USE OF THE PADÉ APPROXIMANTS FOR CALCULATING THE SECOND VIRIAL COEFFICIENT

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The expansions in reduced temperature, occurring in relations for the second virial coefficient of the power-law potentials were expressed by the Padé approximant. For the Kihara potential it is proved that the functions $F_1(T^*)$, $F_2(T^*)$ and $F_3(T^*)$ and consequently the whole virial coefficient can be expressed for reduced temperatures $T^* > 0.6$ with a good accuracy by means of a simple Padé approximant. To describe quantum effects on the second virial coefficient of low-molecular gases at low temperatures a simple approximant was formulated on the basis of the Wigner-Kirkwood expansion allowing to correlate data on the second virial coefficient even in the temperature range where the use of the Wigner-Kirkwood expansion already fails.

The P–V–T behaviour of real gases can be characterized in relatively wide range of temperatures by a virial expansion comprising the second virial coefficient. The relations for calculating the virial coefficient which hold for so-called "realistic" models of intermolecular interactions (*e.g.* for intermolecular potentials of the power--law type, multipole one and so like) are given by expansion in powers of reciprocal temperature[1].

Recently, when solving a number of problems in statistical thermodynamics of fluids, the method of the Padé approximants[2-4] proved to be useful allowing to determine the value of function at arbitrary point on the basis of knowledge of the first terms of expansion. The form of relations for virial coefficient (in the framework of classical description) and the Wigner-Kirkwood expression of quantum effects[5] make it possible to apply the method given to statistical thermodynamics of real gases. The expression of virials by means of the Padé approximants has twofold meaning: It allows — in comparison with expansions with several initial terms — to extend substantionally the temperature range in which the virial coefficient can be determined by a simple procedure and leads to a simple expression of the virial coefficient dependence on temperature. In case of the application to the Wigner-Kirkwood expansion, the temperature range in which it is possible to determine second virial coefficient in a semi-empirical way is substantially extended. Recently, Thakkar[6] has paid attention to the study of this problem and proposed several methods of speeding-up the convergence of the Wigner-Kirkwood expansion. However, these methods are comparatively difficult for practical correlation of the virial coefficient data.

This work is devoted to the formulation of the Padé approximants for the second virial coefficients of gases with power-law type interaction potential. It is divided into three parts: The first one brings the application for the Kihara potential, the

second one is devoted to the formulation of the approximant for the Wigner–Kirkwood expansion for the Lennard–Jones 6−12 potential and the comparison of the data following from it with the results of quantum-mechanical calculations. In the third one the application is given of this approximant (for quantum effects) to the correlation of the second virial coefficient data of low-molecular substances.

THEORETICAL

Second Virial Coefficient for the Kihara Potential

In this section we assume that the pair interactions are given by the general type of the Kihara potential which comprises the Kihara central and the Lennard–Jones 6−12 potentials as special cases for the spherical and point cores. The Kihara potential can be written in the form[7]

$$u(\varrho) = \varepsilon[(\varrho_0/\varrho)^{12} - 2(\varrho_0/\varrho)^6], \tag{1}$$

where ε and ϱ_0 are the characteristic parameters and ϱ is the shortest distance of core surfaces of two interacting molecules. If V, S and R are the geometric functionals of the core (i.e. volume, surface and $1/4\pi$-multiple of the mean curvature integral) then the second virial coefficient is given by the relation[7]

$$B = \tfrac{2}{3}\pi N_A \varrho_0^3 F_3(T^*) + 4\pi N_A R \varrho_0^2 F_2(T^*) + N_A(S + 4\pi R^2) \varrho_0 F_1(T^*) + $$
$$+ N_A(V + RS), \tag{2}$$

where N_A is the Avogadro number and T^* the reduced temperature $T^* = kT/\varepsilon$; it holds for the functions $F_s(T^*)$

$$F_s(T^*) = \int_0^\infty \{1 - \exp\left[-(\xi^{-12} - 2\xi^{-6})/T^*\right]\} \, d(\xi^s) = $$
$$= -\frac{s}{12} \sum_{i=0}^\infty \frac{2^i}{i!} \Gamma\left(\frac{6i - s}{12}\right) T^{*-(6i+s)/12}. \tag{3}$$

