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ENHANCED APPROACH TO CALCULATING CLUSTER INTEGRALS FOR LATTICE MODELS OF MATTER

Ushcats M.V. Doctor of Science, Prof.
Admiral Makarov National University of Shipbuilding
Ukraine, Mykolaiv
mykhailo.ushcats@nuos.edu.ua;

Abstract. *The study is devoted to enhancing the existing techniques of calculating Mayer's expansion cluster integrals for lattice models of matter. Two important optimizations are proposed: reducing the number of integration points (due to eliminating physically identical configurations) and simplification of "per point" computations. Based on those optimizations, new data on high-order cluster integrals are obtained.*
Keywords: *Mayer's expansion, reducible cluster integral, connected diagram, lattice statistics, Wheatley's algorithm.*

Introduction. Theoretical description of phase transitions in many-particle systems still stays a challenging problem of Molecular Physics, Statistical Mechanics, Condensed Matter Physics, Physical Chemistry, and other related areas. Concerning this problem, thermodynamic systems with a discrete configuration phase-space (the so-called lattice models of matter: lattice gases, the Ising model of magnets [1], Lattice Statistics of binary mixtures, etc.) have turned out to be of special interest due to a number of reasons. First of all, there exists a strict definition of phase-transition parameters for the simplest two-dimensional Lee-Yang lattice gas [2], which allows direct comparisons of different analytical or numerical approaches. Secondly, the proved "hole-particle" symmetry of such models [3, 4] as well as recent generalization of the Lattice Statistics [5, 6] allow an exact theoretical prediction of the phase-transition activity for any lattice model of gases, magnets, and binary mixtures. The third reason of such interest to the lattice models is that their cluster integrals (i.e., the power coefficients in Mayer's expansion of the partition function [7]) are defined as finite exact sums in contrast to the models with a continuous phase-space, where cluster integrals can only be evaluated by using numerical integration techniques for each value of temperature. Moreover, a special technique of summation [4] allows defining the Lattice Statistics cluster integral once as an exact function of temperature in a form of some polynomial in powers of Mayer's function [7].

On the other hand, any accurate cluster-based definition of the saturation points (in terms of density and pressure) needs calculation of the corresponding cluster integrals to the orders of hundreds or thousands that, unfortunately, can hardly be performed even by using the modern computational equipment. At the moment, the highest order of calculated integrals reaches 6-7 for various 2D-lattice models and 5 for 3D models [4, 5]. Due to the huge number of the integration (summation) points, any attempt to calculate the integrals of higher orders still turns into a complex computational problem.

The research is aimed at enhancing the algorithm of summation over the lattice configurations in order to calculate the cluster integrals of orders higher than those of integrals known at the moment. Such enhancing involves two major optimizations: the first one is reducing the actual number of integration (configuration) points and the second is simplifying the Wheatley algorithm [8] for reducible cluster integrands at each configuration point by moving its most complex stages to the treatment of the resulting sum (resulting integral).

The main part. Considering the reducible integral of the nth order, b_n, one has to integrate all the possible reducible (connected) diagrams (graphs) over all the configuration phase-space of n particles, where each particle is related (connected) with the others by one Mayer's function [7], $f(r_{ij},T)$, at least (i.e., each particle i must be connected by $f(r_{ij},T)$ with some particle j, but it also may be connected by $f(r_{ik},T)$ with particle k or disconnected with this particle, and so on). Thus, the integrand, $f_C^{\{n\}}$, at each configuration point (a point of the $2n$-dimensional space for 2D models and $3n$-dimensional space for 3D models) is a sum of a huge number of different products of Mayer's functions, where each product corresponds to a possible reducible (connected) diagram (graph).

As to the complexity of such integrand $f_C^{\{n\}}$, there is a recursive algorithm of its calculation proposed by R. Wheatley [8]:

$$f_C^{\{n\}} = f_Q^{\{n\}} - \sum_{\{s\}\in\{n\}} f_C^{\{s\}} f_Q^{\{n\}/\{s\}}, \qquad (1)$$

where $f_Q^{\{m\}}$ is the product of all the possible $(f_{ij} + 1)$ for all the pairs in some $\{m\}$ set of particles. The $\{s\}$ set always includes the 1st (central) particle (for the set of only one central particle, $f_C^1 \equiv 1$). The $\{n\}/\{s\}$ set is always complementary to $\{s\}$ and it does not include the 1st particle (for a set of one particle, $f_Q^{i\neq 1} \equiv 1$).

The original approach means the implementation of the above-mentioned recursion in Eq. (1) (and, hence, computations of all possible $f_C^{\{s\}}$ and $f_Q^{\{n\}/\{s\}}$) at each integration point, however, in some cases, such "per point" computations may be essentially simplified. As the integration (or summation) for $f_C^{\{s\}}$ and $f_Q^{\{n\}/\{s\}}$ in each their product of Eq. (1) is over independent phase-spaces of $\{s\}$ and $\{n\}/\{s\}$ sets of particles, it is possible to sum all $f_C^{\{s\}}$ and $f_Q^{\{n\}/\{s\}}$ for each set separately and then (after the integration over all the points) find the final sum of the corresponding products. Furthermore, as any $\{s\}$ includes the central particle, the correct summation of $f_C^{\{s\}}$ over the integration volume must yield the reducible integral of order s less than n (and, therefore, known from previous calculations). As a result, no computation of $f_C^{\{s\}}$ (and, thus, no computation of the large number of complex recursive relations) is actually needed at each integration point that, in turn, fastens the "per point" computations in many times.

