POTENTIAL ENERGY OF INTERACTION BETWEEN
UNLIKE NONPOLAR MOLECULES

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It is shown that calculations for the (12-7, δ) model of pair interaction potential consistently agree with experimental data on the interdiffusion coefficients and the mixed second virial coefficient for nonpolar mono- and polyatomic gases.

For calculating the thermophysical properties of gas mixtures, one must know the potential pair interaction energy (pair interaction potential) of all like and unlike molecules. The models of interaction potentials must, moreover, consistently (i.e., with unique values of the force constants) agree with various experimental data over the entire range of measurement [1]. For nonpolar molecules of arbitrary symmetry this requirement is met by the quasispherical model potential (12-7, δ)[2]:

$$\varphi(\bar{r}) = \begin{cases} \infty, & \bar{r}^2 \leqslant \delta, \\ 5.1042\varepsilon \left[\left(\dfrac{1-\delta}{\bar{r}^2-\delta} \right)^6 - \left(\dfrac{1-\delta}{\bar{r}^2-\delta} \right)^{7/2} \right], & \bar{r}^2 \geqslant \delta, \end{cases} \tag{1}$$

where ε is the depth of the potential well; σ, molecule "diameter," r_e, characteristic linear dimension ("core" of a molecule); $\bar{r} = r/\sigma$; and $\delta = (r_e/\sigma)^2$, asphericity of a molecule.

For calculating the thermophysical properties of gas mixtures one uses, as a rule, the same model potential as for the pure components. The main difficulty thus is in determining the force constants in the interaction potential of unlike molecules. For this one generally uses the combining rules

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}), \tag{2}$$

TABLE 1. Force Constants in the (12-7, δ) Potential

System	ε/k, K	$\sigma \cdot 10^8$, cm	δ	Λ^*	T_B, K
He—Ar	24,9	3,092	0	1,053	62
He—Kr	24,6	3,271	0	0,976	62
He—Xe	21,8	3,564	0	0,944	55
He—N_2	24,3	3,175	0,0598	1,077	55
He—CO_2	55,4	3,159	0,2707	0,687	95
He—CH_4	27,4	3,250	0,0580	1,017	63
Ne—Ar	70,2	3,070	0	0,329	189
Ne—Kr	74,1	3,218	0	0,277	200
Ne—Xe	71,3	3,465	0	0,253	193
Ne—N_2	68,1	3,156	0,0605	0,347	168
Ne—CO_2	143,8	3,170	0,2688	0,219	262
Ne—CH_4	79,9	3,214	0,0593	0,361	198
Ar—Kr	177,6	3,413	0	0,131	481
Ar—Xe	194,9	3,607	0	0,111	528
Ar—N_2	145,8	3,389	0,0525	0,186	368
Ar—CO_2	272,5	3,398	0,2340	0,121	527
Ar—CH_4	182,1	3,421	0,0524	0,198	459
Ar—SF_6	286,9	3,965	0,3112	0,082	491
Kr—Xe	244,6	3,688	0	0,075	663
Kr—CH_4	216,2	3,521	0,0494	0,163	548
N_2—CO_2	262,7	3,480	0,2729	0,133	479
N_2—CH_4	174,4	3,504	0,0989	0,212	412
N_2—SF_6	274,0	4,038	0,3371	0,096	450
CO_2—CH_4	319,9	3,515	0,2683	0,144	587
CO_2—SF_6	492,9	4,059	0,4609	0,059	655
CH_4—SF_6	349,6	4,056	0,3346	0,107	576

TABLE 2. Comparison of Experimental and Theoretical Values
of the Mixed Second Virial Coefficient for Nonpolar Gases

System	T, K	$|\Delta B_{12}|_m$, $\dfrac{cm^3}{mole}$	$|\Delta B_{12}|_{max}$, $\dfrac{cm^3}{mole}$	Ref.
He—Ne	148—323	1,3	1,7	[6]
He—Ar	148—323	3,4	4,3	[6]
He—N$_2$	148—323	3,4	4,5	[6]
He—CO$_2$	303—373	1,1	2,0	[7]
Ne—Ar	148—323	0,3	0,8	[6]
Ne—N$_2$	148—323	1,5	1,9	[6]
Ar—Kr	117—254	2,7	6,4	[8]
Ar—Kr	213—500	0,8	3,5	[9]
Ar—Xe	213—500	2,0	7,2	[9]
Ar—N$_2$	148—323	0,8	1,4	[6]
Ar—CH$_4$	107—274	1,6	3,7	[8]
Ar—CH$_4$	300—550	1,8	2,5	[10]
Ar—CO$_2$	303—373	3,3	5,0	[11]
Ar—SF$_6$	300—550	11	12	[10]
Ar—SF$_6$	273—323	1,3	2,8	[11]
Kr—Xe	213—500	1,4	4,3	[9]
Kr—CH$_4$	119—271	1,4	3,0	]8]
CH$_4$—SF$_6$	300—550	4,5	9,7	[10]

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}} \qquad\qquad (3)$$

on various more intricate ones [3]. Certain empirical combining rules are, however, unsatisfactory [3].

