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Application of Levin's transformations to virial series

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A new method of estimating high-order virial coefficients for fluids composed of equal three-dimensional rigid spheres is proposed. The predicted B_{11} and B_{12} values are in good agreement with reliable estimates previously reported. A new application of the Levin's transformations is developed, as well as a new way of using Levin's transformations is suggested. For the virial series of packing factor powers, this method estimates the B_{13} value near 173.

Key words: *Levin's transformations, virial series, rigid spheres*

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1. Introduction

The virial series is extremely important for obtaining accurate state equations, because it expands the compressibility factor of a fluid through a power series of an adequate variable. Using the packing factor, η,

$$Z = 1 + \sum_{i=2}^{\infty} B_i \eta^{(i-1)}, \tag{1.1}$$

where Z is the compressibility factor and B_i is the virial coefficient of order i. In the late nineteenth century, van der Waals [1], Boltzmann [2], and van Laar [3], analytically calculated the virial coefficients B_2, B_3, and B_4, of a gas formed by equal three-dimensional spherical rigid particles. So far, there are no analytical expressions to calculate the coefficients after B_4, even considering such simple particles. Thus, the best values for higher-order coefficients are obtained by numerical calculations of the Mayer's functions [4].

Using Mayer's functions, in 1953 the coefficient B_5 was obtained by Rosenbluth and Rosenbluth [5]. Subsequently, the coefficients B_6 and B_7 were calculated by Ree and Hoover [6], and B_8 by van Rensburg [7], and by Vlasov and You [8]. B_9 was obtained by Labík and collaborators [9] in 2005, and B_{10} by Clisby and McCoy in 2006 [10]. Calculations of coefficients after B_{10} were not performed, on account of the huge increase in the number of Mayer's diagrams and integrals to be analyzed. Thus, the coefficients subsequent to B_{10} are estimated (see estimates in [11]).

There are some methods reported in the literature for extrapolating the values of virial coefficients to orders higher than the tenth. Among them, stand out the Padé approximants, the maximum entropy approximation, the density functional method, the series of continuous exponential, molecular dynamics and the differential approximation method. All these methods are considered to be very plausible. Nevertheless, unproved assumptions on the mathematical behavior of the series are imposed in their applications. Indeed, it is not even proved whether the 3D rigid sphere virial series does converge for all physically significant η values, or does not. Then, to avoid such assumptions is a desirable aim.

Slow convergent or even divergent series frequently appear in problems involving the evaluation of integrals, solutions of differential equations, perturbation theory and others [12]. Moreover, in many scientific problems, the series permits the computation of a small number of terms, which is not sufficient

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to obtain the required accuracy. In this context, the sequence transformations play an essential role, since they accelerate the convergence of the series without the need to compute higher-order terms [13].

In 1973, David Levin [14] introduced new sequence transformations, which improved the convergence of slowly convergent series. Moreover, this method is particularly suitable for the summation of strongly divergent series. According to Smith and Ford [15], who compared the performance of several linear and nonlinear series transformations, the Levin-type ones are probably the most powerful and versatile convergence accelerators ever known. Baram and Luban [16] were the first to demonstrate the applicability of the Levin's transformations to the virial expansions of hard discs and rigid spheres through estimates for B_7 [17]. In recent years, many applications of Levin-type transformations have been reported in the literature, though the focus has been mainly in the field of quantum physics (see, for example, [18–23]).

In this work, the Levin's transformations are used to estimate the B_{11}, B_{12}, and B_{13}, virial coefficients for gases composed of 3D equal rigid spheres, assuming the known values of the coefficients up to B_{10}. That is, a completely new methodology for estimating virial coefficients is proposed, and an unused way of using Levin's transformations is suggested. This work is organized into four more sections. In section 2, the Levin's transformations are briefly described, highlighting their mathematical structure. In section 3, the methodology used to estimate the virial coefficients is presented. In section 4, the obtained estimates are indicated and compared to those reported in the literature. Finally, in section 5 the results are commented.

