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Evidence for a first-order phase transition at the divergence region of activity expansions

M. V. Ushcats
Department of Molecular Physics, Taras Shevchenko National University of Kyiv, 2, Prosp. Academician Glushkov, Kyiv 03680, Ukraine and Department of Physics, Admiral Makarov National University of Shipbuilding, 9, Prosp. Heroes of Ukraine, Mykolayiv 54025, Ukraine

L. A. Bulavin
Department of Molecular Physics, Taras Shevchenko National University of Kiev, 2, Prosp. Academician Glushkov, Kiev 03680, Ukraine

S. Yu. Ushcats
Department of Physics, Admiral Makarov National University of Shipbuilding, 9, Prosp. Heroes of Ukraine, Mykolayiv 54025, Ukraine

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In the example of a lattice gas with "hole-particle" symmetry, a convincing confirmation is obtained for the direct relationship between the condensation phenomenon and the divergent behavior of the virial expansions for pressure and density in powers of activity. For such lattice-gas models of arbitrary geometry and dimensions, a general analytical expression is derived for the phase-transition activity (the convergence radius of activity expansions) that, in particular, exactly matches the well-known phase-transition activity of the Lee-Yang model. The study proves analytically the strict equality of pressure for the low-density and high-density virial expansions in powers of density (in terms of irreducible cluster integrals or virial coefficients) exactly at the symmetrical points, where their isothermal bulk modulus vanishes, as well as for the corresponding expansions in powers of activity (in terms of reducible cluster integrals) at the same points (the points of their divergence). It is also shown that Mayer's expansion with the constant (volume-independent) cluster integrals remains correct up to the condensation beginning, and the actual density dependence must be taken into account for the high-order integrals only in more dense regimes beyond the saturation point.

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I. INTRODUCTION

Since the 19th century, there have been many attempts to construct a strict and general theory for the gas-liquid phase transition on the basis of the Gibbs statistics [1,2], however the real success has been achieved only for two extremely specific statistical models: the mean-field approximation of intermolecular interactions (the van der Waals–Maxwell equation of state [3,4]) and the two-dimensional lattice gas with the square-well potential (its condensation parameters were established by Lee and Yang [5] on the basis of Onsager's solution of the Ising problem [6]). Unfortunately, more general approaches have failed in high-density regimes of fluids and, especially, at the phase-transition region [1]: The solution of the Ornstein-Zernike equation [7] vanishes in the transition regimes [8], and various expansions for the partition function (or its logarithm) in powers of a small parameter [1] also have singularities in dense states. For example, the divergent behavior of the well-known virial expansions in powers of activity or density [1,2,9] remains an actual problem of statistical mechanics, mathematical physics, physical chemistry, etc. The situation was well described by the authors of the one-dimensional van der Waals–Maxwell equation: "Many attempts, thus far unsuccessful, have been made to construct a rigorous theory of condensation phenomena from such expansions. In fact, we believe that such a construction is very difficult, if not *impossible*..." [3].

Recent studies of Mayer's cluster expansion [9] for the partition function of realistic interaction models (i.e., the models that include intermolecular attraction as well as repulsion: the Lennard-Jones model [10,11] and its modifications [12,13], square-well [14], Morse [15], Yukawa [16] potentials, etc.) have renewed interest in the problem. In particular, an exact generating function for Mayer's expansion in terms of irreducible cluster integrals (virial coefficients) [17,18] has allowed us to derive the equation of state (UEOS) beyond the adequacy region of the conventional virial expansions [17]. This equation yields the constancy of pressure at any density beyond the point ρ_G, where the isothermal bulk modulus of the virial expansion in powers of density (virial equation of state, or VEOS) vanishes [19,20], which, in turn, may indicate the beginning of the condensation process at the vicinity of this point. Consequent studies of Mayer's expansion in terms of reducible cluster integrals [21–23] (the equation of state in the parametrical form of expansions for pressure and density in powers of activity, AVEOS) have demonstrated its divergence exactly at the same point ρ_G, but the actual character of this divergence [21–24] agrees with the behavior of Mayer's expansion in terms of irreducible integrals (where the activity dependence is excluded) and corresponds to the known thermodynamic signs of the first-order phase transition.

