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APPROXIMATION OF CLUSTER INTEGRALS FOR VARIOUS LATTICE-GAS MODELS

An approximation for cluster integrals of an arbitrary high order has been proposed for the well-known lattice-gas model with an arbitrary geometry and dimensions. The approximation is based on the recently obtained accurate relations for the convergence radius of the virial power series in the activity parameter for the pressure and density. As compared to the previous studies of the symmetric virial expansions for the gaseous and condensed states of a lattice gas, the proposed approximation substantially approaches the pressure values at the saturation and boiling points. For the Lee–Yang lattice-gas model, the approximation considerably improves the convergence to the known exact solution.

Keywords: lattice gas, virial series, cluster integral, hole-particle symmetry, convergence radius, saturation point, boiling point.

1. Introduction

One of the well-known models for the description of substances in statistical physics is the lattice-gas model, in which the particles are confined in separate cells in a spatial lattice. The system has a discrete configuration space, but no restrictions are imposed on the momentum space. On the one hand, this statistical model is closely connected with the theory of ferromagnets (the Ising problem [1]). On the other hand, in essence, this is currently the only example of a rigorous theoretical description of the matter condensation [2, 3] (to say nothing about the van der Waals–Maxwell equation [4, 5], which was derived on the basis of the unrealistic mean-field approximation) with a realistic pair interaction potential, i.e. a potential that involves either the attraction or repulsion for each molecular pair depending on the distance between molecules. Unfortunately, this example is only applicable to the description of the phase transition itself (the Lee–Yang solution [3] only determines the condensation parameters – pressure, activity, and density at the saturation and boiling points – for a two-dimensional lattice gas with a square-well potential) and provides no accurate information about the behavior of the system in the gaseous or liquid state.

Recent researches on the basis of the Mayer cluster expansion of a partition function [6–8] significantly advanced the statistical theory of nonideal gases in general [9–15] and the theoretical description of the lattice-gas behavior in particular [16–18]. New equations derived in terms of irreducible cluster integrals (virial coefficients) [9–13] made it possible to establish the applicability limits of the well-known virial expansion for pressure in powers of density (the virial equation of state, VES [6]) and to obtain a general theoretical criterion that exactly determines the saturation point for various systems of interacting particles. The study of the virial expansions for pressure and density in powers of activity with reducible cluster integrals [14,15,18,19] (the virial equation of state in terms of the activity, VESA [6,13]) completely confirmed those results (obtained in terms of irreducible integrals) and even demonstrated a potential possibility to determine the boiling point in the framework of the Mayer cluster approach [15].

As concerning the lattice gas itself, it was found for a wide number of its models (with an arbitrary geometry and dimensionality and with various interaction potentials) that their partition functions are characterized by the "particle-hole" symmetry (with respect to the particle-hole (an empty cell in the corresponding lattice) interchange [16]. On the basis of this symmetry, the equations of state for the lattice gas were obtained in the high density region in terms of irreducible (the SVES equation, which is symmetric to the VES one) [16] and reducible (the SVESA equation, which is symmetric to the VESA one) [17] cluster integrals. The analysis of those equations proved the complete symmetry of the lattice gas saturation and boiling points (i.e. the symmetry of its binodal, the gas-liquid coexistence curve) and additionally confirmed [19,20] the results presented above for the saturation point. Furthermore, it has been proved very recently that the pressure and activity are identical at the saturation and boiling points for both pairs of symmetric equations (VESA–SVESA and VES–SVES) [14]. Besides that, a general expression was obtained for the phase transition activity. In the case of two-dimensional lattice gas with a square-well potential, this expression exactly coincides with the Lee–Yang solution [3].

However, all those results characterize, first of all, the success of the theory itself, whereas their practical application for the accurate determination of the same phase transition parameters or the calculation of isotherms for specific substance models still remains associated with large technical difficulties. Provided that the complete, i.e. infinite, set of reducible and irreducible integrals is known, theoretical equations really have to exactly determine the saturation and boiling points (the density at those points and the same pressure). But a direct calculation of such integrals (even not of the infinite order, but of a rather high one) for a specific pair interaction potential still remains to be a technically impossible task.