2. Levin's transformations

In this section, the mathematical background of the Levin's acceleration method is summarized. However, for a more detailed mathematical description of the method, references [24] and [25] are suggested. The Levin's sequence transformations are applicable to the model sequence

$$s_r = s + \omega_r \sum_{j=1}^{k} c_j/(r+\gamma)^{j-1}, \qquad k, r \in \mathbb{N}, \tag{2.1}$$

where k represents the order of the transformation, γ is an arbitrary parameter which may not be a negative integer, ω_r is the remainder estimate and s is the limit of the sequence when it converges, or the antilimit if it diverges. The convergence or divergence of the sequence depends on the behavior of ω_r, for $r \to \infty$.

In equation (2.1) there are $k+1$ unknown quantities, that is, the limit or antilimit s and the k linear coefficients $c_1, \ldots, c_k$. Thus, $k+1$ sequence elements $s_r, \ldots, s_{r+k}$, and the corresponding remainder estimates $w_r, \ldots, w_{r+k}$, are required for determining s. Evidently, imposing some kind of remainder estimate, as the three ones considered by Levin, most of the sequences do not follow this model sequence. However, in many cases for which $n \geqslant N$, where $N \in \mathbb{N}$, the sequence can be considered of kth order, namely

$$s_r = s_{kn} + \omega_r \sum_{j=1}^{k} c_{jn}/(r+\gamma)^{j-1}, \qquad n \leqslant r \leqslant n+k, \qquad n \geqslant N, \tag{2.2}$$

where $s = \lim_{n\to\infty} s_{kn}$. Thus, s is both the limit of the sequences $\{s_r\}_{r=1}^{\infty}$ and $\{s_{kn}\}_{n=N}^{\infty}$, whose convergence was accelerated relatively to $\{s_r\}_{r=1}^{\infty}$, or even created if s is an antilimit of $\{s_r\}_{r=1}^{\infty}$.

According to Cramer's rule, the general Levin's transformation is

$$\mathfrak{L}_k^{(n)}(\gamma, s_r, \omega_r) = \frac{\begin{vmatrix} s_n & \ldots & s_{n+k} \\ \omega_n & \ldots & \omega_{n+k} \\ \vdots & \ddots & \vdots \\ \omega_n/(\gamma+n)^{k-1} & \ldots & \omega_{n+k}/(\gamma+n+k)^{k-1} \end{vmatrix}}{\begin{vmatrix} 1 & \ldots & 1 \\ \omega_n & \ldots & \omega_{n+k} \\ \vdots & \ddots & \vdots \\ \omega_n/(\gamma+n)^{k-1} & \ldots & \omega_{n+k}/(\gamma+n+k)^{k-1} \end{vmatrix}}. \tag{2.3}$$

If the sequence elements satisfy equation (2.1), then the Levin's general sequence transformation is exact, i.e. $\mathfrak{L}_k^{(n)}(\gamma, s_r, \omega_r) = s$. But if they satisfy equation (2.2), then

$$\mathfrak{L}_k^{(n)}(\gamma, s_r, \omega_r) = s_{kn}. \tag{2.4}$$

As a ratio of two determinants, the Levin's transformation is unsuitable for practical applications involving reliable evaluations of large order determinants. Therefore, alternative expressions are commonly employed. For example, considering the Vandermonde determinant, the equation (2.3) can be rewritten

$$\mathfrak{L}_k^{(n)}(\gamma, s_r, \omega_r) = \frac{\sum_{j=0}^{k}(-1)^j \begin{pmatrix} k \\ j \end{pmatrix} \left(\frac{\gamma+n+j}{\gamma+n+k}\right)^{k-1} \frac{s_{(n+j)}}{\omega_{(n+j)}}}{\sum_{j=0}^{k}(-1)^j \begin{pmatrix} k \\ j \end{pmatrix} \left(\frac{\gamma+n+j}{\gamma+n+k}\right)^{k-1} \frac{1}{\omega_{(n+j)}}}, \qquad k, r, n \in \mathbb{N}. \tag{2.5}$$

According to [24], the Levin's transformation should work very well for a given sequence $\{s_r\}$ if the sequence $\{\omega_r\}$ of the remainder estimates is chosen in such a way that ω_r is proportional to the dominant term of an asymptotic expansion of the remainder

$$\varpi_r = s_r - s = \omega_r \left[c + O\left(r^{-1}\right)\right], \qquad r \to \infty. \tag{2.6}$$

However, ω_r is not determined by this asymptotic condition, so that it is possible to find a variety of sequences $\{\omega_r\}$ of the remainder estimates for a given sequence $\{s_r\}$. Thus, the practical problem that arises is how to find the sequence of the remainder estimates.