On the other hand, all of the above-mentioned approaches to Mayer's cluster expansion involve serious mathematical

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and technical limitations that make their results questionable. Despite the rapid development of modern computational techniques [25–27], in practice the studied equations always include finite (or roughly approximated [28–30]) sets of cluster integrals (reducible as well as irreducible) that makes an adequate comparison with the experimental data almost impossible. Moreover, the numerical studies of any infinite series cannot be considered as mathematically correct, especially in its divergence region. For a long time, the density ρ_G, where the VEOS isothermal bulk modulus vanishes, used to be considered as a spinodal point (the boundary between metastable and absolutely instable states), because the isotherms of the VEOS, which includes only three to five power terms, have an interval similar to the famous van der Waals loop (the Maxwell construction is still widely used for all theoretical as well as empirical equations despite the fact that it has rigorously been proved only for a specific kind of the mean-field approximation [3,4]). Although the observed behavior of the VEOS with the higher-orders terms completely differs from that of the van der Waals equation, the destruction of such long-standing stereotypes remains a difficult problem that needs strict and persuasive arguments.

In the example of a special statistical lattice-gas model, the present paper provides such a needed simple and obvious confirmation for the above-mentioned results of recent studies (studies of Mayer's cluster expansion in terms of reducible as well as irreducible cluster integrals) concerning the physical meaning of the ρ_G point, the actual character of the AVEOS singularity, and other related disputable questions. Section II presents a general expression for the phase-transition activity (which is exactly the convergence radius of activity expansions for pressure and density) for various lattice gases with the "hole-particle" symmetry. In Sec. III, the symmetry of the corresponding density expansions for pressure (the virial equation of state and the equation in powers of the "hole number density") is considered that finally proves the interpretation of the ρ_G density as a saturation point (and the symmetrical ρ_L density as a boiling point). The generality of the results as to the other statistical models of matter is discussed in Sec. IV, and the last section is devoted to the key conclusions of the work.

II. PHASE-TRANSITION ACTIVITY OF LATTICE GASES

For any classical system of interacting particles (including the lattice-gas model and even certain quantum systems [2,31,32]), Mayer's cluster expansion [9] represents the logarithm of the grand partition function (the pressure, P) and its derivative with respect to the chemical potential, μ (the particle number density, $\rho = N/V$) as the following series (AVEOS):

$$\left.\begin{aligned} \tfrac{P}{k_BT} &= \sum_{n=1}^{\infty} b_n z^n \\ \rho &= \sum_{n=1}^{\infty} n b_n z^n \end{aligned}\right\}, \tag{1}$$

in terms of *reducible cluster integrals* $\{b_n\}$ and powers of activity $z = \lambda^{-3}\exp(\mu/k_BT)$ ($\lambda = h/\sqrt{2\pi m k_B T}$ is the de Broglie wavelength).

Exclusively for the lattice-gas models with "hole-particle" symmetry [33] (where the repulsive hard core of a particle is identical to a lattice cell, and finite attraction may have any form on longer distances), there are expansions for pressure and density (SAVEOS) [34],

$$\left.\begin{aligned} \tfrac{P}{k_BT} &= \rho_0\left(\tfrac{u_0}{k_BT} + \ln\tfrac{\rho_0}{\eta}\right) + \sum_{n\geqslant 1} b_n \eta^n \\ \rho &= \rho_0 - \sum_{n\geqslant 1} n b_n \eta^n \end{aligned}\right\}, \tag{2}$$

in powers of the reciprocal activity,

$$\eta = \frac{\rho_0^2}{z}\exp\left(\frac{2u_0}{k_BT}\right). \tag{3}$$

In Eqs. (2) and (3), ρ_0 and u_0 are parameters of the lattice-gas model: the close-packing density and potential energy per particle in the close-packing state, respectively. It should additionally be noted that the set of reducible integrals, $\{b_n\}$, in Eq. (2) is absolutely the same as that in Eq. (1).

The derivation of SAVEOS (2) based on Mayer's expansion for the partition function of "holes" instead of particles has been presented in a relatively recent paper [22], though some simple but very important aspects of such "hole-particle" symmetry have unfortunately escaped the attention of its authors.

Indeed, the obvious similarity of the series in powers of z and η in AVEOS (1) and SAVEOS (2) automatically means there is a similarity of possible singularities for these series. If the series can diverge at some large enough z (or η), the corresponding convergence radii (say z_G and η_L, respectively) must be *equivalent* for AVEOS (1) and SAVEOS (2). With regard to Eq. (3), such equivalence directly yields the following simple expression for those convergence radii:

$$z_G \equiv \eta_L = \rho_0 \exp\left(\frac{u_0}{k_BT}\right). \tag{4}$$

Recent numerical studies of the AVEOS for various statistical models of matter [22,23] as well as a similar study of both the AVEOS and SAVEOS for the lattice-gas model [21] have indicated the first-order phase transition exactly in the divergence region of these equations at some low (subcritical) temperatures: At a certain activity z_G (i.e., a constant chemical potential), the AVEOS (1) yields a discontinuity of density (i.e., a real divergence of activity series for density beyond the special ρ_G density, which is explicitly related to z_G; see the next section) while the pressure stays finite and constant. Similarly, the SAVEOS (2) yields a discontinuity of density (beneath the special ρ_L density) at some reciprocal activity, $\eta_L = z_G$, and constant finite pressure [21].

