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MODIFICATION OF THE MAYER SAMPLING METHOD FOR THE CALCULATION OF HIGH-ORDER VIRIAL COEFFICIENTS

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A technique for the calculation of high-order virial coefficients, which combines the quadrature integration and the Mayer sampling Monte Carlo method (MSMC), is proposed. Unlike the original MSMC, this technique does not require to know the reference coefficients for the hard-sphere potential and can be used in a wide range of temperatures and for various interaction potentials. In addition, the proposed method has a higher accuracy at lower computational costs. It has been used to obtain some new data on the seventh virial coefficient of the Lennard-Jones (12-6) model.

K e y w o r d s: virial coefficient, irreducible cluster integral, Mayer's function, Mayer sampling, Monte Carlo method.

1. Introduction

The theoretical description of condensed states of matter and, in particular, the first order phase transitions remains a challenging problem for statistical physics [1]. Over a hundred years, one of the widely known approaches with the exact statistical substantiation involves the virial equation of state, in which the power (virial) coefficients are determined in terms of the so-called irreducible integrals of the corresponding order [2],

$$B_{k+1} = -\frac{k}{k+1}\beta_k.$$

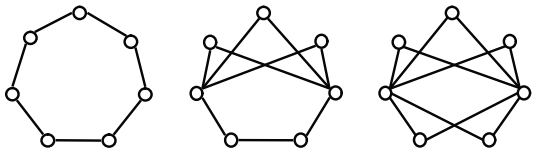
Recently, on the basis of the exact cluster expansion of a configuration integral, another approach has been proposed [3–7], which has a wider range of applicability. In the framework of this approach, both the configuration integral and the equation of state are also expressed in terms of irreducible integrals, which makes the problem of calculating those integrals (or virial coefficients) even more actual.

Unfortunately, this problem still involves considerable technical difficulties even for the simplest model potentials of intermolecular interaction, despite the rapid development of computation facilities. For realistic potentials, which make allowance for both attraction and repulsion, the virial coefficients can be calculated nowadays using quadrature methods only up to the fifth order inclusive [8–10].

An absolutely new approach to the calculation of virial coefficients was proposed by D. Kofke and collaborators [11–13]. It is based on the "umbrella sampling" method, a variant of the Metropolis Monte Carlo algorithm [14], in which the integrand (a sum of various products of Mayer functions [2]) is used as the probability distribution. This method was intended only for the calculation of virial coefficients, and the choice of the probability distribution determined its name, the Mayer Sampling Monte Carlo (MSMC) [11]. Today, this method allowed the values of the sixth and seventh virial coefficients (and even a few values of the eighth coefficient) to be calculated at various temperatures for the Lennard-Jones (12-6) potential [12, 13].

However, the original form of the Mayer sampling has some restrictions. It requires that the value of a reference virial coefficient of the same order should already be known. The virial coefficients for the hard-sphere potential, which are rather precisely determined for today up to the tenth order inclusive, are used for this purpose. At high temperatures, this choice of the reference is quite justified, but at low and near-critical temperatures, the essential difference between the behaviors of the Lennard-Jones and hard-sphere potentials results in considerable calculation errors.

A further development and improvement of the available Mayer sampling method was the aim of this work. A fulfillment of this task would allow us to eliminate its existing restrictions and to raise its



a *b* *c*

Fig. 1. Some of simple graphs of the seventh virial coefficient: No. 1 (*a*), 14 (*b*), and 26 (*c*) according to the enumeration of work [15]

efficiency, while calculating the virial coefficients of higher orders for various potentials of intermolecular interaction.

2. Theoretical Substantiation

The essence of the Mayer sampling consists in the determination of the virial coefficient (or irreducible cluster integral) Γ of the n-th order in terms of an already known reference integral Γ_0 (a version of the direct sampling),

$$\Gamma = \Gamma_0 \frac{\langle \gamma/\pi \rangle_\pi}{\langle \gamma_0/\pi \rangle_\pi}. \tag{1}$$

In Eq. (1), the symbol γ stands for the value of integrand, a complicated sum of products of Mayer functions

$$f(r_{ij}) = \exp\left(-\frac{u(r_{ij})}{kT}\right) - 1 \tag{2}$$

for various molecular pairs ij selected from n molecules at the given interaction potential $u(r)$. The quantity γ corresponds to the required integral, and γ_0 to the reference one. The function π in Eq. (1) is the probability distribution used to accept or reject the given configuration (a point in the configuration space of molecules) according to the ordinary Metropolis algorithm. The angle brackets mean the averaging over the whole ensemble of configurations. The spatial step of the random trial moves of points (configurations) is selected experimentally to provide a 50% acceptance for configurations [14].

