Equation of state for all regimes of a fluid: From gas to liquid

M. V. Ushcats[*]

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

S. Yu. Ushcats

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

L. A. Bulavin and V. M. Sysoev

Department of Molecular Physics, Taras Shevchenko National University of Kyiv, 2, Prosp. Academician Glushkov, Kyiv 03680, Ukraine

The study of Mayer's cluster expansion (CE) for the partition function demonstrates a possible way to resolve the problem of the CE nonphysical behavior at condensed states of fluids. In particular, a general equation of state is derived for finite closed systems of interacting particles, where the pressure is expressed directly in terms of the density (or system volume) and temperature-volume-dependent reducible cluster integrals. Although its accuracy is now greatly affected by the limited character of the existing data on the reducible cluster integrals and, especially, the absence of any information on their density dependence, a number of simple approximations indicate the qualitative adequacy of this equation in various regimes of a fluid: from gaseous to liquid states (including the transition region).

I. INTRODUCTION

Despite considerable advances in statistical description of critical phenomena [1] (second-order phase transitions), the analytical theory of the condensation phenomena (first-order phase transitions) still remains unsuccessful. There are only two specific analytical examples of the condensation phenomenon: the Lee-Yang solution for the two-dimensional lattice gas with the square-well interaction potential [2] and van der Waals–Maxwell equation of state [3,4] (the mean-field approximation of intermolecular interactions). Unfortunately, more general statistical approaches, based on the local particle-distribution functions [5] as well as various approximations for the system partition function [6] have not yielded a general theory that could directly relate the condensation parameters to microscopic features of matter (without additional thermodynamic relations typical for conventional two-phase approaches).

However, recent studies of Mayer's cluster expansion [6–9] (CE) have significantly advanced this cluster-based approach as to the statistical (single-phase) description of the first-order phase transitions. New equations of state in terms of irreducible cluster integrals [10–13] (virial coefficients) have clarified the actual limitations of the well-known virial expansion for pressure in powers of density (virial equation of state [6–8], VEoS) and indicated the beginning of the condensation process at the density, ρ_G, where the VEoS isothermal bulk modulus vanishes [10,11]. Studies of the virial expansions for pressure and density in terms of reducible cluster integrals [14–16] (virial series in powers of activity [7,8], AVEoS)

have established the fact of their divergence at the activity, z_G, which corresponds exactly to the same density, ρ_G [7,9,11,16]. Moreover, the observed character of this divergence directly indicates the beginning of the condensation: Beyond the ρ_G, AVEoS yields a jump of density (while the pressure remains constant) at the mentioned value of activity z_G (i.e., at the constant chemical potential) [14–16].

Thus, the modern statistical theory provides a way to locate the fluid saturation point, ρ_G, analytically on the basis of information about the interaction potential (in principle, the reducible and irreducible integrals can be defined on the basis of this information [7–9]); however, the location of the corresponding boiling point, ρ_L, remains much more difficult to define. As it has been shown in a number of papers [9,10,15], *the CE with constant (density-independent) cluster integrals cannot reproduce the true finite jump of density* (from ρ_G to ρ_L or vice versa) through the phase transition. All the equations mentioned above (in terms of the constant reducible as well as irreducible integrals) yield an essential discontinuity of density (the divergence to infinity) instead of the proper jump discontinuity. Although the main reason for such nonphysical behavior is known in principle (it has been clearly stated in some research [9,14,15]) the problem still remains absolutely unexplored in statistical theory.

For a wide range of lattice-gas models, this problem can simply be avoided due to the "hole-particle" symmetry of the binodal [14,17,18] (i.e., the symmetry between ρ_G and ρ_L). Moreover, such symmetrical statistical models have finally provided a strict analytical confirmation for the physical nature of the $\rho_G(z_G)$ point [19]: It has been proved rigorously that the values of pressure must be absolutely equal at both those points, $\rho_G(z_G)$ and $\rho_L(z_G)$.
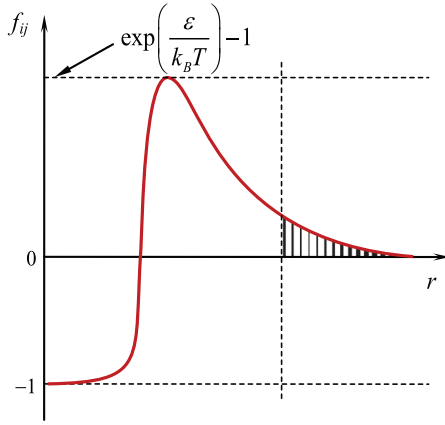
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[*]mykhailo.ushcats@nuos.edu.ua

FIG. 1. Mayer's function for a typical realistic interaction potential (ε is the depth of the potential well). Any limitations of the integration limits would first affect the attractive (positive) component of the function.

