

A SIMPLE POTENTIAL MODEL FOR LINEAR SYMMETRIC MOLECULES

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A simple molecular model is proposed for prediction of second virial coefficients of linear symmetric molecules. The intermolecular potential is substituted by summation of the group-group interactions described by the Lennard-Jones 12-6 potential.

The second virial coefficients of oxygen, carbon dioxide and ethylene predicted in the present study agree with the recommended values of IUPAC within 1% or $1\text{ cm}^3\cdot\text{mol}^{-1}$ for wide temperature ranges. Furthermore, the prediction method proposed is compared with the intermolecular potential model of Lennard-Jones and the corresponding state theory of Tsonopoulos.

The present model is extended to mixtures straightforwardly without any binary parameter. The interaction second virial coefficients predicted by the model are in good agreement with observed data.

Introduction

The second virial coefficient is one of the most important properties in the study of intermolecular potential, and various correlation and prediction methods have been proposed by several investigators. In many cases, the corresponding state principle (abbreviated as CSP) has been applied for correlating virial coefficients. The CSP theory for spherical symmetric molecules and the extension of the theory to *n*-alkanes give empirical formulae for second virial coefficients in terms of the critical properties.

On the other hand, the molecular models are proposed mainly for the purpose of studying intermolecular potential for simple and limited substances. Prediction methods for arbitrary systems based on the molecular model are scarce because of the complexity in calculation and the lack of reliable experimental data in wide temperature ranges. In addition, the intermolecular potential models such as the Lennard-Jones model are not satisfactorily applicable in wide temperature ranges.

Recently, reliable second virial coefficients of oxygen, carbon dioxide and ethylene have been recommended by IUPAC in wide temperature ranges. In the present study, we attempt to propose a molecular model for linear symmetric molecules such as oxygen, carbon dioxide and ethylene.

As a first step in testing the applicability of the model, the second virial coefficients have been correlated with the potential parameters of functional

groups. Thereafter, the interaction second virial coefficients of mixtures have been successfully predicted by mixing rules for group parameters of geometric mean for well depth and of arithmetic mean for collision diameter.

1. Simple Molecular Model

The model proposed is based on the group-contribution concept, and a molecule is divided into each functional group which composes it.

The "bond" length between the groups, l , is defined as the distance between the centroids of each neighboring group in the molecule. For example, we assume that the ethylene molecule consists of two CH_2 groups (E). The normal C-H bond length of 0.109 nm, C=C length of 0.134 nm, and the HCH angle of 117° are given by Sutton¹²⁾ from X-ray analysis. The centroid of CH_2 group is calculated from the above data and the mass of each atom. Therefore a "bond" length between the groups of 0.150 nm is obtained for ethylene that is slightly longer than that of the C=C bond. In a similar way, the "bond" length for each linear molecule is calculated:

$$l = d/(M - 1) \quad (1)$$

where d is the length between two end groups in the molecule considered, and M is the number of functional groups.

Every functional group has two characteristic parameters of the Lennard-Jones potential. The mutual potential of groups is given as

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$$u_{ij}(r_{ij}) = 4(b_i b_j \varepsilon_{ii}^\circ \varepsilon_{jj}^\circ)^{1/2} \times \{(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6\} \quad (2)$$

where ε_{ii}° is the well depth of the Lennard-Jones potential between single group molecules, and b_i is the correcting factor corresponding to the interference effect caused by the neighboring groups in the molecule. The factor b_i is assumed to be represented by the surface ratio of the uncovered sphere to the whole sphere of diameter of σ_i ; then b_i of the i -th group in molecule A is written as follows:

$$b_i = \frac{l_A^2 + (\sigma_i/2)^2 - (\sigma_{i-1}/2)^2}{2l_A \sigma_i} + \frac{l_A^2 + (\sigma_i/2)^2 - (\sigma_{i+1}/2)^2}{2l_A \sigma_i} \quad (3)$$

If $(i+1)$ -th site (the neighboring position of i -th group) is vacant, the second term in Eq. (3) is $1/2$. And $b_i = 0$ when i -th group is wholly covered by the neighboring large group.