Unfortunately, at the moment, such behavior has numerically be confirmed only on a qualitative level: Inaccuracy of the known cluster integrals (in today's practice, the high-order reducible integrals can approximately be evaluated by using the very limited information on the finite number of irreducible integrals or virial coefficients for a certain statistical model) still results in essential quantitative discrepancies between the theory and experiments (or simulations). For instance, the values of constant (phase-transition) pressure significantly differ for the AVEOS and SAVEOS when the reducible integrals, $\{b_n\}$, are calculated only on the basis

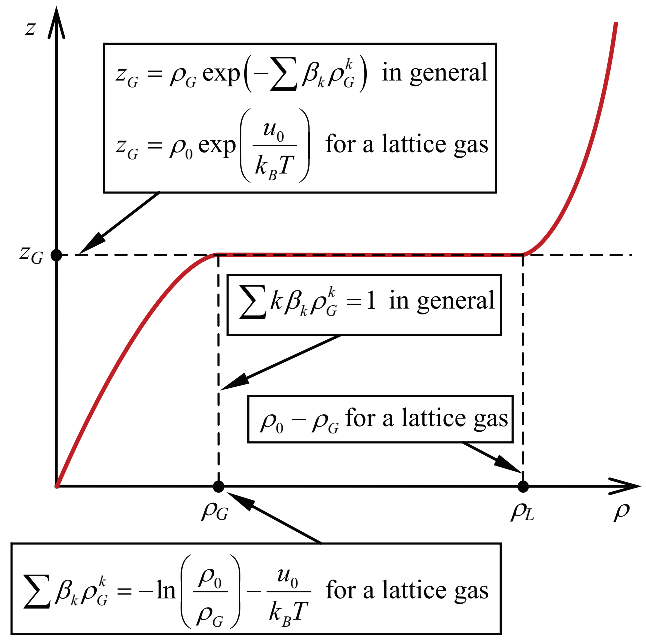

FIG. 1. Typical (schematic) subcritical isotherm of a lattice gas (in the ρ-z plane) that must theoretically be produced by the AVEOS (on the left of the ρ_G point) and SAVEOS (on the right of the ρ_L point) with complete and accurate sets of cluster integrals.

of several irreducible integrals that are actually known in practice [21].

However, the "hole-particle" symmetry analytically confirms the strict equality of the phase-transition pressure in AVEOS (1) and SAVEOS (2) without any numerical evaluation of the actual set of reducible integrals. It is obvious that the difference between the reduced pressure $(P/k_B T)$ values in Eqs. (2) and (1),

$$\rho_0\left(\frac{u_0}{k_B T} + \ln\frac{\rho_0}{\eta}\right) + \sum_{n\geqslant 1} b_n \eta^n - \sum_{n\geqslant 1} b_n z^n,$$

strictly vanishes when $z = \eta$ [and, therefore, both these quantities are defined by Eq. (4)]. Additionally, the sum of densities in Eqs. (1) and (2) always yields the close-packing density, ρ_0, at the same condition $(z = \eta)$.

At supercritical temperatures [when both AVEOS (1) and SAVEOS (2) are always convergent], the activity, z_G, from Eq. (4) simply defines the density, $\rho_0/2$, where the pressure value in Eq. (1) coincides with that in Eq. (2).

At subcritical temperatures, there are two distinct densities, ρ_G and ρ_L [the divergence points of AVEOS (1) and SAVEOS (2), respectively] for *one value of chemical potential* [activity z_G defined by Eq. (4), see Fig. 1] at *one value of pressure* in Eqs. (1) and (2). Therefore, the z_G from Eq. (4) cannot now be interpreted other than *the phase-transition activity* (only the first-order phase transition yields a *density jump at constant pressure and chemical potential*).

It should also be noted that the quantity z_G from Eq. (4) exactly matches the phase-transition fugacity,

$$y_G = \frac{z_G}{\rho_0} = \exp\left(-\frac{4\varepsilon}{k_B T}\right),$$

of the well-known Lee-Yang solution [5] (in their two-dimensional square-lattice model, each particle interacts only with its four nearest neighbors, and, at the close-packing state, the interaction energy per particle, u_0, is -4ε when the depth of the potential well is 2ε).

