A Generating Equation for Mixing Rules and Two New Mixing Rules for Interatomic Potential Energy Parameters

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Abstract: A generating equation for the mixing rules of interatomic potential energy parameters is proposed. It is demonstrated that this equation can, indeed, reproduce many popular mixing rules. A weighting matrix is used with the generating equation. This weighting matrix approach is superior to the present status of mixing rule development. A systematic framework is given for devising new mixing rules and/or comparing them. Two new mixing rules, which are more accurate than the available rules in the literature, are proposed. These rules are capable of reproducing the collision diameter and well-depth parameters for the binary values of noble gases to within their experimental uncertainties.

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Introduction

The application of molecular simulation, whether for insight or quantitative prediction of properties of interest, requires the parameterization of force fields (potential models). These models describe the interactions between different types of molecules. The present status of force field development is based on parameterization using the well-known Lennard–Jones model.[1] There is a trend among some researchers to use the modified Buckingham form (Exp-6).[2–4] Parameterization is based on fits of pure component properties. The unlike interactions are accounted for using mixing (combination) rules. The practice is to use an arithmetic rule for the collision diameter (Lorentz) and a geometric mean for the well depth (Berthelot rule).

Many mixing rules have been proposed in the literature, Maitland et al.[5] provides a good review of the mixing rules literature prior to 1981. More recent rules include these of Pena Diaz and coworkers,[6,7] Tang and Toennies,[8] Bzowski et al.,[9] Halgren,[10] and Waldman and Hagler.[11]

There have not been many studies to assess the effect of mixing rules on the accuracy of the force fields. Two main reasons have contributed to such practice. The common belief is that mixing rules do not appreciably affect the outcome of a computer experiment; and, the development of more accurate rules often requires additional parameters that are not known, or are known to poor accuracy.[1,11] Recent studies suggest that mixing rules do affect the outcome of molecular simulations.[1,12–14]

The main objective of this article is to produce a generating equation for mixing rules. Once such a generating equation is obtained, superior mixing rules can be generated. The first part briefly reviews the available mixing rules. Then, a detailed survey of the available experimental data for the cross interaction collision diameter and well depth for the noble gases is given. Subsequently, a generating equation and two new mixing rules are proposed. The last part provides the results of comparing the mixing rules available in the literature with the rules proposed in this work.

Mixing Rules

For N types of interaction sites, one needs to define $\frac{1}{2}N(N+1)$ interaction parameter sets. This is a huge number, and reduces the versatility of pure site interaction parameters. Instead of specifying the off diagonal terms in such parameter sets, the common practice is to use mixing (combination) rules that allow the use of pure site parameters only. This requires specifying only N parameter sets. In matrix form, the following array depicts these concepts for an N site case, where bold face denotes the vector of parameter sets involved. The boxed elements are the elements that require specification when using mixing rules.

$$\begin{bmatrix} \boxed{\mathbf{a}_{1,1}} & \mathbf{a}_{1,2} & \cdots & \mathbf{a}_{1,N-1} & \mathbf{a}_{1,N} \\ \mathbf{a}_{2,1} & \boxed{\ddots} & \cdots & \mathbf{a}_{2,N-1} & \mathbf{a}_{2,N} \\ \vdots & \ddots & \boxed{\cdots} & \ddots & \vdots \\ \mathbf{a}_{N-1,1} & \ddots & \cdots & \boxed{\ddots} & \mathbf{a}_{N-1,N} \\ \mathbf{a}_{N,1} & \mathbf{a}_{N,2} & \cdots & \mathbf{a}_{N,N-1} & \boxed{\mathbf{a}_{N,N}} \end{bmatrix}$$

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With this in mind, the problem is posed as: consider a system C composed of N components $A_1 \cdots A_N$. Can a property c of the system be predicted from knowledge of the pure constituent properties **a**, where **a** is the vector of pure component properties (**b**, **c**, $\cdots$)?

The mathematical relationship corresponding to the posed problem is called a mixing rule. Mixing rules can be devised either on some theoretical background or purely empirical correlation of experimental data.

Theoretical Rules

Theoretical mixing rules are based on some quantum mechanical derivation. The problem with such an approach is the incorporation of additional parameter sets (e.g., polarizability, ionization potentials, or dispersion force coefficients). This is contradictory to the purpose behind introducing mixing rules. Mixing rules are introduced to reduce the number of parameter sets in any force field, while theoretical rules introduce more parameters and some of them are not easily determined. The most successful equation of this group is the Tang–Toennies.[8]

$$\sigma_{ij}^6 = \frac{(0.5(\varepsilon_{ii}^{1/13}\sigma_{ii}^{12/13} + \varepsilon_{jj}^{1/13}\sigma_{jj}^{12/13}))^{13}}{(\varepsilon_{ii}\varepsilon_{jj})^{1/2}(\sigma_{ii}\sigma_{jj})^3}, \tag{1}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}\left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6}\right)\frac{C_{6,ij}}{(C_{6,ii}C_{6,jj})^{1/2}}. \tag{2}$$

Empirical Rules

Empirical mixing rules attempt to find a suitable mathematical expression capable of reproducing the experimental values for dissimilar interactions. Three rules are widely used in the literature: Lorentz–Berthelot, Halgren HHG, and Waldman–Hagler.

Lorentz–Berthelot

Lorentz–Berthelot rules are the most widely used.[15,16] An arithmetic average is used for the collision diameter, while a geometric average is used for the well depth.