Consequently

$$F_3(T^*) = T^{*-1/4}(1{\cdot}22542 - 1{\cdot}81280T^{*-1/2} - 0{\cdot}61271T^{*-1} + $$
$$- 0{\cdot}30213T^{*-3/2} - 0{\cdot}15318T^{*-2} + \ldots), \tag{4}$$

$$F_2(T^*) = T^{*-1/6}(1{\cdot}12878 - 0{\cdot}89298T^{*-1/2} - 0{\cdot}37626T^{*-1} + $$
$$- 0{\cdot}19844T^{*-3/2} - 0{\cdot}10452T^{*-2} + \ldots), \tag{5}$$

and

$$F_1(T^*) = T^{*-1/12}(1 \cdot 05555 - 0 \cdot 35459T^{*-1/2} - 0 \cdot 17592T^{*-1} + $$
$$- 0 \cdot 09850T^{*-3/2} - 0 \cdot 05375T^{*-2} + \ldots). \tag{6}$$

For the functions F_1 to F_3 we consider the Padé approximant in the form

$$F_s(T^*) = T^{*-s/12} \frac{A + BT^{*-1/2} + CT^{*-1}}{1 + DT^{*-1/2}}, \tag{7}$$

where the constants A, B, C, D are determined from the first four terms of expansions $(4)-(6)$. Then

$$F_3(T^*) = T^{*-1/4} \frac{1 \cdot 22542 - 2 \cdot 41707T^{*-1/2} + 0 \cdot 28120T^{*-1}}{1 - 0 \cdot 49311T^{*-1/2}} \tag{8}$$

$$F_2(T^*) = T^{*-1/6} \frac{1 \cdot 12878 - 1 \cdot 48830T^{*-1/2} + 0 \cdot 09470T^{*-1}}{1 - 0 \cdot 52740T^{*-1/2}} \tag{9}$$

$$F_1(T^*) = T^{*-1/12} \frac{1 \cdot 05555 - 0 \cdot 94561T^{*-1/2} + 0 \cdot 02262T^{*-1}}{1 - 0 \cdot 55991T^{*-1/2}} \tag{10}$$

TABLE I

Comparison of Values of Functions $F_s(T^*)$ Calculated from Eqs $(8)-(10)$ and $(11)-(13)$ with Exact Data

T^*	$F_3(T^*)$			$F_2(T^*)$			$F_1(T^*)$		
	Eq. (8)	Eq. (11)	Exact	Eq. (9)	Eq. (12)	Exact	Eq. (10)	Eq. (13)	Exact
0·6	—4·4597	—4·3824	—4·3826	—2·1658	—1·9935	—1·9932	—0·4801	—0·3191	—0·3189
0·7	—3·3595	—3·3302	—3·3305	—1·4780	—1·3943	—1·3952	—0·1319	—0·0526	—0·0530
0·8	—2·6522	—2·6408	—2·6405	—1·0542	—1·0085	—1·0086	—0·0725	0·1172	0·1171
0·9	—2·1598	—2·1552	—2·1546	—0·7673	—0·7400	—0·7397	0·2066	0·2343	0·2344
1·0	—1·7961	—1·7951	—1·7947	—0·5603	—0·5428	—0·5424	0·3012	0·3196	0·3198
1·2	—1·2976	—1·2981	—1·2982	—0·2823	—0·2738	—0·2736	0·4255	0·4349	0·4351
1·5	—0·8480	—0·8485	—0·8491	—0·0382	—0·0343	—0·0344	0·5317	0·5363	0·5362
2·0	—0·4430	—0·4431	—0·4438	0·1758	0·1776	0·1772	0·6222	0·6242	0·6240
2·5	—0·2205	—0·2210	—0·2210	0·2903	0·2911	0·2909	0·6692	0·6702	0·6701
3·0	—0·0811	—0·0822	—0·0815	0·3604	0·3605	0·3608	0·6973	0·6977	0·6979