The largest number of calculated irreducible integrals are associated with the well-known Lennard-Jones potential [21, 22]. The most powerful computation facilities in combination with modern effective numerical integration methods allowed the virial coefficients to be calculated up to the 14-th order for two subcritical temperatures and up to the 16-th order for only one temperature [23]. Recently, on the basis of data available for such spatially-continuous models, two different approximations of the whole infinite series in a confined temperature interval were proposed [24,25]. These approximations reproduce well the behavior of subcritical isotherms in a vicinity of the saturation point at a qualitative level. In particular, the theoretical isotherms, like real ones, have a cusp at this point. However, a comparison with experimental data still demonstrates appreciable quantitative deviations.

Below, the term Lee–Yang lattice-gas model is used to refer to the two-dimensional model of a square lattice gas with a square-well potential, for which Lee and Yang obtained an exact solution. For this model, the exact temperature dependences for the viral coefficients to the seventh order were obtained recently [17]. The analysis of the corresponding equations with finite-order coefficients (VES and SVES) and the series expansions in the activity parameter (VESA and SVESA), which although contain reducible integrals of very high orders, but were calculated on the basis of a confined set of irreducible integrals [17,18], really demonstrates a gradual convergence to the exact solution [3]. However, the difference still remains rather substantial, and the convergence rate is very slow.

In this work, we propose an approximation for high-order reducible cluster integrals, which is based on recent data for the convergence radius of the activity series for the pressure and density. The subcritical VESA and SVESA isotherms calculated on the basis of this approximation for various lattice-gas models have much closer pressure values at the saturation and boiling points in comparison with the results of previous studies [18]. Additionally, in the case of Lee–Yang model, they also demonstrate a much better convergence to the exact solution.

The theoretical substantiation of the proposed approximation is carried out in Section 2. Section 3 contains the main results of calculations on the basis of this approximation, as well as their comparison with the previous results and the exact Lee–Yang solution. In Section 4, the results obtained are discussed, and the corresponding conclusions are made.

2. Asymptotics of Reducible Integrals and Their Approximation

For a classical system of particles with a pair interaction potential between the molecules, the Mayer cluster expansion [6–8] makes it possible to directly (without further simplifications and assumptions) express the logarithm of the grand partition function (pressure P in the system) and its derivative with respect to the chemical potential μ (average particle density $\rho = N/V$) in terms of the activity $z = \lambda^{-3}\exp(\mu/k_{\rm B}T)$, where λ is the de Broglie wave length of molecules, and the reducible cluster integrals $\{b_n\}$ [6] read

$$\frac{P}{k_{\rm B}T} = \sum_{n=1}^{\infty} b_n z^n, \qquad \rho = \sum_{n=1}^{\infty} n b_n z^n. \tag{1}$$

Below, we will use the abbreviation VESA for this parametric equation of state. The VESA accuracy (in the sense how accurately it reflects the actual behavior of system's partition function) directly depends only on the accuracy of the whole infinite set of cluster integrals. This issue is always associated with certain difficulties of both theoretical and purely technical character. As a rule, those integrals are defined in an infinite integration volume, which makes them independent of the real system volume or density [6, 13]. Actually, this simplification has to be correct only for microscopic particle clusters ($n \ll N$) and, as was recently shown [14], remains applicable only to the saturation point of dry vapor. However, even with this simplification, the determination of high-order reducible integrals still remains a very complicated technical problem.

Formally, every reducible integral b_n of the n-th order (i.e. for a group of n particles), which is defined in an infinite volume, is the sum of products of irreducible integrals $\{\beta_k\}$ ($k < n$) [6]. In its simplest form, the relationship between the reducible and irreducible integrals is expressed by the following recursion formula [18, 20]:

$$n^2 b_n = B_{n,n-1}, \tag{2}$$

where

$$B_{n,i} = n\sum_{k=1}^{i} \frac{k}{i}\beta_k B_{n,i-k}.$$

For today, the considerable experience has been accumulated in calculating the irreducible integrals (i.e. the virial coefficients) for a variety of intermolecular interaction models [26–30], mainly because the practical application of the virial pressure expansion in powers of density [6] (virial equation of state, VES) is much more convenient as compared to the application of the VESA. Indeed, a finite-order VES with a limited set of irreducible integrals (the virial coefficients), which has a very simple form, corresponds to an infinite-order VESA, in which all reducible integrals have to be calculated – e.g., using the recursive relationship (2) – on the basis of the same limited set of irreducible integrals. Of course, this task significantly complicates the practical application of VESA.