Based on purely heuristic arguments, Levin suggested three kinds of the remainder estimates, ω_r, for sequences of partial sums

$$s_r = \sum_{i=1}^{r} a_i, \qquad r \in \mathbb{N}. \tag{2.7}$$

In the case of alternating partial sums, s_r, Levin suggested

$$\omega_r = a_r, \qquad r \in \mathbb{N}. \tag{2.8}$$

Substituting this relationship in equation (2.5), the Levin's t transformation is obtained,

$$t_k^{(n)}(\gamma, s_r) = \frac{\sum_{j=0}^{k}(-1)^j \begin{pmatrix} k \\ j \end{pmatrix} \left(\frac{\gamma+n+j}{\gamma+n+k}\right)^{k-1} \frac{s_{(n+j)}}{a_{(n+j)}}}{\sum_{j=0}^{k}(-1)^j \begin{pmatrix} k \\ j \end{pmatrix} \left(\frac{\gamma+n+j}{\gamma+n+k}\right)^{k-1} \frac{1}{a_{(n+j)}}}. \tag{2.9}$$

In the case of a sequence of partial sums, s_r, satisfying a logarithmic convergence, i.e.,

$$\lim_{r\to\infty} \frac{s_r + 1 - s}{s_r - s} = 1, \tag{2.10}$$

Levin suggested

$$\omega_r = a_r(\gamma + r), \qquad r \in \mathbb{N}, \tag{2.11}$$

which being substituted into equation (2.5) produces the Levin's u transformation

$$u_k^{(n)}(\gamma, s_r) = \frac{\sum_{j=0}^{k}(-1)^j \begin{pmatrix} k \\ j \end{pmatrix} \frac{(\gamma+n+j)^{k-2}}{(\gamma+n+k)^{k-1}} \frac{s_{(n+j)}}{a_{(n+j)}}}{\sum_{j=0}^{k}(-1)^j \begin{pmatrix} k \\ j \end{pmatrix} \frac{(\gamma+n+j)^{k-2}}{(\gamma+n+k)^{k-1}} \frac{1}{a_{(n+j)}}}. \tag{2.12}$$

Finally, Levin also suggested

$$\omega_r = \frac{a_r a_{r+1}}{a_r - a_{r+1}}, \qquad r \in \mathbb{N}, \tag{2.13}$$

which corresponds to the Levin's v transformation

$$v_k^{(n)}(\gamma,s_r)=\frac{\sum_{j=0}^{k}(-1)^j\begin{pmatrix}k\\j\end{pmatrix}\left(\frac{\gamma+n+j}{\gamma+n+k}\right)^{k-1}\frac{a_{(n+j)}-a_{(n+j+1)}}{a_{(n+j)}\,a_{(n+j+1)}}s_{n+j}}{\sum_{j=0}^{k}(-1)^j\begin{pmatrix}k\\j\end{pmatrix}\left(\frac{\gamma+n+j}{\gamma+n+k}\right)^{k-1}\frac{a_{(n+j)}-a_{(n+j+1)}}{a_{(n+j)}\,a_{(n+j+1)}}}. \tag{2.14}$$

Other Levin-type transformations are reported in the literature (see [25]), but only those originally proposed by Levin are listed above, and are used in this work.

3. Methodology

A Levin's transformation can be applied to a well-defined sequence to obtain a new sequence that presents a better convergence than the original one. Still, in this work, the sequence is not completely defined, and the supposition that some Levin's transformation can change the values of lower-order terms to the values of higher-order terms of the same sequence is tested for the virial series. Indeed, the virial series defined by equation (1.1) is a sequence of partial sums in accordance with equation (2.7), i.e.,

$$s_r=\sum_{i=1}^{r}a_i,\quad r\in\mathbb{N},\quad\text{and}\quad Z=\lim_{r\to\infty}s_r\,, \tag{3.1}$$

where $a_i = B_i\eta^{i-1}$ and $B_1 = 1$. In this case, s_r is the value of the virial series truncated at the term proportional to η^{r-1}, whose coefficient is B_r. Then, it is supposed that the application of the Levin's transformation $\mathfrak{L}_k^{(n)}$ to $\{s_r\}_{r=1}^{\infty}$ produces, according to equation (2.4),

$$\mathfrak{L}_k^{(n)}(\gamma,s_r,\omega_r)=s_{kn}=s_{n+k}\,, \tag{3.2}$$

i.e., the nth element of the sequence $\{s_{kn}\}_{n=N}^{\infty}$ is equal to the $(n+k)$th element of the sequence $\{s_r\}_{r=1}^{\infty}$, for all $n\geqslant N$. Thus,

$$\mathfrak{L}_k^{(n)}(\gamma,s_r,\omega_r)=\sum_{i=1}^{n+k}B_i\eta^{i-1}. \tag{3.3}$$