The comparison of the values of functions F_1, F_2 and F_3 calculated from Eqs $(8)-(10)$ with the values resulting from the summation of infinite series for several reduced temperatures is given in Table I. It follows from the comparison that Eq. (8) allows the sufficiently accurate determination of the function F_3 for reduced temperatures $T^* > 0.9$. Since the terms containing F_2 and F_1 are, as a rule, substantially smaller than the term with F_3 it is fair to say that the procedure employing the approximants $(8)-(10)$ is suitable for determining the second virial coefficient at temperatures $T^* > 0.9$.

The fact that the function $F_s(T^*)$ can be expressed well by expression (7) in a wide range of temperatures gives the possibility to use this relation to represent $F_s(T^*)$ in a narrower, practically interesting temperature range $T^* = 0.6-3.0$ with the constants A, B, C, D determined on the basis of exact values of F_s in the given interval. The correlation given leads to the relations

$$F_3(T^*) = T^{*-1/4} \frac{1 \cdot 18163 - 2 \cdot 23086 T^{*-1/2} + 0 \cdot 08095 T^{*-1}}{1 - 0 \cdot 46061 T^{*-1/2}} \qquad (11)$$

$$F_2(T^*) = T^{*-1/6} \frac{1 \cdot 09948 - 1 \cdot 32389 T^{*-1/2} - 0 \cdot 06148 T^{*-1}}{1 - 0 \cdot 47330 T^{*-1/2}} \qquad (12)$$

$$F_1(T^*) = T^{*-1/12} \frac{1 \cdot 03825 - 0 \cdot 80242 T^{*-1/2} - 0 \cdot 07053 T^{*-1}}{1 - 0 \cdot 48277 T^{*-1/2}}. \qquad (13)$$

The values of the functions F_1, F_2, F_3 calculated according to Eqs $(11)-(13)$ are presented in the third, sixth and ninth column of Table I. Excellent agreement in the whole temperature range studied is evident from the comparison with the exact values given in the fourth, seventh, and tenth columns of the same table; the maximum deviation does not exceed 0.001. Approximants $(11)-(13)$ allow thus a sufficiently accurate calculation of second virial coefficient in the whole practically interesting range of temperatures. For example, for the second virial coefficient of argon ($\varepsilon/k = 142.2$ K, $\varrho_0 = 0.3418$ nm, $R = 0.01375$ nm, $S = 0.002376$ nm^2, $V = 0.000011$ nm^3) it follows from Eqs (2) and $(11)-(13)$ for the temperature $T = 101.41$ K the value -178.49 cm^3/mol in comparison with the exact value -178.56 cm^3/mol (experiment[8] -178.72 cm^3/mol) for the temperature $T = 188.2$ K the value -55.95 (exact value -55.97, experimental -54.82) cm^3/mol and for the temperature $T = 423.2$ K the value 0.65 (0.68 and 1.46, respectively) cm^3/mol.

Quantum Correction to Second Virial Coefficient

For low-molecular substances at lower temperatures, the classical statistical-thermodynamic description for determining the second virial coefficient is insufficient.

Unless the temperature considered is too low it is possible to use the semi-classical solution in the form of the Wigner–Kirkwood expansion[5,9]

$$B = B_{class} + (\hbar^2/2\mu) B_1 + (\hbar^2/2\mu)^2 B_2 + (\hbar^2/2\mu)^3 B_3 + \dots + B_{perf} , \quad (14)$$

where μ is the reduced mass, $\hbar = h/2\pi$, h is the Planck constant, B_{class} is the value of second virial coefficient in classical approximation, B_1, B_2, B_3, ... are the quantum corrections of the first, second, etc. order,