The presented interpretation of the z_G point also agrees with other analytical [35] and numerical [36] studies of the lattice-gas model as well as the Ising problem. For example, in the Langer droplet model of a lattice gas [35], the divergence activity of the cluster expansion is also considered as a condensation point of the system.

On the other hand, the definition of z_G in Eq. (4) is *more general* and must be valid for lattice-gas models of arbitrary geometry and dimensions with various (even anisotropic) interaction potentials: The geometry of the model as well as the shape of the potential are simply enclosed in the u_0 and ρ_0 parameters. The sole restriction on Eq. (4) is the "hole-particle" symmetry of the model: The interaction potential must have a hard core identical to a single lattice cell.

III. PHASE TRANSITION IN TERMS OF IRREDUCIBLE INTEGRALS

To exclude the activity dependence, AVEOS (1) is often transformed to the well-known virial equation of state (VEOS) [9] as the following density series for pressure:

$$\frac{P}{k_B T} = \rho\left(1 - \sum_{k\geqslant 1} \frac{k}{k+1}\beta_k \rho^k\right), \tag{5}$$

in terms of *irreducible cluster integrals*, $\{\beta_k\}$ (or virial coefficients, $B_{k+1} = -\frac{k}{k+1}\beta_k$).

In fact, the interchangeability between the VEOS and AVEOS still remains somewhat unclear in various studies. It is conventionally believed that VEOS (5) fares well for repulsive interaction potentials or supercritical temperatures (when repulsion prevails over attraction) in comparison with the activity expansions [AVEOS (1)], but the range of its convergence is relatively poor for attractive potentials or subcritical temperatures (when attraction prevails over repulsion) [37].

The situation looks clearer within the framework of Mayer's diagram approach [9]. Any reducible integral of the nth order, b_n, corresponds to all possible "connected" diagrams for n particles (a cluster) and can be constructed of smaller "biconnected" (rigid) diagrams, i.e., *reduced* to the sum of products of *irreducible* integrals, $\{\beta_k\}$, where $k < n$ (the complex relationship between the reducible and irreducible cluster integrals is described in detail in [9,38]). Therefore, the VEOS with a certain set of irreducible integrals, $\{\beta_k\}$ (this set may even be finite—say all irreducible integrals of orders higher than a certain $k_{\max}$ are supposed to vanish due to the possibility of neglect or just the inability of calculating), always corresponds to the AVEOS with truly infinite activity series where all the reducible integrals (even for $n \to \infty$) are constructed of that (possibly finite) set of irreducible ones. For example, the second-order VEOS (which includes only the second virial coefficient, B_2, or the first-order irreducible integral, β_1) corresponds to the infinite activity series of the AVEOS where each reducible integral,

b_n, must be calculated by summation of all possible chains and stars (as well as their combinations), which are composed of the proper number of β_1 integrals.

For repulsive potentials or high temperatures (when irreducible integrals are mostly negative and the corresponding virial coefficients form a positive decreasing sequence), the usage of the VEOS is naturally preferable in comparison with the infinite alternating activity series of the AVEOS.

However, the applicability of the VEOS for attractive potentials (or subcritical temperatures) is principally limited. It was first shown by Mayer's study [9] and later confirmed in other studies [17–20,22] that the transformation of the AVEOS to VEOS (and, therefore, the validity of the VEOS itself) is strongly restricted by the AVEOS convergence condition: If there is a density, ρ_G, where the VEOS isothermal bulk modulus vanishes, i.e., the following equation:

$$\sum_{k\geqslant 1} k\beta_k\rho_G^k = 1, \tag{6}$$

has at least one real positive root, ρ_G (in the case of several such roots, the ρ_G is the minimum one), the activity series $\sum_{n=1}^{\infty} n^2 b_n z^n$ diverges exactly at this density and corresponding activity (see [9,18,22,38]),

$$z_G = \rho_G \exp\left(-\sum_{k\geqslant 1}\beta_k\rho_G^k\right). \tag{7}$$

As $\lim_{n\to\infty} n^{\frac{1}{n}} = 1$, the activity series of AVEOS (1) must also lose the analyticity beyond the same z_G point [for symmetrical lattice gases, z_G is additionally defined by Eq. (4); see Fig. 1], and VEOS (5) *becomes an incorrect* "substitute" for the AVEOS beyond the corresponding ρ_G density (though the VEOS may stay analytical and, therefore, often gives the impression of a correct equation).