However, the current researches [9, 11, 13] demonstrate that the transformation of a "complicated" VESA into a "simpler" VES has rigorous restrictions. In effect, the VES remains adequate only to the point ρ_G, where the isothermal bulk modulus vanishes. This point is determined as the mimimum positive root of the equation

$$\sum_{k\geq 1} k\beta_k \rho_G^k = 1. \tag{3}$$

Furthermore, it is exactly the density ρ_G that is the saturation point of dry vapor [10, 12, 14, 20] [accordingly, the temperature is subcritical if Eq. (3) has at least one positive root].

The same researches showed that the density ρ_G is directly related to the VESA convergence radius [12, 14, 20]:

$$z_G = \rho_G \exp\left(-\sum_{k\geq 1}\beta_k \rho_G^k\right). \tag{4}$$

As the activity in Eq. (1) approached the z_G-value (4), the density series diverges in the VESA, which leads to a density jump in isotherms at constant values of the chemical potential (activity) and pressure (the pressure series simply has no time to change)

[18, 20]. For a constant set of reducible integrals (determined in the infinite volume), the density has an infinite singularity (an essential discontinuity). In work [15], it was shown that a true finite density jump to the boiling point, which would correspond to the actual physical picture of the first-order phase transition, can still be obtained in the framework of the Mayer cluster expansion, but only if the dependence of the reducible high-order integrals corresponding to macroscopic particle clusters on the real system volume (real integration limits) is taken into account.

Nevertheless, there also exists another approach to define the boiling point ρ_L and describe the condensed states of the lattice-gas model in the framework of the Mayer cluster expansion method. In works [16, 17], the symmetry of the lattice-gas partition function with respect to the particle-"hole" (empty lattice cells) interchange was substantiated, and the equation of state symmetric with respect to the VESA (SVESA) was obtained,

$$\begin{aligned} \frac{P}{k_\mathrm{B}T} &= \rho_0\left(\frac{u_0}{k_\mathrm{B}T}+\ln\frac{\rho_0}{\eta}\right)+\sum_{n\geq 1} b_n\eta^n, \\ \rho &= \rho_0-\sum_{n\geq 1} n b_n\eta^n, \end{aligned} \qquad (5)$$

in terms of the same reducible cluster integrals $\{b_n\}$ and the reciprocal activity

$$\eta = \frac{\rho_0^2}{z}\exp\left(\frac{2u_0}{k_\mathrm{B}T}\right),$$

where ρ_0 is the close-packing density of a lattice gas, and u_0 the potential energy of a particle in the close-packing state.

VESA (1) provides the best accuracy for dilute states, i.e. when the density ρ is close to zero, even with a limited or approximate set of cluster integrals. On the contrary, the accuracy of SVESA (5) is the highest for the states that are close to the dense packing, i.e. when the "hole" concentration $\rho' = \rho_0-\rho$ tends to zero. The both equations have the same convergence radius (the activity z in VESA, and the inverse activity η in SVESA), which is determined by Eq. (4). The corresponding density at the saturation point, ρ_G, is exactly symmetric with respect to the density at the boiling point:

$$\rho_L = \rho_0 - \rho_G.$$

All those peculiarities in the behavior of VESA and SVESA were directly observed in numerical calculations [18] carried out by using a large, although finite, set of reducible integrals $\{b_n\}$ (their order n reached a value of several thousands) calculated, with the help of the recursive relationship (2) on the basis of a limited set of known irreducible integrals $\{\beta_k\}$ (the corresponding set of virial coefficients).