As already mentioned, the values of coefficients are precisely known up to B_{10}. But, for equations (2.9) and (2.12), suppose that the first unknown term is

$$a_{n+k}=B_{n+k}\eta^{n+k-1}\quad\text{for all}\quad 2\leqslant n+k\leqslant 10. \tag{3.4}$$

Then, using (3.3) in equations (2.9) or (2.12), $a_{n+k}=B_{n+k}\eta^{n+k-1}$ can be found for all $n+k$ in $2\leqslant n+k\leqslant 10$. Analogously, for equation (2.14), suppose that the first unknown term is

$$a_{n+k+1}=B_{n+k+1}\eta^{n+k}\quad\text{for all}\quad 2\leqslant n+k\leqslant 9. \tag{3.5}$$

Using the equation (3.3) in (2.14), $a_{n+k+1}=B_{n+k+1}\eta^{n+k}$ can be found for all $n+k$ in $2\leqslant n+k\leqslant 9$. In any case, for a given value of η, the corresponding virial coefficient can be calculated and compared with the values reported in the literature (table 1). It is worthwhile noting that the choice of the values of coefficients reported on table 1 has been made arbitrarily. Indeed, more recent references could be used, such as [26].

In general, the estimation of a virial coefficient can be obtained from several representations of the same Levin's transformation, as shown in table 2. The representations whose virial coefficients values do not deviate more than 1% from the corresponding values in table 1 are used to estimate higher-order coefficients. The representations do not provide good estimates for the coefficients of the order less than B_5, while for higher orders, acceptable values are found. This behavior stems from the lack in information supplied to the representations by the virial series truncated on the terms of the order smaller than the fourth, so that a minimum number of the known terms of the series is required.

The methodology is based on determining simple functions $\eta=f(i)$ (i is the index of B_i) by using the optimal η values which correspond to the best estimates of coefficients from B_5 to B_{10}. These functions

Table 1. The virial coefficients B_i.

i	[9]	[10]
1	1	1
2	4	4
3	10	10
4	18.3647684	18.364768
5	28.2245 ± 0.00010	28.2245 ± 0.0003
6	39.81550 ± 0.00036	39.81507 ± 0.00092
7	53.3413 ± 0.0016	53.34426± 0.00368
8	68.540± 0.010	68.538± 0.018
9	85.80± 0.080	85.813± 0.085
10	...	105.77± 0.39

Table 2. The representations which estimate the terms $a_{n+k} = B_{n+k}\eta^{n+k-1}$, $2 \leqslant n+k \leqslant 10$, by equations (2.9) (transformation t) or (2.12) (transformation u), and $a_{n+k+1} = B_{n+k+1}\eta^{n+k}$, $2 \leqslant n+k \leqslant 9$, by equation (2.14) (transformation v, disregarding the last line in the table).