Mayer and Goeppert-Mayer have explicitly shown in their book [9] that Eq. (6) is an exact boundary of the VEOS adequacy [relation (7) can also be found there]. The other derivations of the VEOS have initially used a somewhat vague "low-density" simplification [39] or complex mathematical transformation of activity series into the density one [1,40], which cannot actually be correct when the former become nonanalytic.

Indeed, the equation of state, UEOS [17,18], based on the recently established exact generating function for the partition function in terms of irreducible integrals absolutely coincides with the VEOS in all regimes except for those beyond the ρ_G density where the UEOS isotherms demonstrate strictly constant pressure instead of the VEOS thermodynamically forbidden intervals with negative compressibility (see Fig. 2 where the isotherms of both equations are shown for the Lennard-Jones fluid [10,11] as a model that, at the moment, has the most explored information on the virial set). On the one hand, such behavior of the UEOS explicitly indicates the VEOS inadequacy beyond the ρ_G point (the virial equation inadequately represents the true behavior of the partition function there) and exactly agrees with the character of the AVEOS divergence described in Sec. II (though there is no activity dependence in the UEOS, and hence it stays analytical even in the AVEOS divergence region). On the other hand, the ρ_G density, where the VEOS isothermal bulk modulus vanishes, used to be considered as a spinodal point for a long time, and such a stereotype is very hard to break down.

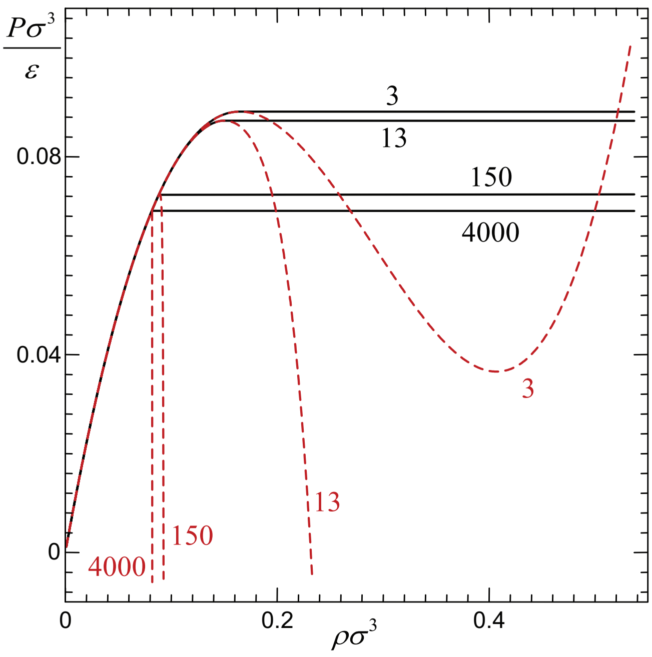

FIG. 2. Lennard-Jones fluid isotherms of the UEOS [17] (solid lines) and VEOS (5) (dashed lines) at the reduced temperature, $k_BT/\varepsilon = 1.2$ (ε and σ are parameters of the Lennard-Jones potential [10,11]). The numbers indicate the maximum order of irreducible integrals in both equations (the high-order integrals are approximated [30]).

Again, the lattice-gas "hole-particle" symmetry provides strict evidence for the true physical nature of ρ_G density. Mayer's expansion in terms of irreducible integrals for the partition function of the lattice-gas "holes" yields the following high-density symmetrical analog of the VEOS (SVEOS) [33,34]:

$$\frac{P}{k_BT} = \rho_0\left[\frac{u_0}{k_BT} + \ln\left(\frac{\rho_0}{\rho'}\right) + \sum_{k\geqslant 1}\beta_k\rho'^k\right] + \rho'\left[1 - \sum_{k\geqslant 1}\frac{k}{k+1}\beta_k\rho'^k\right], \tag{8}$$

where $\rho' = \rho_0 - \rho$ is the "hole" number density.

It is important to note that the derivation of SVEOS (see [33,34]) stays correct only for the "hole" number density, $\rho' \leqslant \rho_G$ (similarly to the VEOS restrictions). The corresponding particle number density,

$$\rho_L = \rho_0 - \rho_G, \tag{9}$$

defines the point where the SVEOS isothermal bulk modulus vanishes and the density series of SAVEOS (2) in powers of reciprocal activity, η, diverges, as is described in Sec. II [i.e., SVEOS (8) becomes inadequate when the density is lower than $\rho_L(\eta_L)$].