The distance r_{ij} between i -group on molecule A and j -group on molecule B is given with the "bond" length l and the distance between the centroids of each molecule r .

$$r_{ij}^2 = r^2 + r(Q_B l_B \cos \theta_2 - Q_A l_A \cos \theta_1) + (Q_A l_A/2)^2 + (Q_B l_B/2)^2 - \frac{1}{2} Q_A Q_B l_A l_B (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi_{12}) \quad (4)$$

where $Q_A = M_A + 1 - 2i$, $Q_B = M_B + 1 - 2j$ and $\phi_{12} = \phi_1 - \phi_2$. The polar coordinates θ_1 , θ_2 and ϕ_{12} are defined as shown in Fig. 1.

The intermolecular potential is assumed to be represented by a summation of pairwise interactions at r fixed.

$$U(r, \theta_1, \theta_2, \phi_{12}) = \sum_{i=1}^{M_A} \sum_{j=1}^{M_B} u_{ij}(r_{ij}) \quad (5)$$

2. Second Virial Coefficient

The second virial coefficient for a linear symmetric molecule can be written from statistical mechanics by use of the above potential model.

$$B(T) = -2\pi N \int_0^\infty F(r) r^2 dr \quad (6)$$

where

$$F(r) = \exp \{ -\Psi(r)/kT \} - 1 = \frac{1}{8\pi} \int_0^{2\pi} \int_0^\pi \int_0^\pi f(r, \theta_1, \theta_2, \phi_{12}) \times \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 d\phi_{12} \quad (7)$$

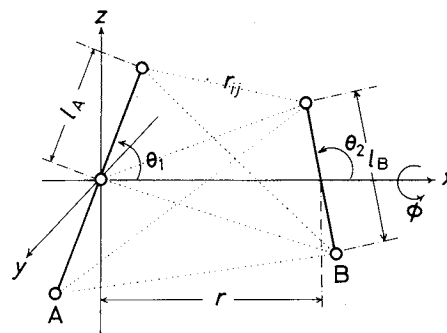


Fig. 1. Coordinates for 2-group molecule and 3-group molecule.

Table 1. Nine types of $f(r, \theta_1, \theta_2, \phi_{12})$ used in Eq. (9)

f	θ_1	θ_2	ϕ_{12}
$f(zz)$	0	0	—
$f(zx)$	0	$\pi/2$	—
$f(xx)$	$\pi/2$	$\pi/2$	0
$f(xy)$	$\pi/2$	$\pi/2$	$\pi/2$
$f(zd)$	0	a	a
$f(xd)$	$\pi/2$	a	$\pi/4$
$f(dd1)$	a	a	0
$f(dd2)$	a	a	$\pi/2$
$f(dd3)$	a	a	π

$$a = \cos^{-1}(\sqrt{3}/3).$$

$$\begin{aligned} f(r, \theta_1, \theta_2, \phi_{12}) &= g(r, \theta_1, \phi_1) g(r, \theta_2, \phi_2) \\ &= \exp \{ -U(r, \theta_1, \theta_2, \phi_{12})/kT \} - 1 \end{aligned} \quad (8)$$

The "effective" intermolecular potential $\Psi(r)$ in Eq. (7) is the averaged potential with angular coordinates and depends on the temperature.

The integral for evaluating $F(r)$ is essentially a numerical integral. However, if the function $g(r, \theta_i, \phi_i)$ is assumed to be an orthogonal function composed of the first-order combination of zeroth-, second- and fourth-order spherical harmonics, the integration by θ and ϕ could be rearranged to an algebraical sum of $f(r, \theta_1, \theta_2, \phi_{12})$ of nine points in space at r fixed.⁷⁾

$$\begin{aligned} F(r) &= (2/5)^2 \{ f(zd) + 2f(xd) \} \\ &\quad + (3/10)^2 \{ f(dd1) + 2f(dd2) \\ &\quad + f(dd3) \} + (2/15)^2 \{ f(zz) \\ &\quad + 4f(zx) + 2f(xx) + 2f(xy) \} \end{aligned} \quad (9)$$

where $zz, zx \dots$ are defined by the angular coordinates as listed in Table 1. The above assumption makes a drastic simplification of the statistical mechanical integral.*)

For the integration in Eq. (6), the numerical in-

*) The assumption of the algebraical sum is satisfied for molecules smaller than seven-groups.