$$B_1 = (\pi N_A/6k^3 T^3) \int_0^\infty \exp \lfloor -u/kT \rfloor (u')^2 r^2 \, dr , \quad (15)$$

$$B_2 = -(\pi N_A/6k^4 T^4) \int_0^\infty e^{-u/kT} \left[\frac{(u'')^2}{10} + \frac{(u')^2}{5r^2} + \frac{(u')^3}{9kTr} - \frac{(u')^4}{72k^2T^2} \right] r^2 \, dr \quad (16)$$

$$B_3 = \frac{\pi N_A}{6k^5 T^5} \int_0^\infty e^{-u/kT} \left[\frac{(u''')^2}{140} + \frac{3(u'')^2}{70r^2} + \frac{(u'')^3}{126kT} + \frac{(u')(u'')^2}{30kTr} + \frac{2(u')^3}{315kTr^3} - \right.$$
$$\left. - \frac{(u')^2 (u'')^2}{120(kT)^2} - \frac{(u')^4}{1\,080(kT)^2 r^2} - \frac{(u')^5}{360(kT)^3 r} + \frac{(u')^6}{4\,320(kT)^4} \right] r^2 \, dr ; \quad (17)$$

the small correction B_{perf} (hereinafter neglected, compare ref.[6]) depends on the fact whether the particle complies with the Bose–Einstein or Fermi–Dirac statistics. Since the difficulty of determining the quantum corrections $B_1, B_2, \dots$ increases rapidly with increasing order it is practically possible to evaluate only two, at most three quantum contributions. This fact imposes limitations on the use of the Wigner–Kirkwood expansion to the region of not too deep temperatures where the expansion converges rapidly. For low temperatures it is necessary to carry out quantum-mechanical calculations which, however, are considerably laborious.

The knowledge of the values of quantum corrections allows to write the Padé approximant which, even at relatively low temperatures, gives (after including the classical contribution, B_{class}) the values of the second virial coefficient in good agreement with the data obtained by the quantum-mechanical calculations.

On the basis of the known B_1 and B_2 or $B_1 - B_3$ it is possible to formulate the following approximants

$$B = B_{class} + \frac{B_1(\hbar^2/2\mu)}{1 - (B_2/B_1)(\hbar^2/2\mu)} \quad (18)$$

and

$$B = B_{class} + \frac{B_1(\hbar^2/2\mu) + (B_2 - B_1B_3/B_2)(\hbar^2/2\mu)^2}{1 - (B_3/B_2)(\hbar^2/2\mu)} . \quad (19)$$

To test the quality of description of the quantum effects in terms of the given approximants the comparison is carried out in Table II of the values of virials calculated by means of Eqs (18), (19) and expansion (14) on the basis of values $B_1 - B_3$ and B_{class} given in ref.[9] with the values from quantum calculations given in the same ref.[9]. It is evident from Table II that expressions (18) and (19) give good prediction of the virial coefficients of low-molecular gases even at comparatively low temperatures where the expansion (14) itself already fails.

Expansion (14) was rewritten for calculating into the form

$$B^* = B^*_{class} + B^*_I \lambda^2 + B^*_{II} \lambda^4 + B^*_{III} \lambda^6 , \qquad (20)$$

where

$$\lambda = h/\sigma \sqrt{(m\varepsilon)} , \qquad (21)$$

TABLE II

Comparison of Values of Second Virial Coefficient with Quantum Correction Given by the Sum of Correction Contributions $\sum_1^3 B_i X^i$ [Eq. (14)], Approximant (18) or Approximant (19); $X = \hbar^2/2\mu$)