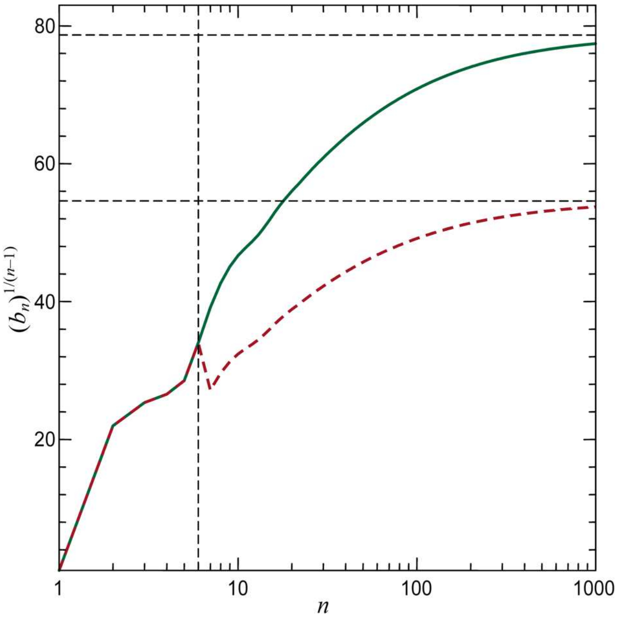

Fig. 1. Asymptotics of reducible integrals of various orders calculated on the basis of five first irreducible integrals $\{b_n^0\}$ (solid line) and approximated by Eq. (8) (dashed line) for the Lee–Yang model ($T = 0.5\varepsilon/k_\mathrm{B}$). The upper horizontal line corresponds to the convergence radius z_G from Eq. (4), and the lower one to the convergence radius z_0 from Eq. (6). The vertical line marks the order n_max, below which the reducible integrals have exact values

The asymptotics of high-order reducible integrals completely corresponds to the Cauchy–Hadamard theorem [31]: with the growth of their order n, the values of integrals (regarded as the power coefficients in the activity series) really approach the value of the reciprocal convergence radius raised to the corresponding power (see Fig. 1). In work [19], we proposed a new method for determining the reducible integrals of very high orders on the basis of the known set of irreducible integrals, but with the help of the corresponding convergence radius z_G from Eq. (4), rather than the recursive relation (2).

Unfortunately, a considerable limitation of the set of known irreducible integrals (virial coefficients) allows VESA and SVESA to reproduce the phase transition in the lattice gas more or less adequately only at the qualitative level. A comparison with the exact Lee–Yang solution [3] in the case of the two-dimensional lattice-gas model with a square-well potential (when each absolutely hard particle attracts only the particles in the nearest four cells of the square lattice) demonstrates rather significant quantitative deviations [18], so that even the pressure values at the phase transition differ substantially from each other in VESA and SVESA. Of course, an increase in the number of accounted reducible integrals gradually changes the convergence radius z_G in Eq. (4) and brings the calculated phase transition points [18] closer to the Lee–Yang solution. However, those changes, as well as the convergence to the exact solution, turned out very slow. The results obtained in work [18] indicate that even if dozens of irreducible integrals, whose calculation still remains a technically impossible task for today, are taken into account, the situation will not be much improved.

At the same time, an exact expression was obtained quite recently for the convergence radius of power series in VESA and SVESA on the basis of the same "particle-hole" symmetry in the lattice-gas models [14],

$$z_0 = \rho_0 \exp\left(\frac{u_0}{k_{\mathrm{B}}T}\right), \tag{6}$$

which opens basically new possibilities for the determination of the set of cluster integrals for any lattice-gas model (the geometry of the model and the parameters of the intermolecular interaction potential are completely determined by the quantity u_0).

On the one hand, the set of irreducible integrals $\{\beta_k\}$ that are already known to a certain order $k_{\max}$ allows one to exactly determine the reducible integrals $\{b_n\}$ only to the order $n_{\max} = k_{\max} + 1$. All other reducible integrals ($n > n_{\max}$) can also be determined with the help of the same recursion formula (2), but with a certain systematic error (in the approximation that all their irreducible components of the orders higher than $k_{\max}$ simply vanish). On the other hand, if the exact value of the convergence radius z_0 in Eq. (6) is known, this allows the asymptotic values of reducible integrals of very high orders to be directly determined using the Cauchy–Hadamard theorem [31],

$$\lim_{n\to\infty} \left(n^2 b_n\right) = z_0^{-(n-1)}, \tag{7}$$

similarly to what was proposed in work [19] for the approximate value of the convergence radius z_G from Eq. (4) determined on the basis of a limited set of known irreducible integrals.

The direct application of Eq. (7) is proper only for integrals of very high orders. Therefore, there arises a logical question: Which orders n can be regarded as sufficiently high? In this situation, only a relatively small number of reducible integrals of the lowest orders (up to the order $n_{\max}$ inclusive), as well as the asymptotic values of the highest-order (thermodynamic) integrals, are known exactly. At the same time, the values of reducible integrals of intermediate orders remain, in essence, unknown.