In order to reduce the scatter of obtained values, i.e. to improve the accuracy and the efficiency of the method, the choice of both reference parameters Γ_0 and γ_0, on the one hand, and the probability distribution π, on the other hand, plays the crucial role. It is important that the configuration spaces for γ and γ_0 should differ from each other as less as possible or overlap in the most contributing regions, and the function π should adequately reflect those contributions. Such methods are most efficient in the cases where the configuration space of one integral is only a part of the space of the other integral, i.e. the former is completely overlapped by the latter (whence the common name of the methods–the umbrella sampling–follows) [14]. Then, the probability distribution π is selected to be proportional to the integrand value of the second integral.

At the Mayer sampling in its original form, the quantities γ and γ_0 are calculated as complete irreducible cluster integrals (for all possible product combinations of Mayer functions). However, γ is calculated for the sought potential, whereas γ_0 for the reference (hard-sphere) one.

For the sixth virial coefficient, the calculation of both γ and γ_0 means the summation over 56 different combinations (different graphs). For the seventh coefficient, the number of different graphs already reaches a value of 468 (!) [15]. As the probability distribution, D. Kofke and collaborators proposed to use $\pi = |\gamma|$.

It should be noted that the principal difference between the potentials forced the authors to use a "transient" function $\gamma_{OS}(\gamma, \gamma_0)$ [16] and, instead of direct sampling, to realize the so-called overlap sampling. In so doing, every coefficient was, in essence, independently calculated two times, with the individual selection of the spatial step and the parameters of the function γ_{OS} in each variant [12, 13].

Instead of introducing the "transient" function, the efficiency of calculations can be improved by selecting the reference integral, i.e. the quantity γ_0. The matter is that, among the set of all possible products of Mayer functions (every product is usually represented by the corresponding graph) that form the complete irreducible integral of any large order, there are always a considerable number of such products that can be calculated rather simply with the use of quadrature methods. For instance, the integration of the 10-connected graph of the seventh virial coefficient (Fig. 1, *c*) is practically not more difficult than the integration of the third virial coefficient [9, 10]. The calculation of integrals represented by graphs *a* and *b* in Fig. 1 by quadrature methods is also not much more difficult.

In general, of 56 graphs for the sixth virial coefficient, the summation of 41 graphs using the quadra-

The seventh virial coefficient in the dimensionless form ($B_7^* = B_7/\sigma^{18}$) for the Lennard-Jones (12-6) potential at various reduced temperatures $T^* = kT/\epsilon$. The magnitudes of 67%-confidence interval, the order of which corresponds to the position of the least significant digit, are indicated in parentheses