Theoretically sound combining rules have been derived by Kong [4]. The expressions relating the force constants σ_{12} and ε_{12} in the interaction potential of unlike molecules to the corresponding force constants for like molecules depend on the form of the model of pair interaction potential which is used for the calculations. Calculations for the (12-7) potential by Kong's combining rules [4] consistently agree with experimental data on the inter-diffusion coefficients and the mixed second virial coefficient for monoatomic gases. This has made it possible to calculate the transport coefficients for binary mixtures of monoatomic gases with low densities at temperatures from 100 to 6000°K [5].

In this study Kong's combining rules have been extended to the quasispherical (12-7, δ) model of pair interaction potential (1) and an evaluation made of the accuracy of describing, on this basis, experimental data on the interdiffusion coefficient and the mixed second

TABLE 3. Comparison of Experimental and Theoretical Values
of the Interdiffusion Coefficients for Nonpolar Gases under
a Pressure of 0.1013 MPa

System	T, K	$|\delta D_{12}|_m$, %	$|\delta D_{12}|_{max}$, %	Ref.
He—Ar	300—1400	1,5	2,0	[12]
He—Kr	300—1100	0,7	1,5	[12]
He—Xe	300—1000	1,0	1,5	[12]
He—N$_2$	298—973	6,5	8,0	[13]
He—CO$_2$	298—973	9,9	12,7	[14]
He—CH$_4$	298—473	3,0	4,7	]14]
He—SF$_6$	298—483	6,7	8,5	[14]
Ne—Ar	300—1400	1,3	2,2	[12]
Ne—Kr	300—1400	1,4	2,3	[12]
Ne—Xe	300—1400	1,2	2,1	[12]
Ne—N$_2$	298—973	5,0	6,5	[15]
Ne—CO$_2$	298—973	9,1	10,6	[14]
Ne—CH$_4$	298—473	0,4	1,1	[14]
Ne—SF$_6$	298—483	2,6	5,2	[14]
Ar—Kr	300—1400	2,0	2,6	[12]
Ar—Xe	300—1400	0,3	0,9	[12]
Ar—CO$_2$	298—873	5,7	6,3	[14]
Ar—CH$_4$	298—473	1,2	2,0	[14]
Ar—SF$_6$	298—483	1,1	1,5	[16[
N$_2$—CO$_2$	298—873	4,7	5,2	[14]
N$_2$—CH$_4$	298—473	1,3	1,6	[14]
N$_2$—SF$_6$	298—473	1,0	1,7	[16]
CO$_2$—CH$_4$	298—473	4,4	5,4	[14]
CO$_2$—SF$_6$	298—478	2,8	3,7	[16]
CH$_4$—SF$_6$	298—473	0,6	0,9	[16]

TABLE 4. Comparison of Experimental Values of the Mixed Second Virial Coefficient and of the Interdiffusion Coefficient for the Argon—Methane System with Calculations for the (12-7, δ) Potential

T, K	$-B_{12}$, $\frac{cm^3}{mole}$			T, K	$[D_{12}]_1$, $\frac{cm^2}{sec}$	
	expt. [8]	calc.	correlation [19]		expt.[14]	calc.
107,10	233,1	236,8	267,7	298,15	0,212	0,210
109,69	222,5	226,1	256,3	323,15	0,246	0,244
113,68	207,5	211,1	240,3	373,15	0,322	0,317
119,48	189,4	192,0	219,5	423,15	0,406	0,398
127,63	168,4	169,4	194,5	473,15	0,489	0,485
138,99	143,3	144,1	166,1			
149,27	126,1	125,9	145,4			
159,88	110,2	110,3	127,9			
174,20	94,0	93,3	108,6			
191,01	78,8	77,6	90,9			
$|\Delta B_{12}|_m$, $\frac{cm^3}{mole}$		1,7	24,4	$|\delta D_{12}|_m$, %	1,2	
$|\Delta B_{12}|_{max}$, $\frac{cm^3}{mole}$		3,6	34,6	$|\delta D_{12}|_{max}$, %	2,0	

virial coefficient for nonpolar mono- and polyatomic gases. The first two terms in the expansion of the (12-7, δ) potential (1) into a series in powers of r_e^2/r^2 were used for the derivation of combining rules, Kong's results [4] not being formally applicable to the model potential (1). Equating the first-order terms in r_e^2/r^2 separately for the repulsion energy and for the attraction energy, we find that

$$r_{e12}^2 = \frac{1}{2}(r_{e11}^2 + r_{e22}^2).$$ (4)

For the zeroth-order terms, using Kong's results [4], we meanwhile obtain

$$a_{12} = \sqrt{a_{11}a_{22}}\,f,$$ (5)

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}f^{-7},$$ (6)

$$f = \left[\frac{(K)^{1/26} + (K)^{-\frac{1}{26}}}{2}\right]^{13/5},$$ (7)

where $a_{ij} = \sqrt{\sigma_{ij}^2 - r_{eij}^2}$, $K = \frac{\varepsilon_{22}}{\varepsilon_{11}}\left(\frac{a_{22}}{a_{11}}\right)^{12}$.