In order to approximately reproduce the actual behavior of reducible cluster integrals with the orders changing from $n_{\max}$ to very large values, the dependences of some already known reducible integrals $\left\{b_n^0\right\}$ on n, which were calculated on the basis of a limited set of irreducible integrals $\{\beta_k\}$, can be used. Hence, we propose to rescale every b_n^0 in such a way that the asymptotic behavior of the resulting series of reducible integrals $\{b_n\}$ should correspond to the exact convergence radius z_0 from Eq. (6) rather than the approximate one z_G from Eq. (4), which was determined on the basis of a finite series of irreducible integrals. Namely,

$$b_n = b_n^0 \left(\frac{z_G}{z_0}\right)^{n-1}, \tag{8}$$

and this rescaling should be applied only to all "doubtful" integrals b_n^0 with the orders higher than $n_{\max}$.

Certainly, the proposed approach can pretend in no way on the absolute precision. In particular, the transition from the exact integral $b_{n_{\max}}^0$ to a few next b_n-values looks rather doubtful (see Fig. 1). But, nevertheless, it can still be regarded as the first approximation, which should adequately describe, in general, the behavior of reducible integrals of rather high orders and, at least, guarantee the asymptotic ($n \to \infty$) convergence of the reducible integrals to exact values, which correspond to the exact value of the convergence radius z_0.

3. Numerical Analysis

The application of the proposed approach to the determination of reducible integrals $\{b_n\}$ in the framework of a definite lattice-gas model involves several steps. First, on the basis of the set of irreducible integrals $\{\beta_k\}$ that are known for this model (at a certain temperature), a set of reducible integrals $\{b_n^0\}$ is determined to the maximum possible order with the help of the recursive relation (2). Then, with the help of the same limited set of irreducible integrals, the density ρ_G at the saturation point is determined from Eq. (3), and the approximate convergence radius z_G from Eq. (4). Finally, the set of reducible integrals $\{b_n^0\}$ is rescaled, starting from the order $n_{\max}+1$, into the set $\{b_n\}$ by applying Eq. (8) and making use of known values for z_G and the exact convergence radius z_0 from Eq. (6). The resulting set $\{b_n\}$ can be immediately used in Eqs. (1) (VESA) and (5) (SVESA) for the calculation of lattice gas isotherms.

On the basis of this algorithm, the VESA and SVESA isotherms were calculated with regard for various numbers of power coefficients (reducible integrals) in those equations for various lattice-gas models in a wide temperature interval. The results obtained for VESA and SVESA in the calculations including 10000 reducible integrals are partially presented in Figs. 2 to 5. The account for a larger number of integrals leads to very small changes, which are practically indistinguishable on the presented scale.

For comparison, the exact phase transition parameters are shown in Figs. 2 and 3 for the two-dimensional lattice gas with a square-well potential calculated according to the Lee–Yang solution [3]. Figure 2 also exhibits VESA and SVESA isotherms with the corresponding set of reducible integrals $\{b_n^0\}$ that were not transformed by Eq. (8).

First of all, the calculation results demonstrate that both VESA (1) and SVESA (5) with the set of reducible integrals $\{b_n\}$ approximated by Eq. (8) have a much better convergence to the exact solution in comparison with the same equations, in which the non-rescaled set $\{b_n^0\}$ was used [it was determined on the basis of a limited set of irreducible integrals $\{\beta_k\}$ with the help of relation (2)]. In particular, the points, at which the density begins to change drastically (VESA and SVESA give a divergence, a density jump) are much closer to the saturation and boiling points (ρ_G and ρ_L) of the Lee–Yang solution just in the case of equations with the approximated set $\{b_n\}$. Moreover, the pressure values given by VESA and SVESA for this density jump (during the phase transition) are much closer to each other and to the

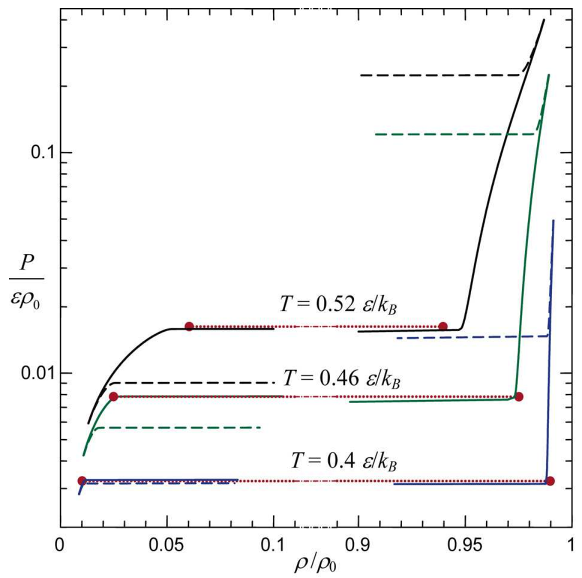

Fig. 2. VESA (Eq. (1), left) and SVESA (Eq. (5), right) isotherms with reducible integrals calculated from five first irreducible integrals (dashed curves) and approximated by Eq. (8) (solid lines) for the Lee–Yang model. Points correspond to the exact solution [3]