Actually, the combination of Eqs. (4) and (7) yields the following additional condition for the lattice-gas virial series at the ρ_G point (see Fig. 1):

$$\sum_{k\geqslant 1}\beta_k\rho_G^k = \ln\frac{\rho_G}{\rho_0} - \frac{u_0}{k_BT}.$$

In turn, this condition makes the values of pressure in VEOS (5) and SVEOS (8) *absolutely equal at the points where their isothermal bulk moduli vanish* (the densities ρ_G and ρ_L, respectively):

$$P(\rho_G) \equiv P(\rho_L).$$

Of course, this equality is mostly a consequence of Eq. (4) concerning the activity series (see Sec. II), but it can serve as a more strict confirmation for the true nature of the densities ρ_G and ρ_L, because VEOS (5) and SVEOS (8) are both analytical in the vicinity of these points (in contrast to the AVEOS and SAVEOS, which, strictly speaking, lose their analyticity there).

Thus, the density ρ_G *is definitely the saturation point* (a binodal point) at least for all the lattice-gas models with "hole-particle" symmetry. The boiling point for such lattice gases, ρ_L, is simply defined in Eq. (9) as a point symmetrical to ρ_G.

It should additionally be noted that Eq. (6) is not only an explicit definition of the above-mentioned saturation density ρ_G, but it also defines implicitly the subcritical temperatures as those where Eq. (6) has at least one real positive root. When Eq. (6) has no such root (i.e., at supercritical temperatures), the activity series in AVEOS (1) and SAVEOS (2) are always converging (there is no phase transition at such temperatures) and Eq. (7) becomes irrelevant.

IV. CONSIDERATIONS FOR NONSYMMETRIC MODELS

In the previous sections, the direct relationship between the first-order phase transition and mathematical divergence of activity series has analytically been established for a class of lattice gases with "hole-particle" symmetry. The next question that naturally arises is whether this result can be generalized on the other statistical models of matter.

In essence, the "hole-particle" symmetry is itself the main feature that formally separates the considered lattice-gas model from the others: Only this symmetry has provided the derivation [33,34] of high-density virial expansions [SAVEOS (2) and SVEOS (8)], symmetric definition of the boiling point [see Eq. (9)], establishment of the analytical expression for the phase-transition activity [see Eq. (4)], and finally the proof of the pressure equality for the low-density and high-density expansions (at the corresponding phase-transition points).

For nonsymmetric statistical models (namely lattice gases, where the hard core of a particle occupies more than one cell of the lattice, or continuous models such as the Lennard-Jones fluid), a strict analytical definition of the boiling point or phase-transition activity is unfortunately absent today. On the other hand, the cluster expansion for the partition function of interacting particles [9] (as well as its consequences, such as AVEOS (1), VEOS (5), or UEOS [17,18]) is formally general for lattice gases, Lennard-Jones fluid, and many other models of matter (even some quantum systems). The principal difference among the models is only in the definition and calculation of the proper cluster integrals (reducible or irreducible), and therefore this *difference is quantitative rather than qualitative*.

Indeed, the behavior of subcritical isotherms of all the considered equations in terms of reducible or irreducible integrals is qualitatively similar for different statistical models with a realistic interaction potential (a potential that includes both attraction and repulsion): The UEOS [17,18] always yields a constant pressure beyond the point, ρ_G, where the VEOS isothermal bulk modulus vanishes (see Fig. 2) for any set of irreducible integrals [if this set provides a proper root of Eq. (6) regardless of the model being considered] and AVEOS always demonstrates the corresponding divergent behavior there (see Refs. [21–23,32] for the Lennard-Jones fluid, the lattice-gas model, and the system of ideal bosons). Some modern approximations of infinite virial series even yield a discontinuity of the isotherm tangent (for UEOS as well as AVEOS) at the ρ_G vicinity [22,28–30] that makes the theoretical isotherms very similar to real ones (see the UEOS isotherm in Fig. 2 when the number of accounted irreducible integrals is very large).

Of course, all the above-mentioned arguments are based on a complex "mixture" of different approaches where strict proofs are mixed with numerical results and approximations. At the moment, only the following facts have really rigorous proofs:

(i) Recent studies have proved that Mayer's expansion in terms of irreducible integrals yields a strict constancy of pressure beyond the ρ_G point where the VEOS isothermal bulk modulus vanishes and AVEOS diverges [see the derivation of UEOS [17,18,38] as well as the strict relationship (7) between z_G and ρ_G [9,17,18,38] for *arbitrary sets of irreducible integrals*].

