x22.40x22.40 | 0.5212         | 280       | 1.466$^e$            | 4.49                | 3.02             |
| n-butane  | 700          | 20.23x20.23x20.23 | 0.5827         | 300       | 7.089$^e$            | -5.1                | -12.19           |

$^a$ From Cristancho et al. [55].
$^b$ From Robertson and Babb [41].
$^c$ From Straty and Tsumura [56].
$^d$ From Straty and Palavra [57].
$^e$ From Kayukawa et al. [58].
5 Concluding Remarks

We have successfully developed a new semi-empirical many-body potential for saturated hydrocarbons based on the modified embedded-atom method. The potential parameterization was performed with respect to a large database of atomization energies, bond distances, and bond angles of a homologous series of alkanes and their isomers up to \( n \)-octane, the potential energy curves of \( \text{H}_2 \), \( \text{CH} \), and \( \text{C}_2 \), \( \text{(H}_2\text{)}_2 \), \( \text{(CH}_4\text{)}_2 \), \( \text{(C}_2\text{H}_6\text{)}_2 \), and \( \text{(C}_3\text{H}_8\text{)}_2 \) and the pressure-volume-temperature \( (PVT) \) relationship of a dense methane system. The new potential successfully predicts the \( PVT \) behavior of representative alkane systems at different densities and temperatures. The significance of this work is in the extension of the classical MEAM formalism for metals and metal hydride, carbide, and nitride systems to saturated hydrocarbons. This is the first step toward its universality for all atomic and molecular systems. The main benefit of using this potential versus other potentials for various atomic and molecular dynamics simulation studies is its vast parameter database for metals. This makes it possible, for example, to study complex polymer-metal systems using the same formalism for both metals and organic molecules. In addition, MEAM is inherently linear scaling, making possible simulations on very large systems. Since MEAM is a reactive potential, numerous possible simulation studies of reactive organic/metal systems as well as void and crack formation and growth in polymer systems are envisioned.

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