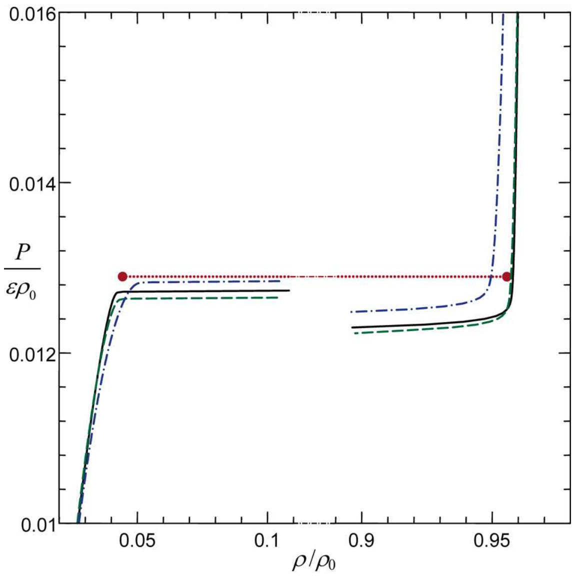

Fig. 3. VESA (Eq. (1), left) and SVESA (Eq. (5), right) isotherms for the Lee–Yang model ($T = 0.5\varepsilon/k_{\rm B}$) with reducible integrals approximated by Eq. (8) on the basis of various sets of irreducible integrals (virial coefficients): $n_{\max} = 6$ (solid curves), 4 (dotted curves), and 2 (dash-dotted curves). Points correspond to the exact solution [3] . The pressure axis scale is mich larger in comparison with Fig. 2)

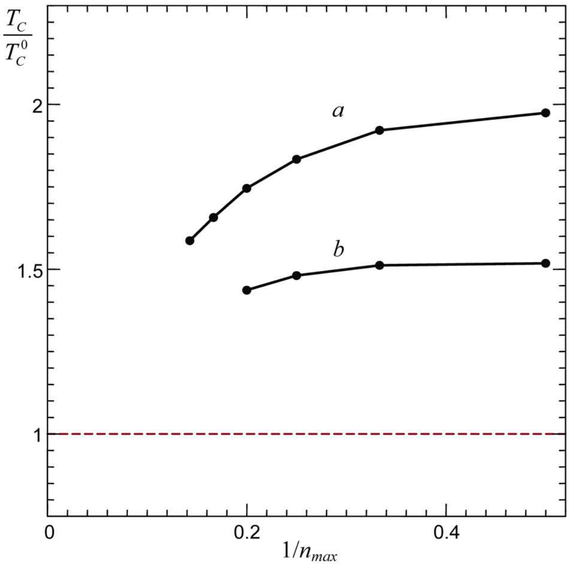

Fig. 4. Critical temperature T_C normalized by T_C^0 calculated for the Lee–Yang model (a) and for the three-dimensional cubic lattice gas (b) with various numbers of irreducible integrals (n_max is the maximum order of corresponding virial coefficients) as a temperature, at which ρ_G for VRSA [Eq. (1)] and ρ_L for SVESA [Eq. (5)] reach a density value of $\rho_0/2$. The value of the temperature T_C^0 for the three-dimensional case corresponds to results of a simulation in work [32]

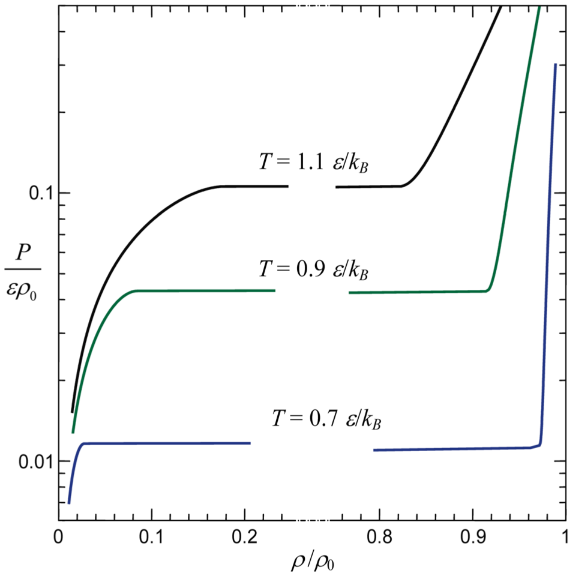

Fig. 5. VESA (Eq. (1), left) and SVESA (Eq. (5), right) isotherms with reducible integrals approximated by Eq. (8) on the basis of three first irreducible integrals for the three-dimensional model of cubic lattice gas with a square-well potential