(ii) The present study proves that the singularity point of activity expansions [z_G defined in Eq. (4)] is the first-order phase-transition activity for lattice gases with "hole-particle" symmetry (in particular, it matches the phase-transition activity in the Lee-Yang *exact solution* [5]), and the ρ_G density is certainly the saturation point of such gases (note that these results are also obtained *without any quantitative information on the actual sets of reducible or irreducible integrals*).

Such arguments as the observed features of the AVEOS divergence at the z_G activity (the jump of density at constant pressure and constant chemical potential) or "realistic" discontinuity of the tangent for some theoretical isotherms [at the $\rho_G(z_G)$ point] are actually based on numerical studies of virial expansions [21–23] with certain sets (finite or approximated to infinity [28–30]) of cluster integrals for various interaction models, and unfortunately they cannot be considered as rigorously grounded. However, they are in good agreement with the stricter evidence mentioned above for the first-order phase transition beyond the ρ_G density (i.e., beyond the AVEOS convergence region), and this agreement is quite expected.

As we still have no grounded reason to distinguish qualitatively the sets of cluster integrals for different statistical models (with realistic interaction potentials), the above-mentioned similarity should be considered as a fundamental feature of the cluster expansion (and virial series) in general. In other words, if the ρ_G density is certainly a binodal point for a lattice gas, there is no reason to consider similar density as a spinodal point for the Lennard-Jones fluid.

There is another important issue concerning the accuracy and generality of the cluster expansion (and hence UEOS, AVEOS, and SAVEOS) in terms of the *constant cluster integrals*. Beyond the ρ_G point, the UEOS isotherms yield constant pressure for an arbitrary high density ($\rho \to \infty$) [17,18], and the AVEOS series for density has an essential discontinuity (to infinity) instead of the physically correct finite jump [21,22]. A possible reason for such nonphysical behavior (the absence of a boiling point on the isotherms) has been stated in a number of papers [21,22,38]: The conventional definition of cluster integrals over absolutely infinite limits (and, therefore, their independence of the real system volume or density) becomes incorrect in very dense regimes (especially for high-order cluster integrals).

Although this issue (concerning the actual density dependence of cluster integrals) remains almost unexplored in modern statistical physics (see the first and very approximate attempts to solve this problem in Ref. [41]), some of its important aspects can be clarified with regard to the "hole-particle" symmetry considered in the present paper. Namely, AVEOS (1) and SAVEOS (2) with "properly defined" (i.e., density-dependent) reducible cluster integrals would absolutely coincide in all regimes of a lattice gas ($0 \leqslant \rho \leqslant \rho_0$). However, they actually coincide only at the phase-transition domain ($\rho_G \leqslant \rho \leqslant \rho_L$) when the "simplified" set of constant (density-independent) reducible integrals is used in practice. Thus, the constancy of cluster integrals becomes invalid somewhere in the phase-transition interval, but *this simplification remains surely correct* for the AVEOS (i.e., the cluster expansion for the partition function of particles) at any lower density ($\rho \leqslant \rho_G$) and SAVEOS (the cluster expansion for the partition function of "holes") at any higher density ($\rho \geqslant \rho_L$). Correspondingly, the equations in terms of irreducible integrals (VEOS and SVEOS) must really be correct within the same symmetrical intervals (ending at the points ρ_G and ρ_L, respectively, where the pressure for both equations is strictly equal, as is shown in Sec. III).

For instance, Lee and Yang even provided a strict definition for the *constant* reducible integrals based on the distribution of the partition function roots in the complex plane of activity [5]. However, they initially considered the symmetrical low-density and high-density expansions (analogs of the AVEOS and SAVEOS) instead of a single expansion for all regimes (where the actual density dependence of cluster integrals must be taken into account). As their conclusions are correct at the points ρ_G and ρ_L, the cluster integrals can really be considered as constant up to those points.

Moreover, such a boundary for the correctness of the density-independent cluster integrals can clearly be explained in view of the AVEOS (and SAVEOS) divergence. The analytical (convergent) behavior of activity series up to the phase transition (while activity does not exceed the convergence radius, z_G) means that the principal contribution to the partition function belongs to the low-order power terms (i.e., reducible integrals for microscopic clusters). For such integrals, the volume of a thermodynamic (macroscopic) system is almost infinite at any state, and the simplification of density independence remains accurate. On the contrary, the divergence of activity series [beyond $\rho_G(z_G)$ for the AVEOS and beneath $\rho_L(\eta_L = z_G)$ for the SAVEOS] means there is an increasing contribution of high-order integrals for which the density dependence cannot be neglected, and the above-mentioned simplification becomes incorrect in the divergence region.