i	Levin's representations, $\mathfrak{L}_k^n(\gamma, s_r, \omega_r)$
2	$\mathfrak{L}_1^1$
3	$\mathfrak{L}_2^1, \mathfrak{L}_1^2$
4	$\mathfrak{L}_3^1, \mathfrak{L}_2^2, \mathfrak{L}_1^3$
5	$\mathfrak{L}_4^1, \mathfrak{L}_3^2, \mathfrak{L}_2^3, \mathfrak{L}_1^4$
6	$\mathfrak{L}_5^1, \mathfrak{L}_4^2, \mathfrak{L}_3^3, \mathfrak{L}_2^4, \mathfrak{L}_1^5$
7	$\mathfrak{L}_6^1, \mathfrak{L}_5^2, \mathfrak{L}_4^3, \mathfrak{L}_3^4, \mathfrak{L}_2^5, \mathfrak{L}_1^6$
8	$\mathfrak{L}_7^1, \mathfrak{L}_6^2, \mathfrak{L}_5^3, \mathfrak{L}_4^4, \mathfrak{L}_3^5, \mathfrak{L}_2^6, \mathfrak{L}_1^7$
9	$\mathfrak{L}_8^1, \mathfrak{L}_7^2, \mathfrak{L}_6^3, \mathfrak{L}_5^4, \mathfrak{L}_4^5, \mathfrak{L}_3^6, \mathfrak{L}_2^7, \mathfrak{L}_1^{(8)}$
10	$\mathfrak{L}_9^1, \mathfrak{L}_8^2, \mathfrak{L}_7^3, \mathfrak{L}_6^4, \mathfrak{L}_5^5, \mathfrak{L}_4^6, \mathfrak{L}_3^7, \mathfrak{L}_2^8, \mathfrak{L}_1^9$

are obtained both by interpolating the five or six optimal η values themselves, and by interpolating their variations (optimal η value for B_6 less optimal η value for B_5, and so forth). The mathematical structures of such functions are determined by using the Mathematica computer program, version 8.0. Once the functions are known, they are used to estimate B_{11} and B_{12}.

4. Estimates of the 11th, 12th and 13th virial coefficients

In this section, the best representations and the corresponding estimates of coefficients are presented. For the t and u transformations, the t_3^n and u_3^n representations, respectively, provide good estimates of coefficients, while for the v transformation, the best estimates are obtained through the v_2^n representations. For the t_3^n representations, the optimal η for estimating the coefficients from B_5 to B_{10} approximately lie between 0.20 and 0.28, while they are approximately in the interval from 0.01 to 0.08 for the u_3^n representations.

Using the v_2^n representations, the optimal η values are, approximately, in the interval from 0.40 to 0.78. This range is about five times broader than the other two ranges, yet a large η variation for low i values is not important, while the η tendency to reduce its variation as the index i increases is fundamental. Moreover, this range presents an upper bound about 5% greater than the physical one (the geometric maximum packing factor for rigid spheres is about 0.74). Nonetheless, the v_2^n representations are retained for this work, because this physical restriction is irrelevant for the present mathematical purpose. Moreover, packing factors above its physical upper bound, and even above 1.0, are frequently considered in the literature.

4.1. T-type representations

Using the t_3^{i-3} representations for $i = 5,6,\dots,12$, the virial coefficients B_i are estimated. Thus, to predict the coefficients B_{11} and B_{12}, the t_3^8 and t_3^9 representations are respectively used. The optimal η values for the t_3^8 and t_3^9 representations are established by using four trial functions, which are obtained by interpolating the optimal η values corresponding to the coefficients from B_5 to B_{10}. These optimal η values are $\eta = 0.2493$ for B_5, $\eta = 0.2591$ for B_6, $\eta = 0.2703$ for B_7, $\eta = 0.2425$ for B_8, $\eta = 0.2172$ for B_9, and $\eta = 0.2053$ for B_{10}. Table 3 shows the values of the obtained virial coefficients, and their percentage deviations from the values reported in the literature.

According to table 3, all B_{12} estimates obtained from the interpolation of the optimal η values themselves deviate more than 6% from the reported values. Thus, the estimates using the η values from the functions of the optimal η variations are the only ones providing virial coefficients close to those reported in the literature. Among the four functions, only the logarithmic and the straight-line functions provide deviations less than 3% for both B_{11} and B_{12}. Comparing these values with those obtained by Padé approximants ($B_{11} = 128.6$ and $B_{12} = 155$) [27] one concludes that both methods lead to similar estimates. Therefore, this comparison, as well as the values reported in [9] and [10], lead to the values of B_{11} and B_{12} obtained from the logarithmic and the straight-line functions of the optimal η variations.

Table 3. Values of the virial coefficients B_{11} and B_{12} estimated by the t_3^8 and t_3^9 representations, respectively. Percentage deviations from the values reported in the literature are also presented. $(\%)^a$ Percentage deviation from the $B_{11} = 129 \pm 2$ and $B_{12} = 155 \pm 10$ values reported by [9]. $(\%)^b$ Percentage deviation from the $B_{11} = 127.9$ and $B_{12} = 152.7$ values reported by [10].