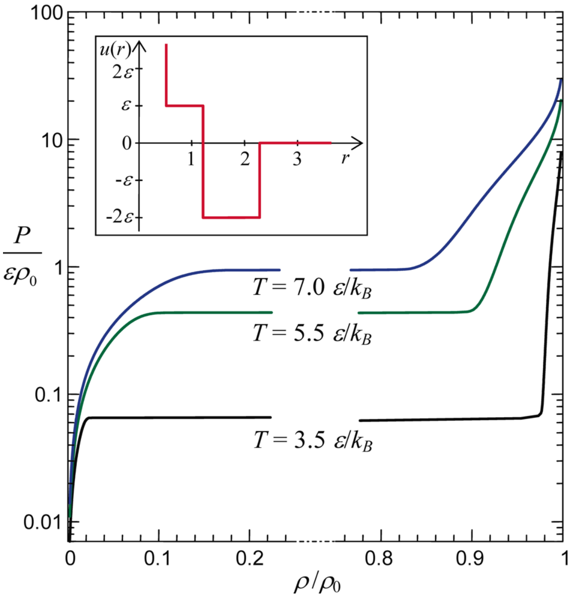

Fig. 6. VESA (Eq. (1), left) and SVESA (Eq. (5), right) isotherms with reducible integrals approximated by Eq. (8) on the basis of four first irreducible integrals for the two-dimensional model of cubic lattice gas with a complicated interaction potential including both the additional finite repulsion (the barrier height ε) and attraction (the well depth 2ε); its form is depicted in the inset

exact solution (see Fig. 2) in comparison with the results of previous calculations [18] performed, by using no information about the exact convergence radius z_0, i.e. making no approximation of reducible integrals with the help of Eq. (8).

Such a behavior confirms once more the correctness of all conclusions concerning the convergence radius of VESA and SVESA, the divergence character of those equations, and the physical meaning of the quantitiesρ_G and ρ_L, which were obtained analytically in [14] and [9–12, 24]. Furthermore, the very accuracy of the results obtained on the basis of a rather crude approximation of the medium-order cluster integrals (the low-order reducible integrals are calculated on the basis of the exact information about the irreducible integrals of the corresponding low orders, and the asymptotics of the integrals of very high orders must also be determined rather precisely by the convergence radius z_0) may indirectly confirm conclusions made in works [13, 15, 18, 20] about the real influence of cluster integrals with various orders on the partition function behavior.

At temperatures lower than the critical one (for the two-dimensional Lee–Yang model, $T_\mathrm{C} = 0.5673\varepsilon/k_\mathrm{B}$, where ε is the depth of the square-well potential), the influence of cluster integrals of relatively low orders (both reducible and irreducible) is crucial only in dilute states up to the saturation point (or symmetrically for SVESA, for low "hole" concentration values above the boiling point). In a vicinity of the saturation point (and, the more so, above this point), the contribution of the highest-order integrals to the partition function becomes dominating. These are a few first integrals and the highest ones that determine, to a large extent, the phase transition parameters (the pressure and the density at the saturation and boiling points). Even significant changes in the number of irreducible integrals that were taken into account did not considerably affect the results obtained (see Fig. 3).

On the other hand, as the temperature increases and approaches the critical one, the situation becomes somewhat different. In particular, the deviations from the exact Lee–Yang solution grow, and the dependence on the number of irreducible integrals that were taken into consideration (i.e. the dependence on the number of exactly determined reducible integrals) becomes stronger. For example, the calculated values of ρ_G and ρ_L differ more and more from those determined by the exact solution, and the critical temperature values are considerably higher than both the exact T_C^0 value in the Lee–Yang model (see curve a in Fig. 4) and the known critical temperature for a similar three-dimensional model [32] (curve b in Fig. 4). The calculations showed that, in a vicinity of the critical temperature, the VESA and SVESA isotherms gradually approach the exact solution, as the number of irreversible integrals that were taken into account grows. The calculated critical temperature also shifts down toward the exact one (see Fig. 4), but this convergence is rather slow, and the observed significant deviations testify that, for the theoretical description of the lattice gas behavior in a vicinity of the critical point to be exact, the information is required about irreducible integrals (virial coefficients) of considerably higher orders.