However, for continuous statistical models of matter, the corresponding symmetry is unfortunately not so obvious, and the relation between ρ_G and ρ_L would have a much more complex character.

In this paper, the important steps are made in a possible way to resolve the problem of the CE inadequacy at very dense regimes of model systems (i.e., regimes that correspond to the condensed states of matter). The key points of the proposed solution are discussed in Sec. II. Section III presents the derivation of a general equation of state (in terms of volume-dependent reducible integrals), which can potentially describe the behavior of a fluid in all regimes: from gaseous to liquid states continuously. Section IV is devoted to some attempts to roughly approximate the volume dependence for high-order reducible integrals. This section also presents the results of the corresponding computations and their discussion. The last section emphasizes the key results of the study and highlights the main directions of possible further developments in the area.

II. THEORETICAL BACKGROUNDS OF THE PROBLEM

A. Limitations on the volume independence of cluster integrals

The first question that naturally arises, when one has to consider the volume dependence of the cluster integrals, is how these integrals may be affected by changing the integration limits on the macroscopic level (in thermodynamic systems, the number of particles, $N \to \infty$, and the volume, $V \to \infty$ from "a microscopic point of view") if their integrand (various products of Mayer's functions, see Fig. 1) vanishes at the microscopic distance between particles.

Indeed, the simplification of the integration limits (their transformation to infinite ones and, hence, the independence of the integrals on the system volume) should be adequate for microscopic (i.e., the low-order, $n \ll N$) clusters even at very dense states while the system volume remains macroscopic. However, this simplification becomes invalid for macroscopic clusters ($n \to N$) at dense states of the system.

This issue is obvious on the example of the well-known expansions for pressure and density in powers of activity

(AVEoS):

$$\frac{P}{k_B T} = \sum_{n=1}^{\infty} b_n z^n$$

$$\rho = \sum_{n=1}^{\infty} n b_n z^n, \tag{1}$$

which include the so-called *reducible cluster integrals* [7,8] $\{b_n\}$. Each b_n is the integral over the configuration phase space of n particles (cluster), which are "connected" to each other by all possible combinations of Mayer's functions (see Fig. 1) but not "connected" with the other particles of the system (its integrand is the sum of all possible products of Mayer's functions, where the index of each particle of the cluster is present at least once).

In fact, the reducible integral for n particles can formally be "reduced" to the sum of various products of *irreducible integrals*, $\{\beta_k\}$, which, in turn, correspond to the "biconnected" diagrams (the strict definition for both kinds of integrals as well as the detailed description of complex relationship between them can be found in a number of sources [6–9]):

$$b_n = n^{-2} \sum_{\{j_k\}} \prod_{k=1}^{n-1} \frac{(n\beta_k)^{j_k}}{j_k!}, \tag{2}$$

where all possible integer sets $\{j_k\}$ must satisfy the condition

$$\sum_{k=1}^{n-1} k j_k = n - 1.$$

Figure 2 demonstrates the weight (or contribution) of various terms, $b_n z^n$, to the logarithm of the grand partition function [the series for pressure in Eq. (1)] and how their weight changes when both the activity and density, $\rho(z)$, increase (the ranges of the order, n, and activity, z, are limited in order to visualize the nature of the series divergence at the vicinity of a certain activity, z_G). There the reducible integrals, $\{b_n\}$, are calculated on the basis of the irreducible ones, $\{\beta_k\}$, for the widely known Lennard-Jones model (the high-order β_ks are approximated in accordance with the recently proposed technique [20]) by using the recursive algorithm [15] which is formally identical to Eq. (2).