T^*	$B_{class}{}^a$	$B_1 X^a$	$B_2 X^{2\ a}$	$B_3 X^{3\ a}$	Eq. (14)	Eq. (18)	Eq. (19)	Quant^a
			^{3}He					
2	−13·22	19·99	−13·54	20·80	14·03	− 1·30	1·43	0·61
4	2·432	6·511	− 1·724	1·258	8·48	7·58	7·94	7·85
6	6·804	3·658	− 0·581	0·280	10·16	9·96	10·07	10·04
			^{4}He					
2	−13·22	15·02	− 7·65	8·83	2·98	− 3·27	− 1·75	−2·13
4	2·432	4·893	− 0·973	0·534	6·89	6·51	6·70	6·67
6	6·804	2·749	− 0·328	0·119	9·34	9·26	9·32	9·34
			Ne					
1	−66·52	3·83	− 0·27	0·03	−62·93	−62·94	−62·93	—
2	−16·45	0·92	− 0·02	0·000	−15·55	−15·55	−15·55	—
4	3·021	0·300	− 0·003	0·000	3·32	3·32	3·32	—
6	8·461	0·169	− 0·001	0·000	8·63	8·63	8·63	—

^{a} Taken over from ref.[9].

the asterisk denotes the value of the given contribution divided by $\frac{2}{3}\pi N_A \sigma^3$ and the contributions $B_I^* - B_{III}^*$ are given by the expansions[5,9,10]

$$B_I^* = T^{*-13/12} \sum_{j=0}^{\infty} -\left(\frac{11 - 36j}{768\pi^2}\right)\frac{2^{13/6} \cdot 2^j}{j!} \Gamma\left(\frac{6j - 1}{12}\right) T^{*-j/2} \qquad (22)$$

$$B_{II}^* = T^{*-23/12} \sum_{j=0}^{\infty} -\left(\frac{767 + 4728j + 3024j^2}{491\,520\pi^4}\right)\frac{2^{23/6} \cdot 2^j}{j!} \Gamma\left(\frac{6j + 1}{12}\right) T^{*-j/2} \qquad (23)$$

and

$$B_{III}^* = T^{*-33/12} \sum_{j=0}^{\infty} \left(\frac{180615 + 491076j + 303216j^2 + 53568j^3}{73\,400\,320\pi^6}\right)\frac{2^{33/6} \cdot 2^j}{j!} \cdot$$
$$\cdot \Gamma\left(\frac{6j + 3}{12}\right) T^{*-j/2} . \qquad (24)$$

The forms of Eqs $(22)-(24)$ offer re-using the Padé approximant method. However, the approximants formed from first four terms of expansions turn out, with regard to bad convergence, to be applicable only for higher reduced temperatures. Analogously to the first part of this work it is, however, possible to consider Eq. (7) as a correlation relation for B_n^* and in a practically interesting range of temperatures $T^* \in (1,3)$

TABLE III
Comparison of Reduced Quantum Contributions of the First, Second and Third Order Calculated from Eqs $(25)-(27)$ with Exact Values

T^*	$B_{I,calc}^*$	$B_{I,ex}^*$	$-B_{II,calc}^*$	$-B_{II,ex}^*$	$B_{III,calc}^*$	$B_{III,ex}^*$
0·8	0·7295	0·7295	0·2031	0·2031	0·0974	0·0973
1·0	0·4151	0·4156	0·0821	0·0822	0·0298	0·0299
1·2	0·2741	0·2741	0·0412	0·0412	0·0120	0·0120
1·4	0·1979	0·1979	0·0237	0·0236	0·0058	0·0058
1·6	0·1517	0·1515	0·0149	0·0149	0·0031	0·0031
1·8	0·1212	0·1212	0·0100	0·0100	0·0018	0·0018
2·0	0·1000	0·1000	0·0071	0·0071	0·0012	0·0012
2·2	0·0845	0·0845	0·0053	0·0053	0·0008	0·0008
2·4	0·0728	0·0728	0·0041	0·0040	0·0005	0·0005
2·6	0·0637	0·0637	0·0032	0·0032	0·0004	0·0004
2·8	0·0564	0·0565	0·0026	0·0025	0·0003	0·0003
3·0	0·0505	0·0506	0·0021	0·0021	0·0002	0·0002

to evaluate the constants A, B, C, D on the basis of exact values. In such a way we arrive at the relations