Again, the formal generality of the cluster expansion (and the qualitative similarity of its behavior for various models) allows for a generalization of all the above-presented considerations about the density dependence of the lattice-gas cluster integrals onto the other statistical models: *Mayer's cluster expansion with constant cluster integrals remains correct up to the saturation point* $\rho_G(z_G)$ (as well as the corresponding equations in terms of reducible or irreducible integrals: UEOS, VEOS, and AVEOS).

V. CONCLUSIONS

Some important but previously unexplored aspects of the "hole-particle" symmetry for a wide range of lattice gases (where the particle hard core is identical to a single lattice cell) provide a number of analytical relations that are important in the modern statistical theory of first-order phase transitions.

In particular, a strict analytical expression of the phase-transition activity has been derived that is general for lattice gases of arbitrary geometry and dimensions with various interaction potentials [see Eq. (4)].

Exactly at this activity (i.e., a certain chemical potential), the symmetrical low-density and high-density equations in terms of reducible cluster integrals [AVEOS (1) and SAVEOS (2)] diverge: their isotherms have similar discontinuities of density [in points $\rho_G(z_G)$ and $\rho_L(z_G)$, respectively] at some constant value of pressure that is absolutely the same for both equations.

The behavior of the corresponding equations in terms of irreducible integrals [VEOS (5) and SVEOS (8)] also exactly matches that described above: The saturation point ρ_G and the boiling point ρ_L are analytically defined as densities where the isothermal bulk modulus vanishes [see Eq. (6)] for the VEOS and SVEOS, respectively, and both equations really yield the same equal pressure at those points.

In fact, all these features provide a much needed strict confirmation for some recently obtained results [17,20–22,28,29] concerning not only the lattice-gas model but other statistical models too, and this confirmation may finally end the long-standing disputes about the adequacy of Mayer's expansion, the nature of its divergence, the character of the ρ_G point (i.e., whether it belongs to the binodal or spinodal), etc. The VEOS and AVEOS are general equations for various pairwise interaction models, and therefore the fact that the density ρ_G from Eq. (6) (the zero point of the VEOS isothermal bulk modulus) is the saturation point for the lattice gas proves that it has the same sense for the other models with realistic interaction potentials.

The difference may only be quantitative (due to the difference of irreducible sets for different interaction models) and not qualitative (at least for realistic interaction models). The equality of pressure and chemical potential (activity) at the saturation and boiling points (ρ_G and ρ_L, respectively) demonstrates that zeros of the VEOS isothermal bulk modulus [see Eq. (6)] really form the binodal (which is additionally the boundary of the VEOS adequacy): ρ_G cannot belong to the spinodal, as was often considered earlier. The divergence region of the AVEOS is exactly bounded by $\rho_G(z_G)$, and this divergence indeed yields the jump of density at constant values of pressure and chemical potential.

Another important result is that Mayer's expansion with the constant (volume- or density-independent) cluster integrals remains correct up to the density ρ_G (activity z_G). As a rule, the cluster integrals are defined in infinite limits, but for the integrals of very high (macroscopic or thermodynamic) orders this is not always correct: At very dense states, they must essentially depend on the real system volume, and their contribution also becomes determinative (this contribution even causes the AVEOS to diverge). In practice, the neglect of such volume dependence for high-order cluster integrals produces the inadequate behavior of the AVEOS (as well as UEOS in terms of irreducible integrals) at very dense states [17,19,20]: Equations with constant cluster integrals actually yield the density jump to infinity (the essential discontinuity of density) instead of the finite jump to the boiling point ρ_L. In the case of the discrete lattice-gas model, the usage of symmetrical equations (SAVEOS and SVEOS) resolves this problem very simply (see Fig. 1), but for continuous models of matter, the "hole-particle" symmetry is not so obvious. This issue still awaits a solution, however the present study directly confirms that *the volume dependence of the cluster integrals may really be neglected at least in the regimes when* $\rho \leqslant \rho_G$.

It should additionally be noted that the presented results do not contradict those obtained in previous analytical [5,35] and numerical [36] studies of the lattice-gas model as well as the Ising problem. Of course, the existing extremely limited data on the virial sets still do not allow an accurate quantitative determination of the condensation parameters [ρ_G and $P(\rho_G)$] even for the simplest statistical models, but this problem may now be considered technical rather than theoretical.

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