Functions	η-variation						η-absolute					
	B_{11}	$(\%)^a$	$(\%)^b$	B_{12}	$(\%)^a$	$(\%)^b$	B_{11}	$(\%)^a$	$(\%)^b$	B_{12}	$(\%)^a$	$(\%)^b$
Logarithmic	127.1	1.47	0.63	156.5	0.97	2.49	133.8	3.72	4.61	170.2	9.81	11.5
Exponential	131.3	1.78	2.66	164.9	6.39	7.99	131.1	1.63	2.50	165.5	6.77	8.38
Straight-line	126.2	2.17	1.33	153.5	0.97	0.52	130.9	1.47	2.35	165.1	6.52	8.12
Potency	126.8	1.71	0.86	147.4	4.90	3.47	133.6	3.57	4.46	169.9	9.61	11.3

Thus, the logarithmic and straight line functions of the optimal η variations are also considered to estimate the value of B_{13}. Using the t_3^{10} representation, the values 183.68 and 175.45 are respectively found. The value from the logarithmic function is very close to those estimated in [10] (181.19) and [11] (180.82), whereas the value obtained from the straight-line function is between those estimated in [28] (177.40) and [29] (171.28). Therefore, this comparison confirms that the logarithmic and straight-line functions can be used to find estimates of the optimal η for high order coefficients.

4.2. U-type representations

Using the u_3^{i-3} representations for $i = 5,6,\dots,12$, the virial coefficients B_i are also estimated. Thus, to predict the coefficients B_{11} and B_{12} the u_3^8 and u_3^9 representations are respectively used. The optimal η values are 0.01714 for B_6, 0.06435 for B_7, 0.07235 for B_8, 0.07209 for B_9, and 0.07819 for B_{10} (the 1% minimal deviation is not attained for B_5). Table 4 presents the values of the obtained virial coefficients.

Table 4 shows that the η values from the logarithmic, exponential and potency functions obtained by interpolating the optimal η variations provide good estimates. In the case of a straight-line function, one can also note a good estimate, but only for B_{11}. Considering the η values obtained from functions of the optimal η values themselves, only the logarithmic function provides a B_{12} value which deviates less than 6% from a reported value. This function also provides the best estimate for B_{11}. However, imposing the smaller percentage deviations as a criterion, the logarithmic, exponential and potency functions obtained by interpolating the optimal η variations are selected to estimate high-order coefficients.

The B_{13} values estimated by using the exponential and potency functions of the optimal η variations are 190.03 and 190.80, respectively. It is impossible to obtain an estimate of B_{13} from the logarithmic function, because the u_3^{10} representation does not support the supplied optimal η value. The estimated

Table 4. Values of the virial coefficients B_{11} and B_{12} estimated by the u_3^8 and u_3^9 representations, respectively. Percentage deviations from the values reported in the literature are also presented.

Functions	η-variation						η-absolute					
	B_{11}	$(\%)^a$	$(\%)^b$	B_{12}	$(\%)^a$	$(\%)^b$	B_{11}	$(\%)^a$	$(\%)^b$	B_{12}	$(\%)^a$	$(\%)^b$
Logarithmic	127.3	1.32	0.47	150.3	3.03	1.57	131.0	1.55	2.42	162.8	5.03	6.61
Exponential	128.9	0.08	0.78	156.6	1.03	2.55	132.9	3.02	3.91	170.9	10.3	11.9
Straight-line	126.2	2.17	1.33	221.5	42.9	45.1	132.4	2.64	3.52	167.9	8.32	9.95
Potency	129.1	0.08	0.94	156.9	1.23	2.75	131.5	1.94	2.82	164.5	6.13	7.73

values are above those obtained by [10, 11, 28, 29]. However, they are close to the values estimated in [30] (190.82) and [31] (185±10).

4.3. V-type representations

In the last test, the v_2^8 and v_2^9 representations are used to estimate the coefficients B_{11} and B_{12}. The optimal η values are 0.4010 for B_5, 0.5445 for B_6, 0.6507 for B_7, 0.7089 for B_8, 0.7464 for B_9, and 0.7783 for B_{10}. Table 5 presents the estimated coefficients B_{11} and B_{12}, as well as their deviations from previously reported values. This table clearly indicates that the η values corresponding to the potency and exponential functions of the optimal η variations, and the logarithmic interpolation of the optimal η values themselves, provide the best estimates for the coefficients B_{11} and B_{12}. Using the v_2^{10} representation and the potency function of the variations, which shows the lowest deviations, the coefficient B_{13} is estimated. The value obtained is 172.65. This estimated value is lower than those presented in [10, 11, 30, 31], but it is placed between those in [28] and [29].

