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INTERACTION POTENTIAL OF NONPOLAR POLYATOMIC MOLECULES

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The extension of the (12—7)-pair potential model to nonpolar polyatomic molecules is proposed. It is demonstrated that this model consistently fits diverse experimental data.

It has been demonstrated in previous studies [1-3] that the (12—7)-pair potential model

$$\varphi(r) = 5.1042\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{7}\right] \tag{1}$$

consistently fits diverse experimental data pertaining to all monatomic gases over the entire range of measurements, except for discrepancies between the results obtained by various authors. With the (12—7) potential, in other words, the law of corresponding states is actually satisfied for equilibrium and transport properties of gases with spherical nonpolar molecules at low temperatures. It has been possible on this basis to calculate the properties of monatomic gases at temperatures at which direct measurements are not possible [3].

Many gases are not monatomic, however, and their molecular structures are most diverse. The potential energy of interaction involving two polyatomic molecules depends not only on the distance between their centers of inertia but also on their orientations. It is well known [4-6] that, by averaging the pair potential of interaction over all possible orientations, one can theoretically calculate the corrections for asphericity of molecules, these corrections depending only on the intermolecular distance. This greatly simplifies calculations of the macroscopic properties, inasmuch as the effective pair potential of polyatomic molecules can be expressed in terms of a spherically symmetric function.

The simplest model of interaction of polyatomic molecules is the Kihara—Midzuno—Kaneko model [5]. Here every molecule is represented as a distribution of potential sources corresponding to individual atoms and the interparticle potential between two molecules represents interaction of the distributed sources which represent these two molecules. According to this model, the effective pair potential can be expressed as a power series in r_e^2 [5]:

$$\varphi = \varphi_0 + \frac{r_e^2}{12}\left(\varphi_0'' + 2\,\frac{\varphi_0'}{r}\right) + \cdots, \tag{2}$$

where φ_0 is the interaction potential of two sources and r_e is a linear dimension which characterizes the asphericity of molecules (core). For homonuclear diatomic molecules (hydrogen, nitrogen, oxygen) and also for the linear symmetric CO_2 molecule, this core dimension is equal to the equilibrium distance between the two extreme nuclei in a molecule.

Strictly speaking, expression (2) is valid for large distances between the cores of molecules ($r \gg r_e$), where the far-range component of potential energy is dominant. Assuming that there

$$\varphi_0 = -cr^{-7}, \tag{3}$$

as is the case in the model potential (1), we have for polyatomic molecules

$$\varphi = -cr^{-7}\left(1 + \frac{7}{2}\,\frac{r_e^2}{r^2}\right) \tag{4}$$

in the first approximation.

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

Gas	ε/k, °K	σ·10⁸, cm	r_e·10⁸, cm	δ	Λ*	T_B, °K
He	10,2	2,537	0	0	2,70	—
Ne	45,5	2,717	0	0	0,531	122
Ar	152	3,304	0	0	0,170	412
Kr	214	3,511	0	0	0,0931	580
Xe	295	3,845	0	0	0,0578	800
N₂	140	3,471	1,098	0,1000	0,201	330
O₂	184	3,195	1,207	0,1427	0,178	407
CO₂	515	3,530	2,324	0,4335	0,0823	718
SF₆	497	4,745	3,120	0,4323	0,0347	693
CH₄	220	3,531	1,107	0,0983	0,209	519
C₂H₆	367	4,083	1,532	0,1408	0,102	817
C₃H₈	523	4,590	2,540	0,3062	0,0628	904
C₂H₄	338	3,863	1,332	0,1189	0,116	777
C₃H₆	534	4,412	2,520	0,3263	0,0661	893
C₆H₁₂	796	5,377	3,116	0,3358	0,0314	1310

Note: $\Lambda^* = h/\sigma\sqrt{m\bar{\varepsilon}}$ is the quantum-mechanical parameter and T_B is the Boyle temperature.

TABLE 2. Consistency in the Description of Experimental Data on Various Properties of Nonpolar Polyatomic Gases with the Aid of the (12—7, δ) Model Potential