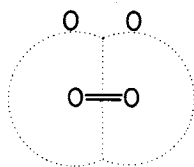


Fig. 2. Model of oxygen molecule: $\text{O}=\text{O}$, 0.121 nm; l , 0.121 nm; σ_{OO} , 0.2976 nm; $\varepsilon_{\text{OO}}^\circ/k$, 75.18 K; b_{O} , 0.703.

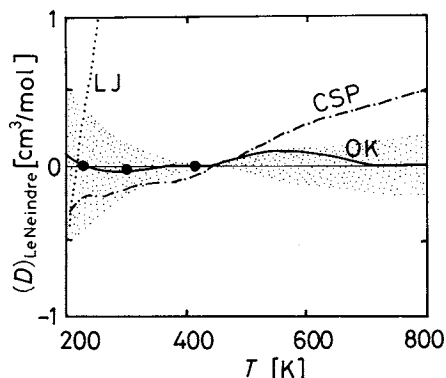


Fig. 3. Deviation from the recommended second virial coefficient of Le Neindre for oxygen.

tegral was carried out from 0 to 2 nm. In addition, for the range longer than 2 nm the Lennard-Jones potential was applied to the intermolecular potential because the second virial coefficient calculated from Eq. (6) was governed by the integral from 0 to 1.5 nm.

3. Results and Discussion

3.1 Oxygen

The model for the oxygen molecule is shown in Fig. 2 with the intramolecular properties and potential parameters. The "bond" length in the model is equivalent to the bonding length between two oxygen atoms obtained from X-ray analysis.

The deviations of the predicted second virial coefficient from the recommended value of IUPAC (Le Neindre and Vodar⁸), $(D)_{\text{Le Neindre}}$, are plotted in Fig. 3. The three circles show the data points where the two potential parameters for the model were evaluated by fitting to the data. The dotted domain in Fig. 3 shows the deviation region smaller than $\pm 1\%$ error.

The prediction method proposed in the present study (OK) shows excellent agreement in the temperature range 200–800 K containing the Boyle temperature (405.88 K).

The corresponding state theory of Tsionopoulos,¹³ (CSP), agrees with the experimental data within $\pm 0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ in the range; however, the result of CSP theory deviates slightly from the recommended values of IUPAC at temperatures higher than the Boyle temperature. The Lennard-Jones model (LJ) ($\varepsilon/k = 109.7 \text{ K}$, $\sigma = 0.3703 \text{ nm}$) cannot correlate the recommended values within $\pm 1 \text{ cm}^3 \cdot \text{mol}^{-1}$ in such a

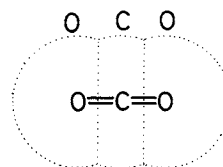


Fig. 4. Model of carbon dioxide molecule: $\text{C}=\text{O}$, 0.116 nm; l , 0.116 nm; σ_{CC} , 0.3146 nm; $\varepsilon_{\text{CC}}^\circ/k$, 145.92 K; b_{C} , 0.440; b_{O} , 0.657; q , $-4.3 \times 10^{-12} \text{ J}^{1/2} \cdot \text{nm}^{5/2}$.

wide temperature range containing the Boyle point.

3.2 Carbon dioxide

The molecular model for carbon dioxide is shown in Fig. 4. The molecule is composed by one carbon and two oxygen atoms and the "bond" length is equal to the length observed by X-ray.

The potential parameters σ_{OO} and $\varepsilon_{\text{OO}}^\circ$ were evaluated in the study of the oxygen molecule. Then σ_{CC} and $\varepsilon_{\text{CC}}^\circ$ are two potential parameters which should be evaluated from the experimental second virial coefficients of carbon dioxide. The factor b_{O} defined in Eq. (3) is slightly different from the value in the case of the oxygen molecule.

For multipolar molecules such as carbon dioxide, the proposed model cannot be directly applied since the expression of pole-pole interaction requires an additional angular coordinate for rotation about the molecular axis.