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}), \tag{3}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}. \tag{4}$$

Halgren HHG

Halgren HHG rules implement a weighted average of the arithmetic-mean rule for σ; the weight factor being the square of the value.[10] For ε, Halgren HHG applies a harmonic mean of the harmonic and geometric mean values.[10]

$$\sigma_{ij} = \frac{\sigma_{ii}^3 + \sigma_{jj}^3}{\sigma_{ii}^2 + \sigma_{jj}^2}, \tag{5}$$

Table 1. Values of Collision Diameter and Well Depth for Pure Noble Gases.

	Kestin[9,17]		Halgren[10]		Tang–Toennies[8]	
	σ (Å)	ε/k_B (K)	r_m (Å)	ε/k_B (K)	r_m (Å)	ε/k_B (K)
He[a]	2.610	10.4	2.963	10.95	2.963	10.95
Ne[a]	2.755	42.0	3.087	42.25	3.087	42.25
Ar	3.350	141.5	3.761	143.3	3.759	143.3
Kr	3.571	197.8	4.012	199.9	4.012	199.9
Xe[a]	3.885	274.0	4.363	282.4	4.363	282.4

[a]Additional values are given below.[25]

He	2.56	10.2
Ne	2.75	35.6
Xe	4.10	222.3
Xe	3.85	230.0

$$\varepsilon_{ij} = \frac{4\varepsilon_{ii}\varepsilon_{jj}}{(\varepsilon_{ii}^{1/2} + \varepsilon_{jj}^{1/2})^2}. \tag{6}$$

Waldman–Hagler

The Waldman–Hagler rule utilizes a sixth power mean for collision diameter and a simplified form of the reduced sixth dispersion coefficient for the well depth[11]

$$\sigma_{ij} = \left(\frac{\sigma_{ii}^6 + \sigma_{jj}^6}{2}\right)^{1/6}, \tag{7}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}\left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6}\right). \tag{8}$$

Experimental Data for σ and ε

Mixing rules can be tested against experimental values of σ_{ij} and ε_{ij}. Unfortunately, such data sets are limited. Three data sets for the binary mixtures composed of the noble gases are available in the literature; Kestin and coworkers,[9,17] Tang and Toennies,[8] and Halgren.[10] These data sets are given in Tables 1 and 2 for pure systems and binary mixtures, respectively. These tables include some partial data sets that are available in the literature.

The data sets of Halgren, and Tang and Toennies for the pure component parameters are essentially the same. However, the mixture properties differ by up to 7% for the lighter systems (up to Ne–Ar), at which point the two systems become essentially the same. The Tang and Toennies values of well depth are higher than those of Halgren, while the opposite is true for the minimum distance. This discrepancy in experimental values needs to be resolved before adopting such data sets to compare mixing rules. To be able to compare the mixing rules on an objective and consistent manner, we need to use a consistent set of values of σ

Table 2. Values of Collision Diameter and Well Depth for Binary Mixtures of Noble Gases.

	Kestin[9,17]		Halgren[10]		Tang–Toennies[8]	
	σ (Å)	ε/k_B (K)	r_m (Å)	ε/k_B (K)	r_m (Å)	ε/k_B (K)
He–Ne[b]	2.691	19.44	3.036	20.89	3.015	21.82
He–Ar[b]	3.084	30.01	3.478	29.65	3.480	29.80
He–Kr[b]	3.267	31.05	3.691	29.50	3.688	30.87
He–Xe[b]	3.533	29.77	3.968	28.00	3.940	30.00
Ne–Ar[a]	3.119	64.17	3.489	67.59	3.417	69.18
Ne–Kr[a]	3.264	67.32	3.621	71.60	3.630	70.70
Ne–Xe[a]	3.488	67.25	3.861	74.20	3.870	72.20
Ar–Kr	3.464	165.8	3.881	167.3	3.881	167.3
Ar–Xe	3.660	182.6	4.067	188.6	4.067	188.6
Kr–Xe	3.753	225.4	4.174	233.5	4.174	233.5

[a]Rotation modified r_m and three-body effects values.[26]

Ne–Ar	3.4849	3.4812
Ne–Kr	3.6430	3.6430
Ne–Xe	3.8898	3.8898

[b]Corresponding states viscosity inversion values as given by[27]

He–Ne	2.695	20.94
He–Ar	3.102	29.57
He–Kr	3.294	30.34
He–Xe	3.559	30.00

and ε. The data provided by Kestin and coworkers[9,17] is consistent, and no combination rule was assumed or invoked to derive the parameters reported for the noble gases.[11]

A practical approach to assess the consistency of experimental sets of data is to test them against a short form or an extended form of corresponding states theory,

$$\varepsilon_{ij}\sigma_{ij}^6 = (\varepsilon_{ii}\varepsilon_{jj})^{0.5}(\sigma_{ii}\sigma_{jj})^3, \tag{9}$$

$$\frac{\varepsilon_{ij}\sigma_{ij}^6}{C_{6,ij}} = \frac{(\varepsilon_{ii}\varepsilon_{jj})^{0.5}(\sigma_{ii}\sigma_{jj})^3}{(C_{6,ii}C_{6,jj})^{0.5}}. \tag{10}$$

One can test for deviations from corresponding states theory by arbitrarily plotting $(\sigma_{ii}\sigma_{jj})^3/\sigma_{ij}^6$ vs. $\varepsilon_{ij}/(\varepsilon_{ii}\varepsilon_{jj})^{0.5}$ or $(\sigma_{ii}\sigma_{jj})^3 C_{6,ij}/\sigma_{ij}^6(C_{6,ii}C_{6,jj})^{0.5}$ vs. $\varepsilon_{ij}/(\varepsilon_{ii}\varepsilon_{jj})^{0.5}$. These quantities are chosen as abscissas because the expected range is around 1.0. Figure 1 shows the short form of the corresponding states theory test, while Figure 2 shows the extended form test. It is clear that the data set of Kestin is the closest to following both corresponding state theories, while both theories underestimate the experimental data sets of Halgren and Tang and Toennies. Including the dispersion force coefficient does not result in significant improvement in the agreement between the corresponding state theory and the experimental values. This might be due to uncertainties in the C_6 values, the inequality of ratios at the well minimum and at zero energy, or the inadequacy of simple corresponding states theory itself.