Along with the above-mentioned simplification of "per point" computations, there is an additional option to optimize the overall computation of a certain b_n by considerable reducing the number of integration points. A conventional calculation of b_n implies the integration over the $V^{(n-1)}$ phase-space volume of $(n-1)$ particles around one particle assumed to be the first (or central) particle and V is the maximum volume, where those n particles may form a connected chain. Say, for the simplest 2D Lee-Yang lattice model [2] (for $n = 4$, the integration volume is shown in Figure 1), the total number of integration points is $[2n(n-1)+1]^{2(n-1)}$. As the particles are actually indistinguishable, the huge number of such points differs only in indices of particles and thus are equivalent.

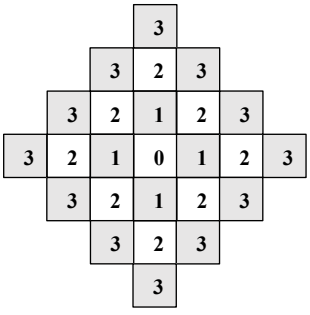

Fig.1. Integration 2D volume per particle for n=4. Numbers correspond to coordination spheres

A possible (and obvious) way to reduce the number of integration points is to make particle distinguishable and, then, account for equivalent configurations due to permutations of their indices. This way, each numbered particle can occupy some limited number of numbered "coordination

spheres" (see Fig. 1), where it can be connected with "preceding" and "following" particles in the other coordination spheres: the first particle always remains at the central cell(sphere 0); the 2nd can be placed in the same center (sphere 0) and all cells (numbered in some way) of sphere 1; the 3rd particle can be placed at the same cell as the 2nd one and all the cells after the 2nd (cells after the 2nd in the sphere, where the 2nd stays at the moment and all cells of all spheres up to sphere 2); the 4th particle can occupy all the cells beginning from the position of the 3rd one up to "the last" cell of sphere 3 and so on.

The integrand of each mentioned configuration must be included to the resulting sum with the integer "weight", which is the number of equivalent configurations due to the actual indistinguishability of particles. This weight can easily be defined for each configuration as $(n-1)!/(k_2 \cdot k_3 \cdot k_4 \cdot \ldots \cdot k_n)$, where $k_2 = 2$ if the 2nd particle occupy the same cell as the 1st one and $k_2 = 1$ otherwise; $k_3 = k_2 + 1$ if the 3rd particle occupy the same cell as the 2nd one and $k_3 = 1$ otherwise; $k_4 = k_3 + 1$ if the 4th particle occupy the same cell as the 3rd one and $k_4 = 1$ otherwise, etc.

Table 1 clearly demonstrate the corresponding reducing of the integration points for the above-mentioned 2D Lee-Yang lattice model.

Table 1. Comparison between non-optimized and enhanced approach for the Lee-Yang model

Integral order, n	No optimization, points number	Optimization, points number
3	169	55
4	15 625	995
5	2 825 761	25 720
6	844 596 301	875 946
7	377 149 515 625	37 305 195
8	235 260 548 044 817	1 916 172 535
9	195 408 755 062 890 625	115 608 738 525

In order to check the effectiveness of the proposed optimizations, computations of reducible cluster integrals were performed for a number of different lattice-gas models in a form of exact polynomials in powers of Mayer's function. For comparison, the previous CPU computations were only possible up to the 5th order for 2D models and 4th order for 3D ones and computing the integrals of higher orders required the usage of multithread GPU calculations [4, 5] (for b_6 and b_7 of the Lee-Yang model, the non-optimized multithread GPU computations took minutes and hours, respectively).

Applying only one optimization – reducing the number of integration points – has allowed computations of the Lee-Yang b_7 on CPU (it took about 43 minutes on Intel Core i7-7700). Adding the simplification of the Wheatley algorithm has additionally reduced the time of such computations to 4 seconds!

Moreover, even CPU computations based on the proposed enhanced approach have provided a new information on reducible integrals for a number of different lattice-gas models in a form of exact polynomials in powers of Mayer's function f: in particular, such integrals were calculated for the Lee-Yang model up to the 9th order (see Table 2, where the b_9 computation took about 5 hours); for 2D square model with 8 nearest neighbors – up to the 8th order; 3D square model with 6 neighbors – up to the 7th order; 3D square model with 26 neighbors – up to the 6th order.

Table 2. New data on reducible integrals of the Lee-Yang model

n	$nb_n\rho_0^{n-1}$
8	$48\cdot f^{10} + 1552\cdot f^9 + 13364\cdot f^8 + 24912\cdot f^7 - 186104\cdot f^6 + 243472\cdot f^5 - 126740\cdot f^4 + 29456\cdot f^3 - 2968\cdot f^2 + 112\cdot f - 1$
9	$9\cdot f^{12} + 756\cdot f^{11} + 12582\cdot f^{10} + 73440\cdot f^9 + 36981\cdot f^8 - 1034496\cdot f^7 + 1816362\cdot f^6 - 1272348\cdot f^5 + 423342\cdot f^4 - 68376\cdot f^3 + 5040\cdot f^2 - 144\cdot f + 1$

Conclusions. As a result, the proposed enhancement has allowed extending the information on reducible cluster integrals by one/two orders depending on the model that, overall, considerably improves the theoretical description of phase transitions for various models of matter and, in particular, the obtained data can be useful in further studying the volume dependence of cluster integrals. It may additionally be emphasized that, at the moment, the proposed enhancement has only been applied to CPU calculations and further advances are fairly possible by applying the same approach to multithread GPU computations in future studies.

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