T^*	B_7^*	B_7^* with [13]	T^*	B_7^*	B_7^* with [13]	T^*	B_7^*	B_7^* with [13]
0.200	$-5(2)\times10^{26}$		0.9250	$-3.08(4)\times10^{4}$		1.450	−1.1(6)	
0.250	$-3.8(2)\times10^{20}$		0.9500	$-1.75(4)\times10^{4}$		1.475	−0.1(8)	
0.300	$-8.19(9)\times10^{16}$		0.9750	$-10.0(2)\times10^{3}$		1.500	2(1)	
0.400	$-4.64(1)\times10^{12}$		1.0000	$-5.8(2)\times10^{3}$	$-5.4(2)\times10^{3}$	1.525	4(1)	
0.500	$-1.342(2)\times10^{10}$		1.0250	$-3.1(1)\times10^{3}$		1.550	2(1)	
0.550	$-1.466(3)\times10^{9}$		1.0500	$-2.0(1)\times10^{3}$		1.575	0.6(8)	
0.575	$-5.448(10)\times10^{8}$		1.0750	$-1.01(8)\times10^{3}$		1.600	3(2)	2(1)
0.600	$-2.153(3)\times10^{8}$	$-2.13(3)\times10^{8}$	1.1000	−680(70)		1.650	4.1(9)	
0.625	$-9.01(2)\times10^{7}$		1.1250	−340(50)		1.700	4(1)	
0.650	$-3.97(1)\times10^{7}$		1.1500	−200(40)		1.800	5.2(7)	
0.675	$-1.809(5)\times10^{7}$		1.1750	−110(30)		1.900	5.2(6)	
0.700	$-8.62(3)\times10^{6}$		1.2000	−30(10)	−60(20)	2.000	5.2(4)	5.5(2)
0.725	$-4.23(2)\times10^{6}$		1.2250	−12(9)		2.100	4.9(3)	
0.750	$-2.114(9)\times10^{6}$		1.2500	−10(7)		2.250	4.2(3)	
0.775	$-1.102(5)\times10^{6}$		1.2625	−4(6)		2.500	3.2(2)	
0.800	$-5.84(3)\times10^{5}$	$-5.87(10)\times10^{5}$	1.2750	4(5)		3.000	1.67(9)	1.77(1)
0.825	$-3.15(2)\times10^{5}$		1.2875	6(5)		4.000	0.71(3)	0.728(4)
0.850	$-1.71(1)\times10^{5}$		1.3000	4(4)		5.000	0.34(4)	
0.875	$-9.7(1)\times10^{4}$		1.3500	1(4)		7.000	0.13(3)	
0.900	$-5.38(7)\times10^{4}$		1.4000	−0.7(5)		10.00	0.05(2)	0.0698(2)

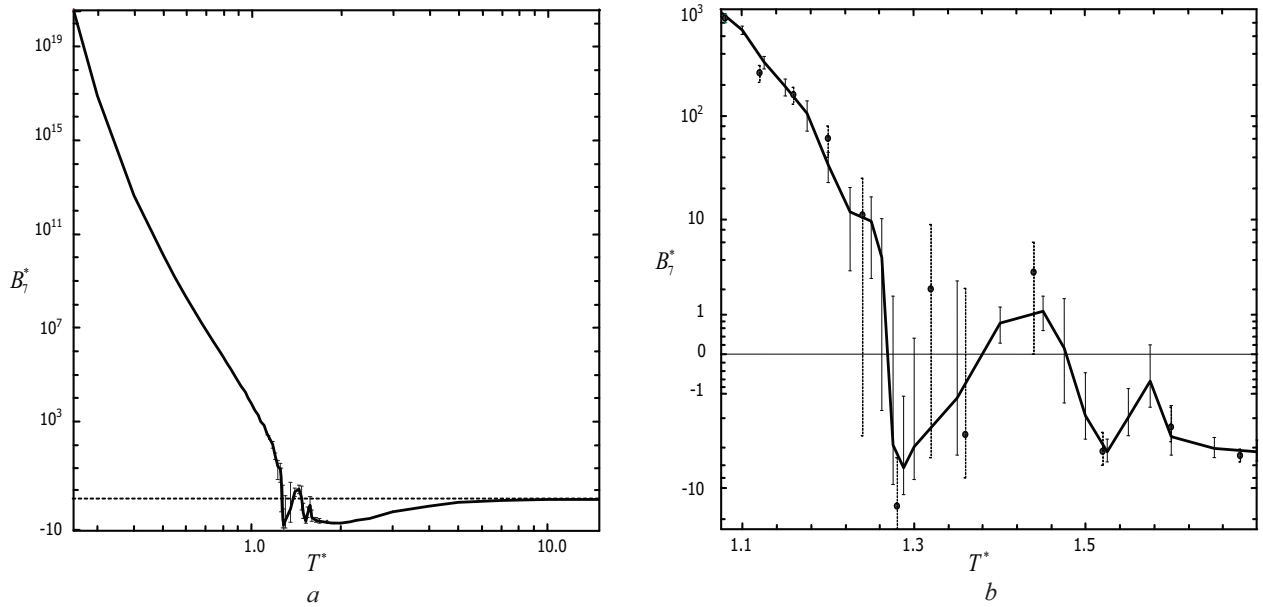


Fig. 2. Seventh virial coefficient of the Lennard-Jones potential (a) in the reduced temperature range (0.25,...,15) and (b) in the near-critical region. Vertical solid segments mark 67%-confidence intervals. Points in panel (b) correspond to the data of work [13] with the same confidential interval (dotted segments)

ture methods is not more difficult than the calculation of the fourth virial coefficient [9, 10]. The same concerns more than 200 of 468 graphs for the seventh virial coefficient.