Gas (formula)	Property	T, °K	T*	Mean deviation	Max. deviation	Ref.
Nitrogen (N₂)	I	100—2000	0,714—14,29	0,8%	4,0%	[10]
	I	100—2000	0,714—14,29	1,1%	3,6%	[11]
	II	75—700	0,536—5,00	1,3	3,1	[18]
	II	100—1000	0,714—7,14	1,6	3,1	[19]
Oxygen (O₂)	I	110—300	0,597—1,63	0,7%	2,0%	[12]
	I	100—2000	0,543—10,87	1,5%	2,7%	[11]
	II	90—400	0,489—2,17	2,1	6,3	[18]
	II	100—400	0,543—2,17	2,2	3,7	[19]
Carbon dioxide (CO₂)	I	250—1200	0,485—2,33	2,7%	4,9%	[13]
	I	250—2000	0,485—3,88	4,0%	6,9%	[14]
	II	250—1000	0,485—1,94	1,1	5,6	[19]
	II	250—1000	0,485—1,94	0,6	1,5	[14]
Sulfur hexafluoride (SF₆)	I	300—1000	0,604—2,01	2,4%	3,6%	[15]
	I	250—1000	0,503—2,01	2,3%	3,5%	[16]
	II	280—520	0,563—1,05	1,9	4,2	[18]
	II	300—550	0,604—1,11	2,4	3,8	[20]
Cyclohexane (C₆H₁₂)	I	300—900	0,377—1,13	2,3%	4,6%	[13]
	III	310—430	0,389—0,540	1	3	[21]
	II	310—430	0,389—0,540	2	5	[21]
Methane (CH₄)	I	120—500	0,545—2,27	1,4%	2,5%	[17]
	I	100—1000	0,455—4,54	1,6%	3,1%	[10]
	II	110—600	0,500—2,73	1,0	10,0	[18]
	II	110—600	0,500—2,73	4,1	2,0	[19]
Ethane (C₂H₆)	I	200—900	0,545—2,45	1,0%	1,9%	[13]
	II	220—500	0,599—1,36	4,4	9,8	[18]
	II	199—251	0,543—0,684	4,5	7,6	[22]
Propane (C₃H₈)	I	300—600	0,574—1,15	2,3%	3,0%	[13]
	II	260—550	0,497—1,05	3,2	6,5	[18]
	II	211—274	0,404—0,524	2,4	6,1	[22]
Ethylene (C₂H₄)	I	200—800	0,592—2,37	1,5%	4,5%	[13]
	II	238—448	0,704—1,33	2,0	3,8	[23]
	II	273—423	0,808—1,25	1,3	3,1	[24]
Propylene (C₃H₆)	I	300—600	0,562—1,12	3,5%	5,7%	[13]
	II	280—500	0,524—0,943	1,0	6,2	[18]

Notes: I) Viscosity; II) second viral coefficient (in cm³/mole); III) Joule—Thomson coefficient (in cm³/mole).

Using this result, one can propose the following extension of the (12-7)-pair potential to nonpolar polyatomic molecules:

$$\varphi(r) = \begin{cases} \infty & \bar{r} \leqslant \sqrt{\delta}, \\ 5.1042\,\varepsilon\left[\left(\dfrac{1-\delta}{\bar{r}^2-\delta}\right)^6 - \left(\dfrac{1-\delta}{\bar{r}^2-\delta}\right)^{7/2}\right] & \bar{r} \geqslant \sqrt{\delta}, \end{cases} \tag{5}$$

where the dimensionless parameter $\delta = r_e^2/\sigma^2$ characterizes the asphericity of molecules and $\bar{r} = r/\sigma$.

Potential (5) is formally very similar to the Smith–Takkar potential [7]. Beside the different power exponents in the far-range term there also other differences between the two potentials. The kernel of infinitely strong repulsion ($r \leqslant r_e$) in potential (5) is due to finite dimensions of polyatomic molecules. In the Smith–Takkar potential [7] proposed for monatomic molecules, on the other hand, the kernel of infinitely strong repulsion has no physical meaning.

The force constants in potential (5) for several nonpolar molecules are given in Table 1. The core dimensions have been calculated from data on the geometry of those molecules [8]. For molecules of hydrocarbons (except methane) the largest distance between carbon atoms forming the skeleton of a molecule was used as the core dimension [4,9]. The two other constants (ε and σ) were calculated by an analysis of experimental data on viscosity [10-17] and on the second virial coefficient [18-24]. Those experimental data were, as a rule, generalized ones and had been applied to various models of the pair interaction potential.

For the calculations we used well-known expressions from the molecular theory of gases [4]. In calculations of the second virial coefficient the first quantum correction was included and in calculations of the viscosity the correction for higher-order approximations was included.

A comparison of calculated and measured data on viscosity and the second virial coefficient for several polyatomic gases is shown in Table 2. It is evident here that with the values selected for the force constants ones can describe both these properties of gases over the entire range of measurements ($T^* = 0.4$-14). The discrepancy between calculation and experiment is smallest (within $\pm 2\%$ for the viscosity) at the 300°K temperature, moreover, and the largest discrepancy does not exceed the difference between readings obtained by various authors (as large as 5-7% for the viscosity [13,14]). It should be noted that until now it has not been possible to reconcile experimental data on viscosity and the second virial coefficient [4,14,25,26] with the aid of known models of the pair interaction potential (12-6 Lennard–Jones, Kihara, Buckingham, Stockmeier, et al.).

The authors have also compared these results with calculations based on the universal Kestin correlation [25,26]. This empirical correlation, originally proposed by Kestin and coauthors for monatomic gases [25], was subsequently extended to cover also polyatomic gases [26]. An analysis has revealed that this correlation does not portray experimental data on viscosity better than the (12-7, δ) potential (the mean deviation from the data in [11] on nitrogen, e.g., is 1.7% and the maximum deviation is 5.2%). As to the second virial coefficient, the correlation [26, 27] is satisfactorily accurate only for monatomic gases. For polyatomic gases the deviations are approximately one order of magnitude larger than those of calculations based on the (12-7, δ) potential (the mean deviation from the data in [18] on nitrogen is 12 cm³/mole and the maximum deviation is 37 cm³/mole). This is not at all surprising, since the universal correlation [26,27] is a biparametric one and does not take into account the structure of molecules.

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