It should be emphasized that similar results (the pressure values at the boiling and saturation points that are closer to each other by orders of magnitude for the approximated set of reducible integrals $\{b_n\}$ in comparison with those for the usual set $\{b_n^0\}$) take place for quite different models of lattice gas: with different dimensionalities (the relevant calculations were carried out for both two- and three-dimensional models), an arbitrary geometry (triangular or square cells), and various interaction potentials. For example, Fig. 5 illustrates the behavior of the VESA and SVESA isotherms for a three-dimensional lattice gas with a square-well potential, when each absolutely hard particle attracts only particles located in the nearest six cells of the cubic lattice. Figure 6 demonstrates the same, but for a two-dimensional square lattice gas with a complicated interaction potential. Namely, the nearest four particles are repulsed (the corresponding barrier height equals ε), and next sixteen particles in the "second coordination sphere" are attracted (the well depth equals -2ε) by the central particle. At the qualitative level, this behavior does not differ in essence from that described above for the two-dimensional Lee–Yang model. This circumstance, in turn, makes it possible to apply the proposed method of reducible integral approximation, while researching a wide range of lattice-gas models, for which there is no reliable information from other sources.

4. Conclusions

The analysis of modern approaches to the statistical description of the behavior of non-ideal gases in general and the first-order phase transitions in particular allows a conclusion to be drawn that, despite the considerable recent progress in those issues of statistical theory as a whole, a reliable quantitative description of the condensation on the basis of the information about the intermolecular interaction still remains problematic even for the simplest models of real substances. In this work, a method is developed that allows a set of reducible cluster integrals $\{b_n\}$ to be approximated for a wide range of lattice-gas models on the basis of the information concerning a limited set of virial coefficients (a few first irreducible cluster integrals $\{\beta_k\}$) and the known convergence radius z_0 of the corresponding virial power expansions in the activity (a method for the exact determination of this convergence radius for various lattice-gas models was recently proposed in work [14]). The reducible integrals obtained in the framework of this approximation can be directly used in the corresponding equations of state – VESA (1) and SVESA (5) –

to describe the lattice gas behavior at subcritical temperatures in the density interval extending from dilute to condensed states (including the condensation region).

The numerical studies showed a relatively high accuracy of the proposed approximation in comparison with traditional methods used to determine reducible integrals. In particular, for various lattice gas models, both the VESA and SVESA equations with the approximated set $\{b_n\}$ give similar pressure values at the theoretical saturation and boiling points. For the two-dimensional lattice-gas model with a square-well potential, both the indicated pressure values and the density values at the saturation (ρ_G) and boiling (ρ_L) points coincide well with the known exact Lee–Yang solution [3].

Furthermore, our researches confirm previously obtained theoretical results concerning the origin of divergence for the virial expansions in powers of activity (VESA and SVESA), the influence of cluster integrals of various orders on the behavior of the partition function in dense states, and the statistical description of the physical phenomenon of condensation in whole. One of the promising directions for the further development of the proposed approach may be the solution of the inverse problem, i.e. the analysis of the behavior of high-order irreducible integrals (virial coefficients) on the basis of the information about reducible ones.

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АПРОКСИМАЦІЯ ГРУПОВИХ ІНТЕГРАЛІВ ДЛЯ РІЗНИХ МОДЕЛЕЙ ҐРАТКОВОГО ГАЗУ

Резюме

В роботі пропонується апроксимація звідних групових інтегралів необмежено високих порядків для відомої статистичної моделі ґраткового газу довільної геометрії та вимірності. Апроксимація ґрунтується на нещодавно отриманій точній інформації стосовно радіусу збіжності віріальних серій для тиску й густини за степенями активності. У порівнянні з попередніми дослідженнями симетричних віріальних розкладів у газоподібних та конденсованих станах ґраткового газу, запропонована апроксимація робить значення тиску у відповідних точках насичення та кипіння суттєво ближчими одне до одного, а для моделі ґраткового газу Лі–Янга значно підвищує збіжність до відомого точного розв'язку.