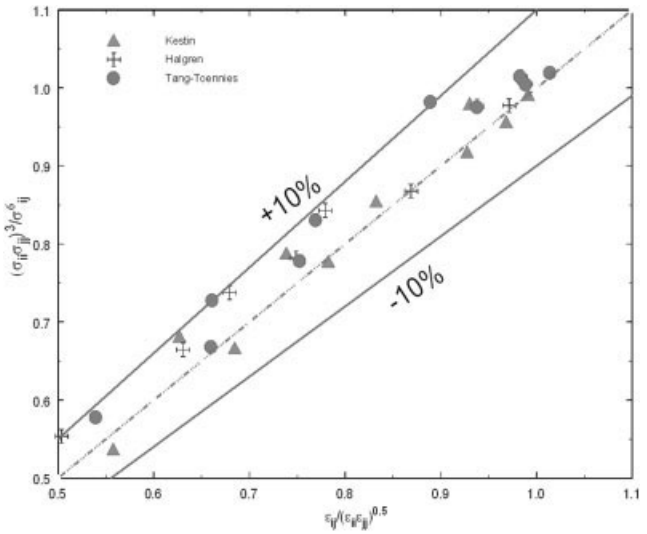


Figure 1. Short form of corresponding states theory plot for different binary noble gas data sets.

Development of Generating Equation for Mixing Rules

Current mixing rules implement homogeneous pure site terms. If a quantity is to be represented in terms of its components, we need to include the nonhomogeneous contributions in addition to devising a methodology to obtain weighting parameters. In this manner, we can devise a framework for generating mixing rules or comparing them efficiently. Some of the most popular mixing rules (Lorentz–Berthelot, Halgren HHG, and Waldman–Hagler) are special cases of the general formula proposed here. There are few experimental values for the interaction parameters that are based on binary pairs. Consequently, we focus our attention on the two component case.

The problem is posed as: consider a system C composed of N components $A_1 \cdots A_N$. Can a property c of the system be pre-

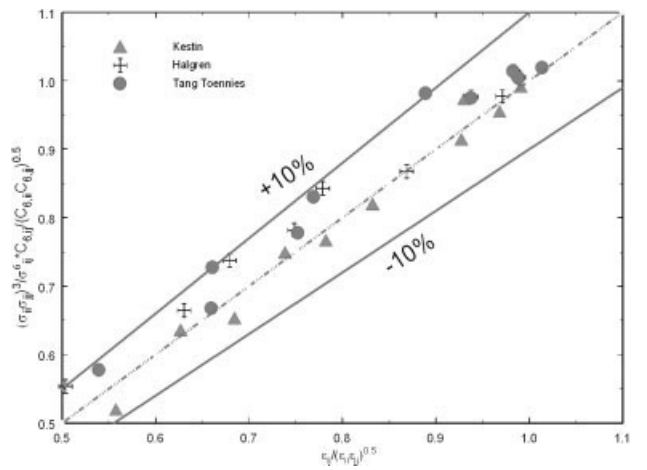


Figure 2. Extended form of corresponding states theory plot for different binary noble gas data sets.

dicted from knowledge of the pure constituent properties **a**, where **a** is the vector of pure component properties (**b**, **c**, $\cdots$)? This problem needs to be addressed while keeping in mind that an N^{th} order interaction may depend on all lower order interactions up to $(N-1)^{\text{th}}$ order interactions. The first order is assigned to pure component interaction.

A summary of the reasoning of Waldman and Hagler[11] regarding the requirements for the existence of such a function follows. The mathematical treatment is generalized and a fourth condition is added.

1. Symmetry
$$f(\mathbf{a}) = f(\mathbf{a}^T) \tag{11}$$
is essential to reduce the number of parameter sets involved. In principle, the method proposed can be used without this constraint. However, it will require specifying $2N$ parameter sets instead of N sets,
2. The function is scalable or invariant with uniform scaling of **a**, and **c**. This is important for the model to be useful among different systems of units,
$$sc = f(s\mathbf{a}). \tag{12}$$
3. Identity relationship for a mixture composed of the same components should predict the properties of the pure component,
$$c = f(\mathbf{a}_{\text{pure}}) = \|\mathbf{a}\| = a. \tag{13}$$
4. If composition dependence is to be included, avoid the Michelsen–Kistenmacher syndrome.[18] This implies the rule must be invariant to the division of a component into identical subcomponents.

In addition to these rigorous mathematical constraints, one can think of other *desirable* features the mixing rule should possess. Simplicity of the mixing rule is the most desirable feature. Computational efficiency and the lowest number of adjustable parameters (if any) are other desirable features.

One can think of the system properties for a two component system as being the result of four kinds of interactions, A_1–A_1, A_1–A_2, A_2–A_1, and A_2–A_2. Due to the symmetry, eq. (11) imposed on the combination rule, we must set the dissimilar interactions of A_1–A_2 is equal to A_2–A_1.