Table 5. Values of the virial coefficients B_{11} and B_{12} estimated by the v_2^8 and v_2^9 representations, respectively. Percentage deviations from the values reported in the literature are also presented.

Functions	η-variation						η-absolute					
	B_{11}	$(\%)^a$	$(\%)^b$	B_{12}	$(\%)^a$	$(\%)^b$	B_{11}	$(\%)^a$	$(\%)^b$	B_{12}	$(\%)^a$	$(\%)^b$
Logarithmic	131.5	1.94	2.81	166.5	7.42	9.04	127.8	0.93	0.08	149.1	3.81	2.36
Exponential	130.8	1.39	2.27	162.2	4.52	6.09	116.6	10.1	8.84	106.8	31.1	30.1
Straight-line	135.1	4.73	5.63	187.6	21.1	22.9	119.2	7.60	6.80	117.1	24.5	23.3
Potency	128.9	0.08	0.78	152.5	1.61	0.13	124.9	3.18	2.35	137.7	11.2	9.82

5. Conclusions

Only representations with $k = 2$ for the Levin's v transformation, and $k = 3$ for the t and u Levin's transformations, are acceptable. This interesting result guided the choice of the representations used to estimate the high order virial coefficients. Moreover, the estimates also depend on the dimensionless η value. This is an expected dependence, because the Levin's convergence accelerators modify the terms from the series, not just the coefficients included within these terms.

The B_{11} and B_{12} values have been confirmed in the literature, by using distinctive methodologies, which imply different assumptions on the mathematical behavior of the virial series. Thus, such values are reliable. Meanwhile, the values reported in the literature are in accordance with some representations of the Levin's transformations, highlighting these transformations usefulness in the prediction of virial coefficients.

Should a Levin's transformation be able to change the values of lower order terms to the values of higher-order terms of the considered virial series, then it is expected that: (i) such ability is enhanced for high order terms of the series, which are favored by high η values, and (ii) the η value variation caused by substituting $i+1$ for i decreases as i increases (η tends to some unique value for high-order coefficients). Accordingly, note that, in table 3 to 5, the functions are not selected to achieve the best fit to the B_5 to B_{10} values in table 1 (for instance, functions with more than two parameters are not used), but to test the asymptotic behavior of the functions. An interesting result is that all the functions selected in section 4 by comparing the obtained values to previously reported ones, except the straight line function, are asymptotic to the i axis, that is, they satisfy the above condition (ii).

The η values corresponding to the u transformation refer to the gaseous state, whose description is accurate enough by using only the low order terms of the series, and the η values corresponding to the t transformation concern the liquid state, whose description is accurate enough by using the low and medium order terms of the series. However, the η values corresponding to the v transformation refer to the overcooled liquid and vitreous states, whose accurate descriptions also demand the high order terms of the series. Note that the v transformation is the only one producing good results not exclusively from the interpolation of the η values variations, but also from the interpolation of the optimal η values themselves, confirming the above condition (i). Thus, the v transformation, which is the least specific one among those originally presented by Levin, is preferable. As a consequence of this choice, the B_{13} value near 173 is proposed in this work. Note that the 13 terms long, virial series for rigid spheres developed in this work should be useful in describing the repulsive pressure of overcooled liquids and vitreous transitions. However, this series will not reproduce crystallization, which involves drastic changes in entropy and volume.

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Застосування перетворень Левіна до віріальних рядів

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Запропоновано новий метод оцінювання віріальних коефіцієнтів високого порядку для плинів, що складаються з однакових тривимірних жорстких сфер. Передбачені значення для B_{11} і B_{12} добре узгоджуються з надійними оцінками, отриманими раніше. Розвинуто нове застосування перетворень Левіна, а також запропоновано новий спосіб використання перетворень Левіна. Для віріальних рядів за степенями упакування сфер цей метод дає оцінку для значення B_{13} близько 173.

Ключові слова: *перетворення Левіна, віріальні ряди, жорсткі сфери*