Therefore, the quadrupole-quadrupole potential is treated according to the next assumption; the quadrupole moment is located at the centroid of carbon dioxide and is written by Eq. (10):

$$U_Q(r, \theta_1, \theta_2, \phi_{12}) = -\frac{3q_1q_2}{4r^5} \{1 - 5(\cos^2 \theta_1 + \cos^2 \theta_2) + 17 \cos^2 \theta_1 \cos^2 \theta_2 + 2 \sin^2 \theta_1 \sin^2 \theta_2 \cos^2 \phi_{12} - 16 \sin \theta_1 \sin \theta_2 \cos \theta_1 \cos \theta_2 \cos \phi_{12}\} \quad (10)$$

where the angle coordinates are equivalent to those of spatial orientation in Fig. 1. The "total" intermolecular potential at distance r is assumed to be expressed as a sum of the intermolecular potential $U(r, \theta_1, \theta_2, \phi_{12})$ in Eq. (5) and the potential of polarities. The value of the quadrupole moment of carbon dioxide is given by Stogryn and Stogryn.¹¹

The result predicted is shown in Fig. 5 as in the case of the oxygen molecule. The two circles show the experimental second virial coefficients reported previously^{6,10} where the two potential parameters were obtained.

The two series for second virial coefficient of carbon dioxide are recommended by IUPAC: one is the recommendation of Le Neindre and Vodar,⁸ the other is the value of Angus *et al.*² From the previous experimental study,¹⁰ it was found that the recommendation of Le Neindre and Vodar was superior to

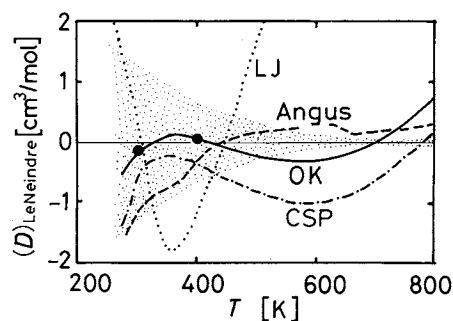


Fig. 5. Deviation from the recommended second virial coefficient of Le Neindre for carbon dioxide.

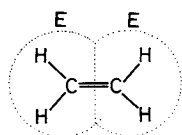


Fig. 6. Model of ethylene molecule: $\angle \text{HCH}$, 117.3° ; $\text{C}=\text{C}$, 0.134 nm ; $\text{C}-\text{H}$, 0.109 nm ; l , 0.150 nm ; σ_{EE} , 0.3872 nm ; ϵ_{EE}^0/k , 125.53 K ; b_{E} , 0.694 .

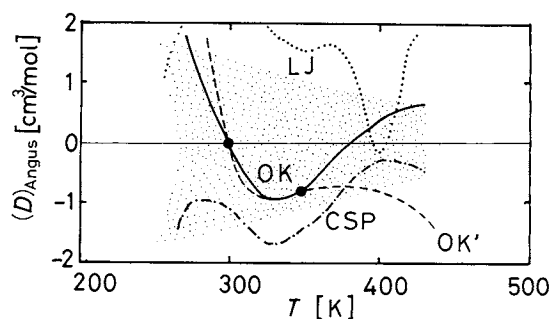


Fig. 7. Deviation from the recommended second virial coefficient of Angus for ethylene.

that of Angus *et al.* in the temperature range lower than 400 K . The Boyle temperature predicted is about 715 K and in good agreement with the literature value of 714.81 K .

The prediction result of the model proposed is superior to the results of the Lennard-Jones model ($\epsilon/k = 189.8 \text{ K}$, $\sigma = 0.4469 \text{ nm}$) and the CSP theory. The deviation from the recommended value of Le Neindre is smaller than $\pm 0.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ in the temperature range $250\text{--}800 \text{ K}$.

3.3 Ethylene

The ethylene molecule is assumed to be composed by two E-groups as shown in Fig. 6. The “bond” length between the centroids of E-groups is slightly longer than the double bonding length between the two carbon atoms. The plus value of quadrupole moment is reported for ethylene and the assumptions for carbon dioxide are not suitable for the case of the ethylene molecule.* Therefore, the ethylene molecule

*) The calculation result considered the quadrupole moment for ethylene (OK', $\epsilon^0/k = 141.2 \text{ K}$, $\sigma = 0.276 \text{ nm}$) is less satisfactory than the result obtained from the non-polar model as shown in Fig. 7.