The second logical step is to consider any property of the system as the weighted average of the vector of pure component properties. The weighting is arbitrary, and *average* does not necessarily refer to *arithmetic average.* Any functional form can be used as long as it satisfies the above mentioned constraints. For an N component mixture, we can arbitrarily represent the mixture property of interest as the summation of weighting factors and functions:

$$c = \frac{[\sum_{i=1}^{N}\sum_{j=1}^{N}\cdots\sum_{m=1}^{N}\sum_{n=1}^{N} w_{ij\cdots mn} f_{ij\cdots mn}(\mathbf{a}, \mathbf{b}, \cdots)]^M}{[\sum_{i=1}^{N} g_i(a_i, b_i, \cdots)]^L}, \tag{14}$$

where the f functions are referred to as the weighting functions, while the g functions are referred to as the normalizing functions. For the two component case, this equation reduces to

$$c = \frac{[\sum_{i=1}^{N=2}\sum_{j=1}^{N=2} w_{ij} f_{ij}(\mathbf{a}, \mathbf{b}, \cdots)]^M}{[\sum_{i=1}^{N=2} g_i(a_i, b_i, \cdots)]^L}. \tag{15}$$

For example, we can arbitrarily use a generalized power average to describe the function f with the dissimilar contributions arbitrarily assumed to follow a multiplicative form of the pure contributions. Consequently, the general equation to generate such an average takes the form:

$$c = \left(\frac{\sum_{i=1}^{N}\sum_{j=1}^{N}\cdots\sum_{m=1}^{N}\sum_{n=1}^{N} w_{ij\cdots mn} a_i^{M/N} a_j^{M/N}\cdots a_m^{M/N} a_n^{M/N}}{\sum_{i=1}^{N} a_i^L}\right)^{1/(m-L)}, \tag{16}$$

where M and L are arbitrary powers. This freedom in choosing the powers is advantageous to generate weighted averages closer to one of the pure components. The weighting factors are included in **w**, which is an N-dimensional matrix which reduces to a 2×2 matrix for the two component case. This matrix contains the weight coefficients that are used to adjust the value of the average. It is clear that as the number of components increases, the weighting matrix demands significant storage requirements. However, it is still a sparse matrix for which efficient storage algorithms exist.[19] This equation can serve as a good starting point to study reducing not just binary interaction, but also ternary and higher order interactions, into pure component properties. Applying the logic adopted here, ternary interactions require knowledge of pure and binary interactions. Similarly, quarternary interactions require the knowledge of ternary, binary, and pure interactions. However, it would be interesting to study the reduction of ternary and higher interactions into only a double summation containing pure interactions instead of an N summation with all orders of interactions up to $N-1$.

For consistency, the indexing starts with the lower valued component and ends at the highest valued component. This approach can be applied for any property regardless of the terminology. This is essential to avoid swapping problems when reversing the order of components and their associated weighting factors.

Many force fields define two parameters that characterize the potential energy surface: the collision diameter (σ, distance at which potential energy becomes zero) and the well depth (ε, the minimum value of energy). Tables 3 and 4 summarize some mixing rules as obtained using eq. (15) for a two-component collision diameter and well depth, respectively. These tables clearly demonstrate that eq. 15 can be used to generate many forms of mixing rules in the literature.

Table 3. Summary of the Mixing Rules for the Collision Diameter Using the Generating Equation as Applied to a Two-Component Mixture.

Combining rule	M	f_{ij}	L	g_i
Lorentz–Berthelot	1	σ_{ij}	1	1
Halgren HHG	1	σ_{ij}^3	1	σ_{ii}^2
Waldman–Hagler	1/6	σ_{ij}^6	1/6	1
Tang–Toennies	13/6	$\frac{\varepsilon_{ij}^{1/13}\sigma_{ij}^{12/13}}{(\varepsilon_{ii}\varepsilon_{jj})^{6/26}(\sigma_{ii}\sigma_{jj})^{36/26}}$	13/6	1

$w = \begin{pmatrix} 1.0 & 0.0 \\ 0.0 & 1.0 \end{pmatrix}$ for all rules

It is interesting to note that in all these combining rules, equal weights are assumed for the like-term interactions. This may give an indication why such simple averaging models do not perform well. From a theoretical point of view, it is expected that the pure interactions are weighted by a certain factor that is dependent on the properties of the pure components. Intuitively, these weighting factors must be different for different components. The current models do not take this into consideration. Analogous to this idea is the coordinates of the center of mass of two objects, which is a weighted average of their coordinates. The weighting is done utilizing the mass of the two objects. The same rationale can be utilized with the mixing rules here. However, no theoretical significance to the values of the weighting factors is provided in this effort. Probably, these parameters must depend on certain pure constituent parameters.

The Tang–Toennies Rule is evidence of this kind of rationale. Based on theoretical considerations, the collision diameter ultimately is weighted by a certain power similar to other rules. It is also weighted by the well depth. This may explain the success of the Tang–Toennies Rule (relative to other models) in determining the collision diameter. This rule not only reduces the average error, it has the lowest maximum absolute error relative to all of the other models (Table 5).