The force constants in the (12-7, δ) interaction potential (1) of like nonpolar molecules are given elsewhere [1]. These values were used here for calculating the force constants in the (12-7, δ) interaction potential (1) of unlike molecules. With the exception of sulfur hexafluoride, i.e., for which more precise values of the force constants were used: $\varepsilon/k = 560$, $\sigma = 4.520 \cdot 10^{-8}$ cm, $r_e = 3.128 \cdot 10^{-8}$ cm, $\delta = 0.4789$, $\Lambda^* = 0.0339$, and $T_B = 722°K$. The calculated force constants in the (12-7, δ) potential (1) for several systems of nonpolar molecules are given in Table 1. There are also given calculated values of the Boyle temperature for the mixed second virial coefficient.

Theoretical and experimental values of the mixed second virial coefficient [6-11] were compared and so were those of the interdiffusion coefficients [12-16] for nonpolar gases, the results of these comparisons being summarized here in Tables 2 and 3, respectively.

In the case of the mixed second virial coefficient, there is a smaller discrepancy between theoretical and experimental values [6-11] here than with other model potentials [17, 18] or with the universal correlation according to Kestin and coauthors [16, 19] (Tables 4 and 5).

The experimental values of the interdiffusion coefficients for nonpolar gases used in the comparison with corresponding theoretical data (Table 3) had been obtained by two methods. For monoatomic systems, the experimental data according to Hogerworst [12]

TABLE 5. Comparison of Experimental Values of the Mixed Second Virial Coefficient and of the Interdiffusion Coefficient for the Argon—CO_2 System with Calculations for the (12-7, δ) Potential

T, K	B_{12}, $\dfrac{cm^3}{mole}$			T, K	$[D_{12}]_1$, $\dfrac{cm^2}{sec}$	
	expt[11]	calc.	correlation [19]		expt[14]	calc.
303,15	—36,6	—41,6	—27,4	298,15	0,147	0,138
313,15	—33,2	—38,1	—24,7	373,15	0,224	0,210
323,15	—31,1	—34,9	—22,1	473,15	0,343	0,322
343,15	—26,6	—29,1	—17,6	573,15	0,479	0,453
373,15	—22,0	—21,9	—11,8	673,15	0,634	0,601
				773,15	0,807	0,764
				873,15	0,998	0,941
$\|\Delta B_{12}\|_m$, $\dfrac{cm^3}{mole}$		3,3	9,2	$\|\delta D_{12}\|_m$, %	5,7	
$\|\Delta B_{12}\|_{max}$, $\dfrac{cm^3}{mole}$		5,0	10,2	$\|\delta D_{12}\|_{max}$, %	6,3	

ranked among the most accurate ones [20] (error estimated at ±2%). For other systems the data according to Kestin and coauthors [13-16] were used, which had been obtained from measurements of the viscosity of binary gas mixtures.

On the whole, the discrepancies between theoretical and experimental data on both the mixed second virial coefficient and the interdiffusion coefficients are within the range of discrepancies between readings taken by different authors, which should be regarded as an objective estimate of the error of the experimental data. Moreover, binary systems were studied here with molecules of most diverse geometrical structures (monoatomic, linear, regular tetrahedral, octahedral, etc.). This legitimizes using the quasispherical (12-7, δ) model of pair interaction potential (1) and modified Kong's combining rules (4)-(8) for calculation of equilibrium and transport properties of nonpolar gases of arbitrary symmetry with low densities.

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STATISTICAL THEORY OF STRUCTURAL AND THERMODYNAMIC
PROPERTIES OF MOLECULAR CRYSTALS

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A crystal theory is constructed on the basis of the statistical method of conditional distributions. A closure procedure is suggested, making it possible to take into account the correlation of various orders, and several structural and thermodynamic quantities are calculated

Along with the traditional approach of describing the crystalline structure of matter, based on Born's ideas [1], several variations of the statistical theory of crystals have been actively pursued lately, based on the apparatus of particle distribution functions [2-7]. The latter tendency is particularly due to the trend of characterizing the high-temperature region of the crystalline phase, as well as due to the fact that, unlike the theory of lattice dynamics, the distribution function formalism is applicable, in principle, to all phases of matter, thus creating the prerequisites for describing the region of the crystal-disordered phase transition.

The biggest difficulty of this approach is associated with the necessity of developing a closure procedure, without destroying the validity of the original equations in relation to any phase. This closure was suggested within the statistical method of conditional distributions [8]. It was based on the approximation of integral terms, having the meaning of average force potentials, and allowed to provide a unified description of all first-order phase transitions [9].

It was shown within this closure [7] that, retaining the general features of the approach, one can construct for the crystalline phase an analytic theory making it possible to calculate a wide set of crystal characteristics.

Based on a modified closure procedure [10] and physical ideas used in [7], in the present paper we construct a statistical theory of molecular crystals with central pair interactions.