At dilute states up to the saturation point [while the activity does not exceed the convergence radius, $z \leqslant z_G$, and the particle number density is correspondingly low, $\rho \leqslant \rho_G(z_G)$], the weight of different terms is a decreasing function of the order, n, i.e., the principal contribution to the partition function belongs to the relatively low-order reducible cluster integrals ($n \ll N$). In these regimes, the neglecting of the volume dependence for high-order cluster integrals (and even the neglect of those integrals themselves) does not lead to any losses of accuracy at the thermodynamic limit ($N \to \infty$; $V \to \infty$). This fact has recently obtained a strict confirmation [19] for various lattice-gas models and, in particular, the Lee-Yang [2] model.

However, the situation turns contraverse at more dense states beyond the saturation point ($\rho > \rho_G$), when the weight of cluster integrals becomes a nondecreasing function in the
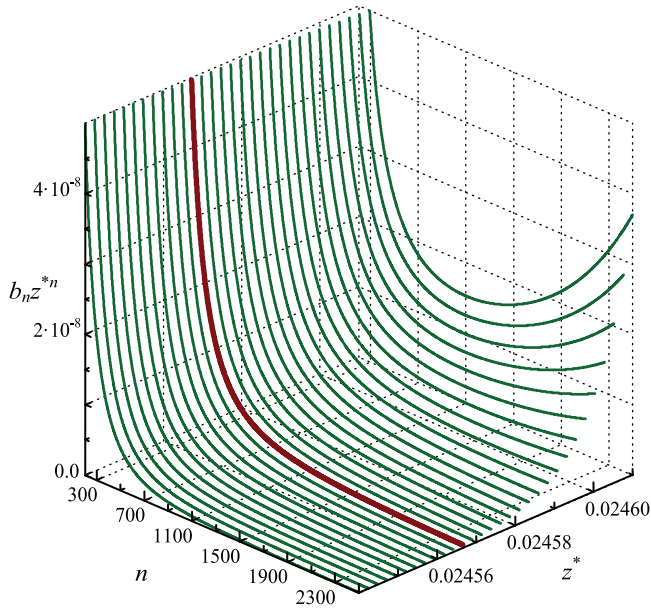
FIG. 2. Contribution of various terms, $b_n z^{*n}$, to the logarithm of the grand partition function [the series for pressure in Eq. (1)] at various activities (in a dimensionless form, $z^* = z\sigma^3$) for the Lennard-Jones fluid ($T = 0.9\varepsilon/k_B$). Cluster integrals are calculated by using the existing techniques [15,20]. The bold line corresponds to the divergence activity, z_G.

high-order region (see Fig. 2). The contribution of the high-order integrals becomes essential there (for infinite series, the contribution tends to infinity for $n \to \infty$ and causes the mathematical divergence) and, at the same time, their volume dependence cannot be neglected in such dense regimes.

The positivity of reducible cluster integrals at subcritical temperatures means that the intermolecular attraction (the positive part of Mayer's function in Fig. 1) prevails over repulsion (the negative part of Mayer's function in Fig. 1). Therefore, it is not surprising that the system compression yields the physical phenomenon of condensation at some high-enough density (and mathematical divergence of the AVEoS at the vicinity of a certain high-enough activity). On the other hand, the volume independence of cluster integrals means that they remain positive at any state (even very dense ones)—attraction always dominates over repulsion, and, hence, the physical phenomenon of condensation cannot stop (the mathematical divergence is to infinity—it yields an essential discontinuity of density instead of a jump).

Thus, the observed nonphysical behavior of the AVEoS (and other related equations in terms of reducible as well as irreducible cluster integrals) is a direct result of neglecting the actual volume dependence of cluster integrals (at least high-order ones).

In real substances, an additional effect can influence the balance between intermolecular attraction and repulsion: The interaction parameters may substantially change in condensed regimes due to the nonadditive character of real intermolecular forces. However, this effect is beyond the scope of the present research which is initially focused on statistical models of matter with pairwise interactions (such as the Lennard-Jones fluid, etc.).

B. Choice of integrals to regard for the volume dependence

Another important issue that has to be considered is what kind of cluster integrals, reducible or irreducible, can properly exhibit the real dependence of the partition function on volume in principle.

A great amount of evidence has been accumulated for calculating irreducible integrals (i.e., virial coefficients) [21–23] for various interaction models [24–28], and their volume dependence would technically be much simpler to explore and apply. Nevertheless, the right choice should be reducible cluster integrals that are rarely used by researchers in comparison with irreducible ones, and the other option would be incorrect, unfortunately, because, on the basis of all the existing approaches (diagram based [7] or others [6,8]), *the irreducible integrals can be well defined only for truly infinite systems* (or for microscopic reducible clusters of macroscopic systems).