Two sets of parameters can generate the Waldman–Hagler model. The $m = 12$ case is more logical than the $m = 6$ case. A matrix of equal weights is the most obvious choice in the absence of any information about cross interaction contribution. It is not surprising that the sixth power works well for mixing rules, because from quantum mechanics it is known that the attractive portion of dispersion energy is proportional to the sixth power in separation.[20]

The framework laid can, in principle, be extended to classical thermodynamics. Cubic equations of state depend on using two adjustable parameters. A parameter related to attractive forces (a) and a parameter related to the excluded volume (b). Not very surprising, Lorentz–Berthelot type rules are used for determining these parameters

$$a_{ij} = (a_{ii}a_{jj})^{1/2}, \tag{17}$$

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2}\right). \tag{18}$$

To improve the accuracy of mixing rules, an empirical binary interaction parameter is fitted to the experimental data.[18,21]

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1 - k_{ij}), \tag{19}$$

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2}\right)(1 - l_{ij}). \tag{20}$$

The method of using a weighting matrix is a general case for such an approach. This is apparent by equating the w_{ij} in eq. (15) with the $(1 - k_{ij})$ or $(1 - l_{ij})$. The approach proposed can lead to defining asymmetrical mixing rules in which $k_{ij} \neq k_{ji}$ or $l_{ij} \neq l_{ji}$.

Table 4. Summary of the Mixing Rules for the Well Depth Using the Generating Equation as Applied to a Two-Component Mixture.

Combining rule	M	f_{ij}	L	g_i
Lorentz–Berthelot	1	$\varepsilon_{ii}^{1/2}\varepsilon_{jj}^{1/2}$	1	1
Harmonic	1	$\varepsilon_{ii}\varepsilon_{jj}$	1	ε_{ii}
Halgren HHG	1	$2\varepsilon_{ii}\varepsilon_{jj}$	2	$\varepsilon_{ii}^{1/2}$
Waldman–Hagler	1	$4\varepsilon_{ii}^{1/2}\varepsilon_{jj}^{1/2}\left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ii}^6 + \sigma_{jj}^6}\right)$	1	1
Tang–Toennies	1	$2\varepsilon_{ii}^{1/2}\varepsilon_{jj}^{1/2}\left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6}\right)\frac{C_{6,ij}}{(C_{6,ii}C_{6,jj})^{1/2}}$	1	1

$w = \begin{pmatrix} 0.0 & 1.0 \\ 1.0 & 0.0 \end{pmatrix}$ for all rules

Table 5. Errors in Estimation of Collision Diameter of the Binary Noble Gases Using Different Mixing Rules.

Rule	RMS (Å)	Max error (%)	RMS (%)
Arithmetic	0.137	8.10	4.02
Halgren HHG	0.020	1.26	0.595
Waldman–Hagler	0.018	1.23	0.524
Tang–Toennies	0.017	0.80	0.522
This work functional	0.019	1.46	0.537
This work fit	0.017	1.00	0.502

This is advantageous, and can avoid resorting to composition-dependent mixing rules. However, this needs to be tested using experimental data. Furthermore, successful mixing rules of the interatomic potential parameters such as the rules we propose or the Waldman–Hagler can be tested to check if they can give any improvement over the classical mixing rules given in eqs. (17), (18), (19), and (20). An additional advantage to use the generating equation in the case of EOS is there is only one adjustable parameter for all symmetric systems and two for asymmetric case. This is contrary to the binary interaction parameters, which are system specific and need to be fitted for each system.

Another future prospect of applying such an approach is to equations of state derived from statistical mechanical theories. Examples include SAFT with all its variants[22,23] and perturbed hard-sphere chain.[24] These models essentially divide the Helmholtz free energy into a reference fluid and a perturbation contribution.[24] Within these models a combination rule is assumed and Lorentz–Berthelot rules are still widely used. This forces such EOS to utilize binary interaction parameters to match experimental data.

Two New Mixing Rules

Having demonstrated that eq. (15) can indeed generate many forms of mixing rules, the second logical step is to test if such an equation can be used to optimize the weighting factors for mixing rules. This is carried out for the interatomic potential energy parameters. The following two rules proposed can be used with a slight improvement for predicting the values of mixture parameters.

Functional Mixing Rule

The functional rule is derived based on extensive functional analysis of the behavior of the available experimental data. It takes the form:

$$\sigma_{ij} = \frac{1}{3}\sum_{L=0}^{2}\left(\frac{0.25(\sigma_{ii}^3 + \sigma_{jj}^3)^2}{\sigma_{ii}^L\sigma_{jj}^L}\right)^{1/(6-2L)}, \tag{21}$$

$$\varepsilon_{ij} = 3(\varepsilon_{ii}\varepsilon_{jj})^{1/2}\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sum_{L=0}^{2}\left(\frac{0.25(\sigma_{ii}^3 + \sigma_{jj}^3)^2}{\sigma_{ii}^L\sigma_{jj}^L}\right)^{6/(6-2L)}}. \tag{22}$$

Fit Mixing Rule

A least-squares analysis was carried out for both σ and ε to determine the weight factors matrix for eq. (15). The data set of Kestin and coworkers was used throughout. The power was fixed to the sixth power for theoretical considerations; however, it can be treated as an adjustable parameter. The final equations take the form

$$\sigma_{ij} = \left(\frac{0.5640\sigma_{ii}^6 + 0.9464\sigma_{ii}^3\sigma_{jj}^3 + 0.4896\sigma_{jj}^6}{2}\right)^{1/6}, \tag{23}$$

$$\varepsilon_{ij} = \left(\frac{0.0799\varepsilon_{ii} + 1.912939769(\varepsilon_{ii}\varepsilon_{jj})^{1/2} + 0.0071\varepsilon_{jj}}{2}\right) \times \left(\frac{\sigma_{ii}^3\sigma_{jj}^3}{\sigma_{ij}^6}\right). \tag{24}$$