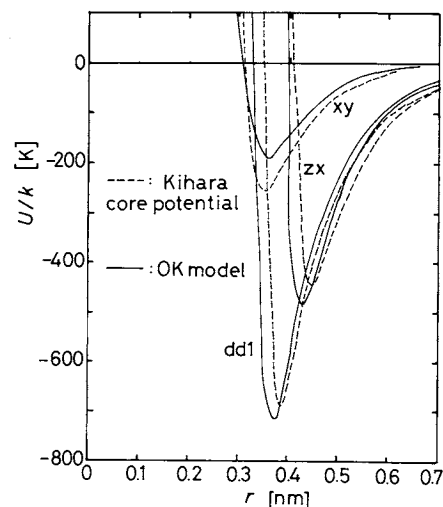


Fig. 8. Molecular potential for each orientation.

was treated as a nonpolar substance in the present study.

The prediction result is shown in Fig. 7 with the same procedure as in the case of oxygen, where $(D)_{\text{Angus}}$ means the deviation from the recommended value of Angus *et al.*¹⁾ For oxygen as well as for the other cases, the model proposed is superior to the LJ model ($\epsilon/k = 199.6 \text{ K}$, $\sigma = 0.4466 \text{ nm}$) and CSP method.

3.4 Potential energy for each orientation

It was shown in Section 2 that the potentials for the nine orientations give the “effective” potential energy between the molecules.

The potentials of carbon dioxide for typical orientations are shown in Fig. 8.

The potential calculated from the model for each orientation was in good agreement with that of the Kihara core potential counting the multipole moments.⁷⁾

It is known that solid carbon dioxide is a primitive crystal having a glide-reflection plane and third-order rotary axis ($\text{Pa}3$), and the most stable orientation is dd1 (see Table 1). This fact is consistent with the result of crystal analysis.

In the cases of oxygen and ethylene, the difference in potential energy for each orientation was not so notable as in the case of carbon dioxide. However, the most stable orientation for oxygen and ethylene is a skew shape (xy).

3.5 Temperature dependence of effective potential

The effective potential defined by Eq. (7) depends on the temperature essentially as shown in Fig. 9.

With increasing temperature the collision diameter and the well depth of the effective potential, respectively, become larger and shallower.

3.6 Extension to mixtures

As the present model stands on the concept of group contribution, this method is extended to mix-

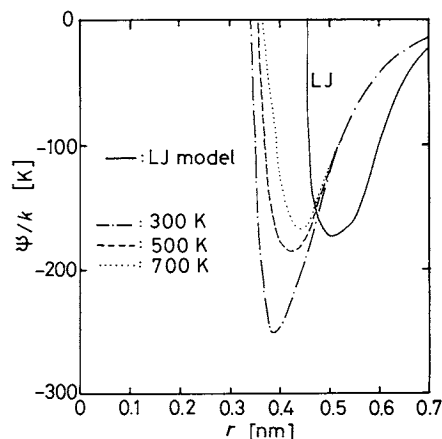


Fig. 9. Effective molecular potential of carbon dioxide at each temperature.

Table 2. Comparison of interaction second virial coefficients

System	T [K]	Present work OK	B_{12} [$\text{cm}^3 \cdot \text{mol}^{-1}$] CSP	Ref.
$\text{CO}_2\text{--C}_2\text{H}_4$	298.15	-117.2	-115.3	-122.2 \pm 0.6 ⁽⁹⁾
		-184.1*	($k_{12}=0.06$)	
	398.15	-60.9	-56.8	-60.7 \pm 0.3 ⁽¹⁰⁾
$\text{O}_2\text{--CO}_2$		-77.4*		
	303.15	-40.5	-51.8	-41.5 \pm 0.2 ⁽⁵⁾
			($k_{12}=0.0$)	-36.8 \pm 5.2 ⁽³⁾
	363.15	-23.8	-30.9	-25.6 \pm 4.4 ⁽³⁾

* Quadrupole moment of ethylene is considered.

tures straightforwardly by using suitable mixing rules for the group parameters ϵ and σ . Therefore, the interaction second virial coefficients for binary systems composed of linear symmetric molecules are easily predicted by only the potential parameters obtained for the pure gases.

The prediction results from the present model and the CSP theory are compared with the experimental data in Table 2. Both prediction methods are in good agreement with the literature values for the carbon dioxide-ethylene system. However, the present method is more satisfactory than the CSP theory for the oxygen-carbon dioxide system.