As mentioned above [see Eq. (2)], each reducible integral, b_n, of a certain order, n, is a complex combination (sum of various products) containing the irreducible integrals $\{\beta_k\}$ of all possible orders less than n ($k \leqslant n - 1$). The actual volume dependence of a high-order reducible integral ($n \to N$) automatically means that all its components are also volume dependent even the irreducible integrals of the lowest orders (for example, β_1, β_2, etc.), must depend on the volume as they are parts of the volume-dependent reducible integral of a very high order. On the other hand, each low-order reducible integral ($n \ll N$) is volume independent in practice, and all its components (i.e., the same β_1, β_2, etc.) must not depend on volume, either.

To make this issue clear, one may consider the different parts (summands) of some b_n [see Eq. (2)]: β_{n-1}, $\beta_1\beta_{n-2}$, $\beta_1^2\beta_{n-3}$, $\beta_2\beta_{n-3}$, ..., β_1^{n-1}. For a macroscopic cluster ($n \to N$) in dense regimes, the first-order irreducible integrals (β_1) of *various summands* (even belonging to the same b_n) would actually be *different integrals*. As to the irreducible integrals belonging to different clusters (large and small ones), they must differ even more essentially, so that *there is no certain β_1 for the system as whole*.

Unfortunately, the irreducible integrals belonging to different reducible ones become *absolutely indistinguishable* when they are used in all the known equations in terms of virial coefficients (the conventional VEoS [6–8] or relatively new equations based on the exact generating function [9–11]).

In these circumstances, the irreducible integrals cannot be used at all, and the corresponding equations mentioned above will always remain inapplicable to condensed states of matter (with rare exceptions like the equations based on the "hole-particle" symmetry for some specific models of matter [17,18]). The only possibility to make the CE behavior adequate in high-density regimes is to use *the equations in terms of reducible cluster integrals as certain functions of volume* (or density), $\{b_n(V)\}$.

Although the AVEoS formally meets this criterion, the volume dependence of reducible integrals makes its practical usage almost impossible because the density in Eq. (1) is a series with the power coefficients which depend on density in turn. Therefore, the problem solution needs another equation of state in terms of reducible cluster integrals where the activity is excluded as a parameter.

III. EQUATION IN TERMS OF VOLUME-DEPENDENT REDUCIBLE INTEGRALS

A. Generating function in terms of reducible integrals

The initial form of Mayer's CE exactly represents the configuration part of the partition function (the so-called configuration integral, Q_N) as a complex sum of products of reducible integrals mentioned above, $\{b_n\}$:

$$Q_N = \sum_{\{m_n\}} \prod_{n=1}^{N} \frac{(b_n V)^{m_n}}{m_n!}, \tag{3}$$

where all possible integer sets $\{m_n\}$ must satisfy the condition

$$\sum_{n=1}^{N} n m_n = N.$$

For the canonical ensemble (a closed system with the constant number of particles), the differentiation of the configuration integral directly yields the equation of state:

$$\frac{P}{k_B T} = \left[\frac{\partial (\ln Q_N)}{\partial V} \right]_T = \frac{1}{Q_N} \left(\frac{\partial Q_N}{\partial V} \right)_T, \tag{4}$$

and the main problem is to obtain an analytical expression for that configuration integral.

For a known set of reducible integrals, $\{b_n\}$, Eq. (3) formally provides such an expression, but its direct usage is too complex in practice (especially for large systems where the N reaches hundreds or thousands). A more convenient way is to use the generating function for the Q_N in Eq. (3),

$$F(y) = \exp\left(V \sum_{n=1}^{\infty} b_n y^n \right) = \sum_{i=0}^{\infty} Q_i y^i. \tag{5}$$

Although this function is not new (it was introduced by the Mayers themselves [7]), and its form is much simpler than that of the generating function in terms of irreducible integrals [9–11], it has not been used explicitly to derive the equation of state in terms of reducible integrals.

In particular, Eq. (5) allows defining the Q_N of an arbitrarily high order, N, in the corresponding recursive differentiation:

$$Q_i = \left. \frac{F^{(i)}(y)}{i!} \right|_{y=0} = \frac{V}{i} \sum_{n=1}^{i} n b_n Q_{i-n}, \tag{6}$$

where $Q_0 = 1$.