It is interesting to see how the weighting matrices for the collision diameter and well depth behave.

$$\mathbf{w}_\sigma = \begin{bmatrix} 0.2820 & 0.2366 \\ 0.2366 & 0.2448 \end{bmatrix}, \quad \mathbf{w}_\varepsilon = \begin{bmatrix} 0.0400 & 0.4783 \\ 0.4783 & 0.0040 \end{bmatrix}$$

The collision diameter weighting matrix shows that the lighter component has slightly more weight. However, due to the lower numerical value and the sixth power dependency, it appears that the collision diameter is not appreciably shifted towards the lighter component. There is approximately equal contribution between like and unlike terms. This trend is not the case for the well depth. The lighter component weighting element is 10 times higher than that of the heavier component. Also, unlike terms dominate the like terms; like terms contribute less than 5% of the total sum of the elements of the weighting matrix.

A comparison of different mixing rules is subsequently performed consisting of evaluating the binary interactions from pure component properties. Kestin's data set was used to determine these values. The root-mean-square (RMS) error, maximum error and RMS percent error for the collision diameter and well depth are given in Tables 5 and 6, respectively. Figures 3 through 7 give the relative errors of each mixing rule with the five possible binary series, beginning with helium and ending with xenon, respectively. Note that the Lorentz–Berthelot values are multiplied by a factor of 0.1 to amplify the scale.

The Ar–Kr system clearly provides the system easiest for mixing rules to describe. This can be explained by the relatively

Table 6. Errors in Estimation of Well Depth of the Binary Noble Gases Using Different Mixing Rules.

Rule	RMS (K)	Max err (%)	RMS (%)
Geometric	19.5	79.3	40.2
Halgren HHG	8.80	29.0	13.4
Waldman–Hagler	1.59	6.11	2.52
Tang–Toennies	2.44	6.70	4.60
This work functional	1.48	6.22	2.93
This work fit	1.40	4.94	2.21

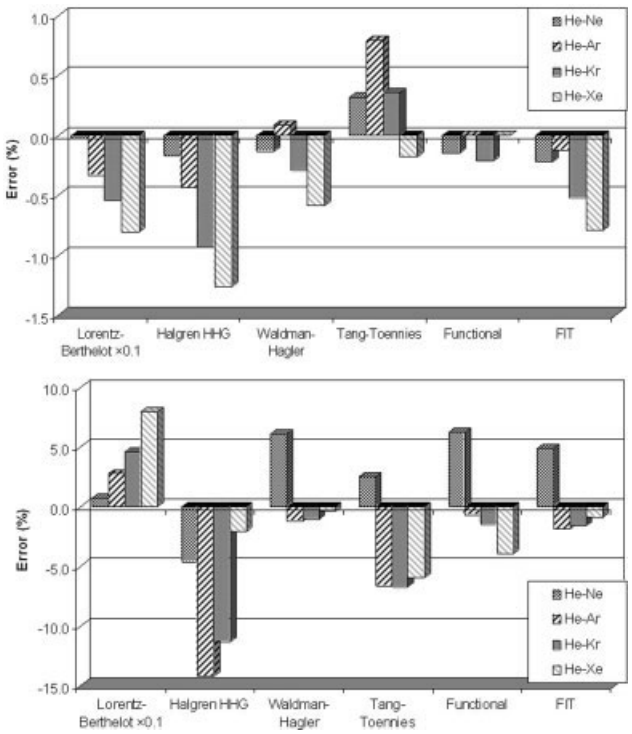


Figure 3. Relative errors using different mixing rules for the helium–noble gas binaries. The upper figure is collision diameter, while the lower figure is well depth.

similar size of the two atoms, and the absence of quantum effects. The Ne–Xe seems to be the most difficult system for the mixing rules to determine the collision diameter. One can speculate that this might be due to electronic cloud distortion effects. The system for which the well depth is the most difficult to describe is the He–Ne system. This might be attributed to the quantum effects inherent in such a light system.

All rules except the Lorentz–Berthelot yield similar results for the collision diameter. These results have an RMS within 0.02 Å or 1% of the experimental values. Distinction can be made, however, using the well depth. It appears that the rule based on fitting the weighting matrix yields slightly better agreement with the data for the well depth. This is true whether using the RMS or the maximum absolute error. Waldman–Hagler, Tang–Toennies, and the functional form of this work seem to be equivalent in their predictions. The following sections discuss the performance of different mixing rules studied in this work.

Results and Discussion

Lorentz–Berthelot

The figures clearly show that the L-B mixing rules consistently underestimate the collision diameter and overestimate the well depth. The underestimation of the collision diameter is proportional to the difference in size between the binary components. The well depth follows the opposite trend, which is consistent with the findings of other researchers.[8,10,11] The error in collision diameter is reasonable at a maximum of 8%; while the errors are erroneous for the well depth amounting to 79%. If (1) corresponding states theory applies, and (2) a scaling as the sixth power with no errors assumed in the pure values of the collision diameter and the well depth then around a 60% error is observed. This is within the error range expected for the L-B rules. This can be used to correct for the well depth without altering the value of collision diameter. However, the results of L-B rules stress the need to resolve the correlation between the collision diameter and well depth. It also sheds some light on the more complicated nature of the well depth compared to the collision diameter. The L-B rules can be used as a starting point for the systematic development of mixing rules. The residual errors can be compensated for by using an additional form to improve the agreement with experimental data. Hence, any mixture property can be written as

$$P_m = P_{\text{L-B}} + P_r, \tag{25}$$

where the subscript m is used to denote a mixture property, L-B for the Lorentz–Berthelot estimate and r for the residual.