$$B_I^* = T^{*-13/12} \frac{0.09762 - 0.05001 T^{*-1/2} + 0.12234 T^{*-1}}{1 - 0.59054 T^{*-1/2}} \qquad (25)$$

$$B_{II}^* = -T^{*-23/12} \frac{0.01652 - 0.04156 T^{*-1/2} + 0.05579 T^{*-1}}{1 - 0.62571 T^{*-1/2}} \qquad (26)$$

and

$$B_{III}^* = T^{*-33/12} \frac{0.00711 - 0.02134 T^{*-1/2} + 0.02424 T^{*-1}}{1 - 0.66457 T^{*-1/2}} . \qquad (27)$$

The comparison of values of $B_I^* - B_{III}^*$ calculated from Eqs $(25)-(27)$ with the values obtained by summing the infinite series $(22)-(24)$ is presented in Table III. Relations $(25)-(27)$ turn out to be practically useful in the entire range of reduced temperatures $T^* > 0.8$.

Correlation of Second Virial Coefficient Data for H_2, D_2, He and Ne

The data taken over from ref.[8] (excepting He whose data are given in ref.[11]) were used to verify the possibility of using approximants (18) and (19) for correlating virial coefficient data of the gases mentioned in the low-temperature region. The program employed computes the exact values of contributions $B_I - B_{III}$ and B_{class} for the given values of the LJ potential parameters and determines in an iterative way the parameters of the LJ potential. From the study carried out it follows that when using expansion (14) with the quantum corrections of the first, second and third

TABLE IV
Values of the Lennard–Jones 12—6 Potential Parameters

Substance	ΔT, K	$\sqrt{\sum(B - B_{exp})^2/(N-1)}$	ε/k, K	σ, nm
H_2	30—400	1.56	39	0.297
H_2	50—400	0.93	37	0.300
D_2	98.16—423.16	0.13	36	0.293
He[a]	14.16—48.2	3.82	11	0.304
Ne	60—600	0.43	37	0.275

[a] Taken over from ref.[11], the others from ref.[8].

order, it is not possible in case of H_2 to correlate responsibly the data for temperatures $T < 50$ K whereas the Padé approximants (18) and (19) allow to correlate the data down to $T \approx 30$ K. The corresponding conclusions follow as well for the other gases studied. In Table IV we summarize the calculated L–J $12-6$ potential parameters following from the correlation employing Eq. (19). In the following Table V, the correlation results of the hydrogen virial coefficient data are summarized.

It is evident that the use of the Padé approximant for calculating the quantum effect on second virial coefficient allows to extend considerably the temperature interval studied. In fact, it is possible to consider still substantially lower temperatures (down to $T^* \approx 0.6$), however, the shortcomings of the L–J $12-6$ potential and the insufficient description of the quantum effect result in the increase of parameter σ on including the data with decreasing temperature value.

CONCLUSION

The possibilities were proved of using the Padé approximant for correlating experimental data of the second virial coefficient of gases with interactions of the power-law type. It appears that the use of relations found on the basis of these approximants allows to speed up considerably the computation procedures (data correlation) of the second virial coefficient in the region of classical behaviour without losing accuracy and, for low-molecular substances, to include even relatively low-temperature data into the classical approximation. At the same time in comparison with the methods of speeding-up the expansion convergences discussed by Thakker[6], the method used by us (essentially a particular case) is substantially simpler.

TABLE V

Comparison of Values of the Second Virial Coefficient of Hydrogen (cm^3/mol) Calculated from Eq. (19) with Experimental Data; $\varepsilon/k = 39$ K, $\sigma = 0.297$ nm

T, K	B_{exp}	B_{calc}	ΔB
30	—85	—83.5	1.5
40	—54	—54.1	—0.1
50	—35	—36.8	—1.8
75	—12	—14.5	—2.5
100	— 1.9	— 4.0	—2.1
150	7.1	5.9	—1.2
200	11.3	10.4	—0.9
300	14.8	14.5	—0.3
400	15.2	16.2	1.0

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