Mathematically, both the definitions of the Q_N in Eqs. (3) and (6) are absolutely identical; however, the last equation is much more convenient for computations.

B. Recursive equation of state

In order to find the derivative of the Q_N with respect to volume in Eq. (4), one can first define the corresponding derivative of the generating function in Eq. (5):

$$\frac{\partial F}{\partial V} = \sum_{i=0}^{\infty} \frac{\partial Q_i}{\partial V} y^i = F \sum_{n=1}^{\infty} \left[b_n + V \left(\frac{\partial b_n}{\partial V} \right) \right] y^n$$

$$= \left\{ \sum_{n=1}^{\infty} \left[b_n + V \left(\frac{\partial b_n}{\partial V} \right) \right] y^n \right\} \left(\sum_{k=0}^{\infty} Q_k y^k \right).$$

In this expansion, the power coefficient at y^N is

$$\frac{\partial Q_N}{\partial V} = \sum_{n=1}^{N} \left[b_n + V \left(\frac{\partial b_n}{\partial V} \right) \right] Q_{N-n} = \sum_{n=1}^{N} b_n^*(V) Q_{N-n},$$

where the following designation is used:

$$b_n^*(V) = b_n + V \left(\frac{\partial b_n}{\partial V} \right). \tag{7}$$

As a result, Eq. (4) is transformed to *the searched equation of state in terms of volume-dependent reducible integrals*,

$$\frac{P}{k_B T} = \frac{\sum_{n=1}^{N} b_n^*(V) Q_{N-n}}{Q_N}. \tag{8}$$

In comparison with the VEoS and other equations in terms of irreducible integrals (or virial coefficients), the practical usage of Eq. (8) is additionally complicated by a laborious stage of determining the set $\{b_n\}$ on the basis of a certain already known irreducible integrals, $\{\beta_k\}$ [besides the recursive determining the set of $\{Q_i\}$ in Eq. (6)] even in cases when the reducible integrals are considered as constant. On the other hand, Eq. (8) meets all the criteria stated in Sec. II: It contains the reducible integrals, which can potentially be volume dependent, and expresses the pressure as a function of density (actually, it explicitly involves the number of particles, N and the system volume, V).

In 1980s, a similar equation was derived in somewhat different (and more complex) manner [29,30]: Generating function (5) was not directly used in the derivation, and the volume dependence of the reducible integrals was not studied. Unfortunately, the complexity of the equation in combination with technical limitations of the computational equipment at that period imposed substantial restrictions on the size of the studied systems ($N \leqslant 1024$), and the obtained results even caused some doubts for a long time. Although the recent studies of Mayer's CE with constant cluster integrals [10,11,15] have completely confirmed those results, the actual behavior of Eq. (8) with regard for the volume dependence of $\{b_n\}$ has never been explored.

IV. APPROXIMATION OF THE VOLUME DEPENDENCE

A. Phenomenological ansatz for the volume dependence

Provided that the set of volume-dependent reducible integrals, $\{b_n(V)\}$, is completely and exactly known for a certain model of matter, Eq. (8) should theoretically be accurate in all possible states of this model from dilute to condensed regimes. Indeed, this equation does not have any theoretical restrictions on density or temperature at least for models where Mayer's CE remains valid.

At the moment, there is no realistic statistical model (which includes intermolecular attraction as well as repulsion) with the completely known set of cluster integrals. Some truncated sets of irreducible integrals (virial coefficients) have been calculated for widely used interaction models (such as the Lennard-Jones model [24,28], its modifications [25,26], Morse [27] and square-well [31] potentials, etc.). There are also a number of approximations for infinite virial sets [20,27,32]. For the reducible cluster integrals, the achievements are even more modest: The techniques of calculating the reducible integrals on the basis of irreducible ones still continue to improve [14–16,29].

As to the volume dependence of those integrals, it has already been mentioned in the previous sections that the problem remains absolutely unexplored in modern physics. There are a number of possible reasons for such ignoring the problem over the years. The calculations of the cluster integrals still involve considerable technical difficulties, and consideration of the volume dependence can only additionally complicate the calculations. Until recently, Mayer's CE did not reach such dense states of systems, where the volume dependence becomes really essential: There was no need to consider the volume dependence for low-order cluster integrals, and only recent studies have raised the issue of calculating the relatively high-order integrals.