On the one hand, in order to determine the coefficient, the sum over a smaller number of graphs remains to be calculated using the Mayer sampling, which means a simpler and faster algorithm. On the other hand, the already known – i.e. previously calculated by the method of quadratures – simple integrals can be used as reference ones for the determination of Γ_0 and γ_0.

For the seventh coefficient, all graphs that cannot be calculated using the method of quadratures are more complicated variants of only three simple graphs depicted in Fig. 1. The difference consists in the presence of various additional "connections" between particles (Mayer functions). The absence of such a "connection" can be regarded as the function $f_0 \equiv 1$ in the product. Since the Mayer function (2) vanishes rapidly, as the distance grows, its presence in the product efficiently confines the configuration space of the corresponding integral in comparison with the case where this function is substituted by $f_0 \equiv 1$.

From this viewpoint, the integral that corresponds to the simplest graph in such a hierarchy has a configuration space that is common for all its derivatives, i.e. graphs with additional "connections", and can serve as a reference for them, and its integrand can be a function of γ_0. The choice of a simple γ_0, in turn, simplifies and accelerates the calculation algorithm. As the probability distribution for such a variant, it would be the most reasonable to use $\pi = |\gamma_0|$ or $\pi = |\gamma_0| + |\gamma|$.

For a higher accuracy, it is desirable to select the reference integrals of the highest complexity, with the configuration space as close to the sought sum of integrals as possible. However, the separate calculations of several integral groups can hardly be characterized as an efficient method for the determination of the entire virial coefficient. It is the more so that the resulting error, which is a sum of errors of separate calculations, may turn out too large even if every contribution to it is small.

Taking the aforesaid into account, the following modifications are proposed to be made in the method of calculation of virial coefficients with the help of the Mayer sampling.

(i) All integrals in the coefficient are preliminary divided into two groups: to be determined by the quadrature method or the Mayer sampling. In order to reduce the error, it is important that the contribution of the second group to the total sum should be as small as possible (just the total sum produced by complicated integrals in the second group rather than their number). Test calculations showed that the exclusion of only one integral from this group very strongly affects the total sum. In order to diminish this sum, it is even possible to remove one or a few integrals from one group to the other.

(ii) From the first group, a minimum possible number of reference integrals is selected, in terms of which all integrals of the second group are expressed (by adding new "connections" to them). The integrands in those reference integrals are used as γ_0 in the subsequent calculations of integrals belonging to the second group using the Mayer sampling method. Since the behavior of the corresponding γ and γ_0 is very complicated, in order to guarantee the correct account for all weighty configurations, the most pertinent choice for the probability density is the function $\pi = |\gamma_0| + |\gamma|$.

3. Practical Implementation

In order to analyze the efficiency and adequacy of the proposed complex procedure for the calculation of virial coefficients, the seventh coefficient for the Lennard-Jones (12-6) potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

was chosen. On the one hand, there are already the data on this coefficient for comparison [12, 13]. On the other hand, the body of those data, as well as their accuracy (especially, in the near-critical region), is still rather confined, so that the additional calculations could substantially increase the available information.

Of 468 integrals entering the seventh virial coefficient [15], 156 integrals were calculated using the Gauss method [10] (two of them, partially). Such a number was selected to reduce the sum of other integrals in the low-temperature interval (in the high-temperature interval, the data [12, 13] have rather small errors and do not require to be calculated more precisely).

Modern graphic processors can support hardware multithreading, which makes repeated operations with float numbers hundreds times more effective in comparison with similar calculations on the basis of central processor unit. The capabilities of graphic processor computation functions are provided today by the CUDA platform and the DirectX11 library (with the help of ComputeShader technology), approximately in the equal proportion.