3.7 Extension to hydrocarbons

The potential parameters of this model to be determined are very sensitive to the values of second virial coefficients used for the calculation. Therefore, accurate data for hydrocarbons such as ethane, propane and butane are necessary to evaluate fundamental group parameters for CH_3 and CH_2 .

It is possible to predict second virial coefficients of hydrocarbons with moderate parameters for CH_3 and CH_2 groups estimated by way of trial. The predicted results for some hydrocarbons are reasonable and are described in Appendix.

It seems effective to introduce C_2H_5 and C_2H_4 groups into this model for simplifying the calculation to hydrocarbons longer than hexane.

4. Conclusion

The simple potential model proposed in the present study is applicable to the prediction of pure and interaction second virial coefficients of linear symmetric molecules. Furthermore, the model can be easily extended to mixtures without binary parameters.

If accurate second virial coefficients of alkanes are available, the potential parameters for groups such as methyl, methylene, \cdots etc. might be rigorous.

Appendix

The prediction of second virial coefficients for some hydrocarbons

The proposed method is extended to linear hydrocarbons straightforwardly by using the group parameters for CH_3 and CH_2 . Even for ethane, however, literature values of the second virial coefficient have considerably large uncertainty. By way of trial, we obtained the parameters for the methyl group from the data of ethane ($l=0.169$ nm) reported by Dymond and Smith.⁽⁴⁾ The parameters for the methylene group should be determined from accurate data of propane or butane by use of the parameters for the methyl group. In the present work, the parameters obtained from ethylene were tentatively used as those of the methylene group in further calculation. The parameters used in the calculation are listed in Table A.

The predicted results are compared with the experimental data for some hydrocarbons in Fig. A. In the calculation, the methane molecule was treated as CH_3 and the propylene molecule as $\text{CH}_3\text{--CH}_2\text{--CH}_2$ ($l=0.134$ nm). For alkanes longer than propane, the bond length is almost constant ($l=0.137$ nm).

Table A. Group parameters used in the prediction

Group	ϵ°/k [K]	σ [nm]
CH_2	125.53	0.3872
CH_3	133.23	0.4101

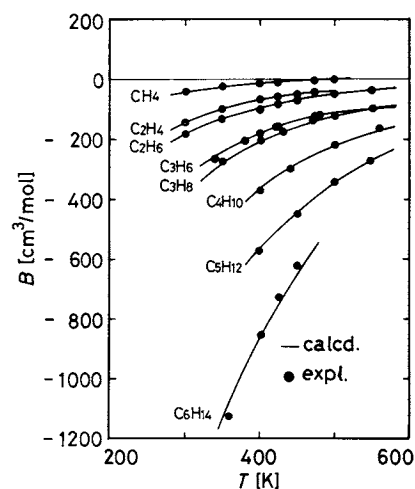


Fig. A. Comparison between predicted and experimental second virial coefficients for some hydrocarbons.

All results except for hexane are predicted satisfactorily in this temperature range. If more accurate second virial coefficients of ethane and propane are available, the prediction might be more satisfactory.

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Nomenclature

B	= second virial coefficient	$[\text{m}^3 \cdot \text{mol}^{-1}]$
B_{12}	= interaction second virial coefficient	$[\text{m}^3 \cdot \text{mol}^{-1}]$
b	= factor of neighboring group effect	[—]
d	= "molecular" length	[m]
k	= Boltzmann constant	$[\text{J} \cdot \text{K}^{-1}]$
k_{12}	= characteristic binary constant	[—]
l	= "bond" length	[m]
M	= number of functional groups	[—]
N	= number of molecules	[—]
q	= quadrupole moment	$[\text{J}^{1/2} \cdot \text{m}^{5/2}]$
r	= intermolecular separation	[m]
r_{ij}	= distance between the groups	[m]
T	= temperature	[K]
U	= "total" potential	[J]
u	= group-group potential	[J]
θ	= polar coordinate	[rad]
ϕ_{12}	= polar coordinate	[rad]
ε	= well depth in the potential function	[J]
σ	= collision diameter	[m]
ψ	= "effective" potential	[J]

<Subscripts>

A, B = A, B molecule

C = carbon group
 E = E group
 i, j = i -th, j -th group
 ij = i - j pair
 O = oxygen group
 Q = quadrupole moment

<Superscript>

° = non-covered

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