Halgren HHG

Halgren HHG rules seem to follow a cyclic trend with the system used. Generally, errors increase in magnitude with the difference in atomic size. The well depth follows a trend similar to that of the

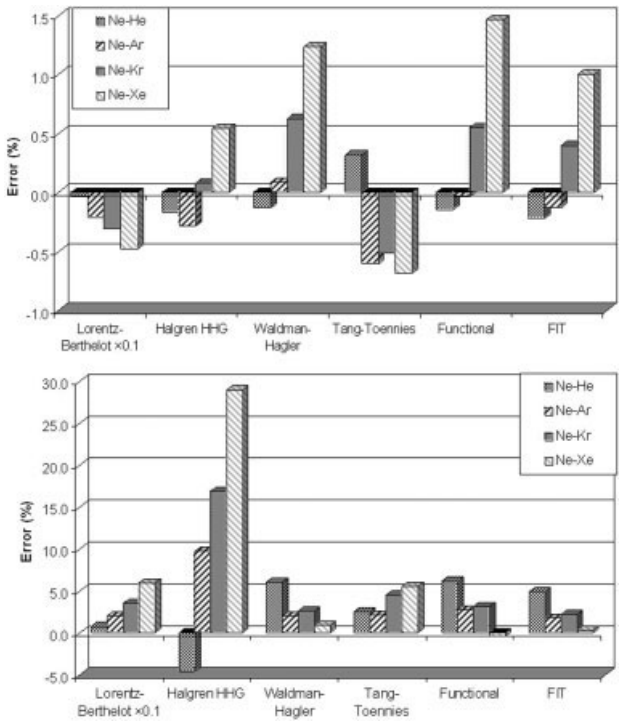


Figure 4. Relative errors using different mixing rules for the neon–noble gas binaries. The upper figure is collision diameter, while the lower figure is well depth.

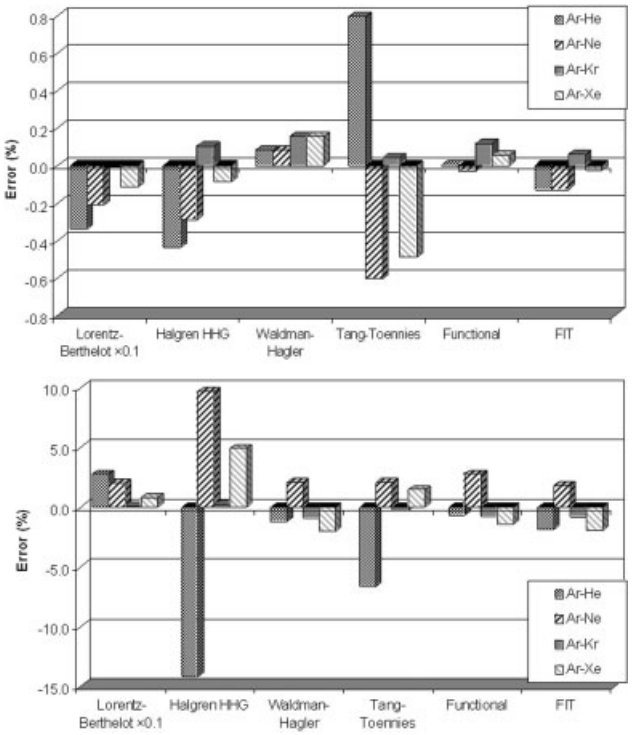


Figure 5. Relative errors using different mixing rules for the argon–noble gas binaries. The upper figure is collision diameter, while the lower figure is well depth.

collision diameter. This cannot be explained solely by the correlation between collision diameter and well depth. Another reason would be the combined effect of this correlation and the behavior of the function describing the mean. It may be advantageous if a combined average, with a rule that follows the opposite trend, is identified. Although these rules are an improvement over the L-B rules, they do not provide a superior alternative to Waldman–Hagler, Tang–Toennies, or the rules proposed in this research.

Waldman–Hagler

The Waldman–Hagler rules generally underestimate the collision diameter for light systems and overestimate it for heavier systems. This underestimation increases with size difference. The Ne binaries in general, and the Ne–Xe system in particular, pose a hard problem for collision diameter predictions from the Waldman–Hagler rules. If quantum effects or electronic cloud distortion alone are responsible for such difficulty, then one would expect the He binaries to follow the same trend. Nonetheless, the He binaries do not follow such a trend. This may hint at experimental errors in such binaries, or even pure component parameters. The Waldman–Hagler rules provide one of the best set of rules, whether considering collision diameter or well depth. Generally, it yields satisfactory results within expected experimental errors.

Tang–Toennies

Tang–Toennies rules provide the best approach for estimating the collision diameter. It has the lowest RMS and the lowest maximum error. This can be attributed to the weighting using the well depth. However, there are no guarantees that the Tang–Toennies rule will perform better than other rules when used for other systems. The derivation of this mixing rule was carried out using a 12th power dependence in the repulsive region. This is generally valid for the noble gases, while other systems have optimum powers other than 12.

It is interesting to note that the Tang–Toennies rules follow the same cyclic trend as those of Halgren HHG. The inclusion of the sixth dispersion coefficients do not necessarily improve the agreement of the results of these rules with experimental data. Although these rules provide the best rule for collision diameter, they do not perform as well for the well depth. However, they do yield satisfactory results within the expected experimental errors.