To accelerate the calculations, the second variant with DirectX11 was used. A single procedure was used to calculate both the sum of all 156 integrals and separate reference integrals for their use at the next stage of calculations. For every of the selected temperatures, the integral values were calculated using the Gauss quadrature formula with 30, 60, and 120 nodes; and the error was evaluated by Aitken's process [17].

The other integrals of the seventh coefficient (314 integrals, including 2 incomplete ones) were divided into three groups: 148 integrals that can be obtained by adding connections to the simple integral represented by graph (a) in Fig. 1, 122 integrals that are derivatives of graph (b), and 44 integrals that are derivatives of graph (c). Just those three integrals were selected as the reference ones.

At the computer realization of the Mayer sampling algorithm, the ComputeShader multithread technology of DirectX11 library was also used. In every thread, a separate sample of seven molecules was simulated, and a separate generator of random numbers was used. Since it is impossible to realize the Mersenne twister in the multithread mode, some authors [13] use a linear congruent generator in such cases. However, a relatively short period of this generator (of about 2^{32}) may result in a considerable correlation of the results. Therefore, a little more complicated generator Taus88 with a longer period of about 2^{88} [18] was used in every thread.

Three different variants of direct Mayer sampling were implemented:

(i) Three quantities–the sum of 148 integrals (taken as γ) at the reference integral (a) in Fig. 1 (taken as γ_0), and the sum of 122 integrals with the reference integral (b) in Fig. 1 together with the sum of 44 integrals with the reference integral (c) in Fig. 1 – were determined independently by formula (2);

(ii) two independent sums were determined: 148 integrals with the reference integral (a) and 166 integrals with the reference integral (b) in Fig. 1;

(iii) the sum of all other 314 integrals (γ) was determined with the reference integral (γ_0) calculated as the sum of integrals (a) and (b) in Fig. 1.

Despite that the convergence of some results was better in variants (i) and (ii), the total error turned out of the same order as in variant (iii). Therefore, in specific calculations, the variant with the calculation of the total sum was used as the most efficient.

The results of calculations are presented in the dimensionless form ($B_7^* = B_7/\sigma^{18}$) in Table and Fig. 2. For every reduced temperature $T^* = kT/\epsilon$, from 50 to 400 simulations were carried out, with 5×10^9 points (configurations) in each sampling. For comparison, the data of work [13], which were obtained using the overlap (!) Mayer sampling in its original form for 432 to 18800 separate simulations with 10^9 points in each, are also shown.

The results obtained allow us to draw a conclusion that the proposed technique is more efficient than the ordinary Mayer sampling, at least – expectedly – at low temperatures. With its help, the values of the seventh virial coefficient for the Lennard-Jones potential were obtained for the first time for temperatures below $0.6\epsilon/k$, and the body of data in the near-critical region was enriched.

4. Conclusions

Substantial modifications were made to the well-known calculation method of high-order virial coefficients based on the so-called Mayer sampling. The developed technique combines the advantages of both quadrature methods and the Mayer sampling. The most important advantages are flexibility and universality: the method does not require that the reference virial coefficient of the same order obtained by other methods for more simple potentials should be known, and it can be applied in any temperature range and to various interaction potentials. In addition, the proposed technique has a higher accuracy at lower computational expenses, which plays a key role while calculating the virial coefficients of high orders. A relative complexity of the method can be classed as its shortcoming: the method requires a considerable research work at its preliminary stage, but those efforts are compensated by the efficiency of calculations.

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МОДИФІКАЦІЯ МЕТОДУ ВИБІРКИ МАЙЕРА ДЛЯ РОЗРАХУНКУ ВІРІАЛЬНИХ КОЕФІЦІЄНТІВ ВИЩИХ ПОРЯДКІВ

Р е з ю м е

Запропоновано комплексну методику обчислення віріальних коефіцієнтів вищих порядків, що поєднує в собі квадратурні методи інтегрування і сучасний статистичний метод вибірки Майера. На відміну від оригінальної вибірки Майера дана методика не вимагає наявності вже відомих еталонних віріальних коефіцієнтів для потенціалу твердих сфер і може використовуватися в широкому діапазоні температур при будь-яких потенціалах взаємодії. Крім того, запропонована методика має більшу точність при менших обчислювальних витратах. За її допомогою були отримані нові дані по сьомому віріальному коефіцієнту для потенціалу Леннард-Джонса (12-6).