Functional and Fit Rules

The Waldman–Hagler rule is slightly better than the functional form, while the fit rule is slightly better than any other rule. This success of the fit rule cannot be attributed to the form. Rather, it is attributed to the extra two parameters fitted to the data. However, these two parameters should be applicable to any system, as long as the same functional form is used. The weighting matrix is expected to be slightly altered if other binary systems are included in the fitting procedure. The Ne–Xe system contributes most of the error to these two rules. The error would be reduced roughly by 50% if this system was excluded from the data fitting. Also, the functional form would be more accurate than the Waldman–Hagler rules by about 30%. Over-

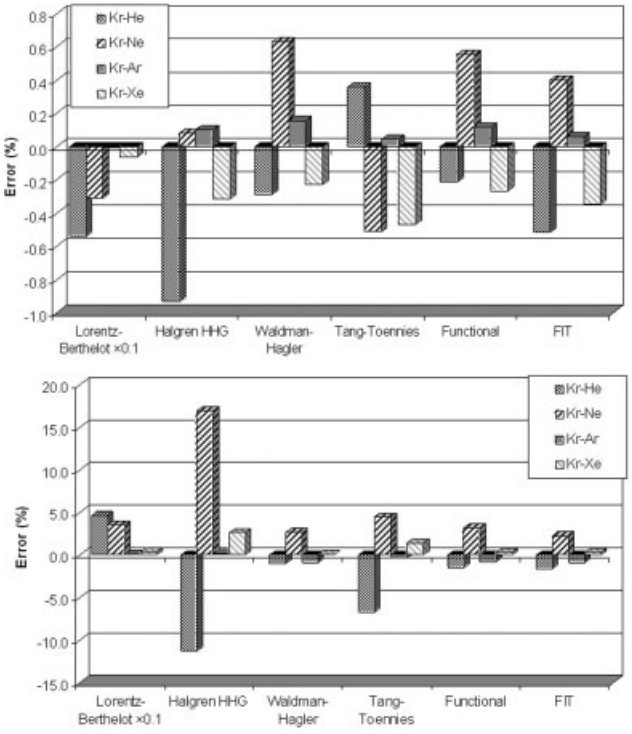


Figure 6. Relative errors using different mixing rules for the krypton–noble gas binaries. The upper figure is collision diameter, while the lower figure is well depth.

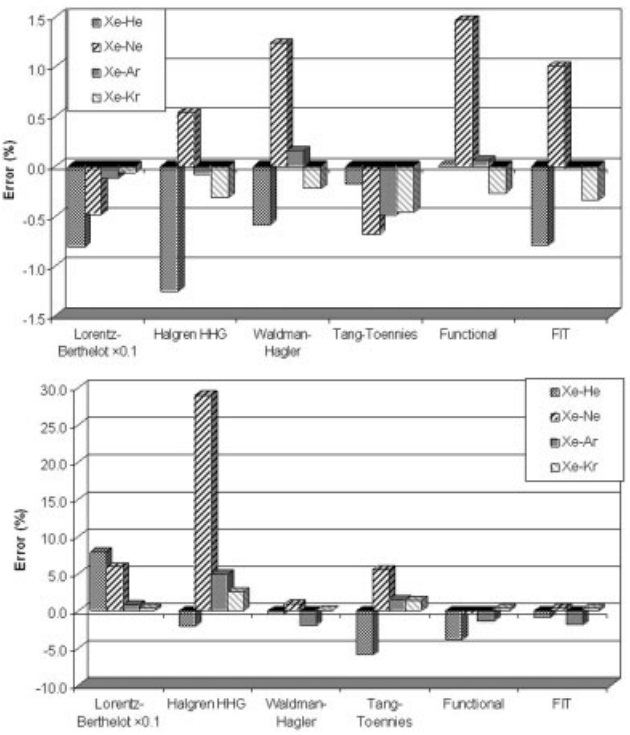


Figure 7. Relative errors using different mixing rules for the xenon–noble gas binaries. The upper figure is collision diameter, while the lower figure is well depth.

all, these two rules are able to provide estimates of collision diameter and well depth within expected experimental uncertainty.

Conclusions and Future Research

An evidence of the inadequacy of the Lorentz–Berthelot mixing rules is produced in this research. Lorentz–Berthelot rules do not perform better than other available mixing rules even when compared against experimental collision diameter and well depth. This research tried to overcome this inadequacy by first providing a systematic framework for the development of mixing rules. This framework was then used to produce a generating equation for mixing rules. Consequently, the generating equation is used to produce a mixing rule superior to the available mixing rules in the literature. This approach was shown to be successful in generating such a mixing rule. This mixing rule was found to perform better than any of the other mixing rules considered. However, this improvement, in agreement with experimental data, came at the expense of two additional adjustable parameters. A functional form was also provided, which is slightly less accurate than the fitted form. However, this functional form is comparable to Waldman–Hagler and better than Tang–Toennies rules.

It is recommended to use either the Waldman–Hagler [eq. (7)], or the Functional [eq. (21)] form proposed in this research. These models are expected to improve the accuracy of computer experiments, be it molecular dynamics or Monte Carlo.

Another direction is to resolve the correlation between the collision diameter and well depth, and collision diameter and dispersion coefficients. If such correlations are resolved by developing accurate relationships then a convergence between empirical and theoretical mixing rules is to be expected. Furthermore, it is recommended that more complicated forms of corresponding states theory be tested. This might require the use of eighth and higher dispersion coefficients to improve theory predictions with experimental data. The success of eq. (21) for the collision diameter can be extended further to include well depth using higher order dispersion coefficients.

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