On the other hand, a simple qualitative analysis of Mayer's function may help to predict the main features of the searched volume dependence on the corresponding qualitative level. Of course, such considerations do not have a firm basis and cannot be accurate in practical calculations; however, they may indicate some important directions of further developments and invigorate future research.

Formally, there would be no loss of generality and accuracy to express the searched dependence in the following form:

$$b_n(V) = b_n^0 g(n, T, x), \qquad (9)$$

where b_n^0 is the nth-order reducible integral defined over infinite limits (i.e., the conventionally defined reducible integral); $g(n, T, x)$ is a certain function of the order, temperature and special variable, x, that is related to *the real integration limits*.

Some key simplifications and inaccuracies may appear in Eq. (9) due to possible approximations being used in function g or its variable x on the basis of certain analytical or empirical considerations.

B. Approximation on the qualitative level

The decreasing of integration limits (under compression of the system) must first affect the positive part of Mayer's function (i.e., the long-distance attractive component of intermolecular forces, see Fig. 1). Therefore, the reducible integrals, which are initially positive (when defined in infinite limits at subcritical temperatures), should decrease or even change the sign when the integration volume decreases.

As a result, the positive (in dilute regimes) set of reducible integrals may become the complex alternating one in very dense regimes—the primarily attractive contribution to the partition function (that leads to condensation under compression at subcritical temperatures) may become the primarily repulsive one (that is similar to the supercritical virial

series which cannot yield the condensation). Mathematically, it should stop the density divergence of the AVEoS at very dense states and means the end of the pressure constancy. Physically, it should stop the condensation and indicates the presence of a certain balance between attraction and repulsion in condensed regimes of matter.

Due to the absence of any reliable and accurate information on such complex behavior of reducible integrals, one can suppose that, on average, the reducible integral vanishes (or its positive value significantly decreases) when its integration volume becomes small enough ($V \to V_0$), i.e., the specific volume per particle, $\frac{V}{n}$ (it is important to distinguish this cluster quantity from the system specific volume, $\frac{V}{N} = \rho^{-1}$), reaches a certain small quantity, v_0 (or the cluster density, $\frac{n}{V}$, reaches a certain large quantity ρ_0). Furthermore, as the volume dependence would be essential for the high-order integrals only, and the behavior of various high-order integrals should not differ fundamentally, the v_0 may be the same for those integrals and therefore can be used as a key parameter in the x variable mentioned above [see Eq. (9)]:

$$x = \frac{V_0}{V} = \frac{n v_0}{V} = \frac{n}{N} \frac{\rho}{\rho_0}. \qquad (10)$$

For microscopic clusters ($n \ll N$), x is always very small ($x \to 0$ even in very dense regimes, when $\rho > \rho_0$). For macroscopic clusters ($n \to N$), this variable vanishes ($x \to 0$) only at dilute (gaseous) states, but $x \simeq 1$ in dense (condensed) regimes.

Correspondingly, the expected dependence of function g on variable x [see Eq. (9)] should satisfy the following criteria:

(i) $g(x = 0) = 1$—assures that $b_n \to b_n^0$ at dilute states;

(ii) $\left(\frac{\partial g}{\partial x}\right)_{x=0} = 0$—smoothes the transition from the b_n constancy to the volume dependence;

(iii) $\left(\frac{\partial g}{\partial x}\right)_{x>0} < 0$—corresponds to the decreasing of the function.

A specific form of function g would influence the results rather quantitatively rather than qualitatively. Thus, two principally different functions are proposed to approximate the $b_n(V)$ dependence (9) in order to study the behavior of Eq. (8) on the qualitative level:

$$g(x) = [1 - x^i (2 - x)^i]; \qquad (11)$$

$$g(x) = \frac{1}{1 + x^i \exp(x - 1)}. \qquad (12)$$

The behavior of both functions for various values of the power factor, i, is illustrated in Fig. 3. In general, both functions satisfy the listed above criteria; however, the points of their vanishing essentially differ.

C. Results of computations and discussion

A great number of computations have been performed on the basis of Eq. (8) for various interaction models [for the Morse [33], Lennard-Jones [34,35], modified Lennard-Jones [36,37] models, the truncated sets of known irreducible integrals [24–28] as well as the sets approximated to infinite orders [20,27,32] have been used to calculate the corresponding constant values of reducible integrals $\{b_n^0\}$, see Eq. (9)]
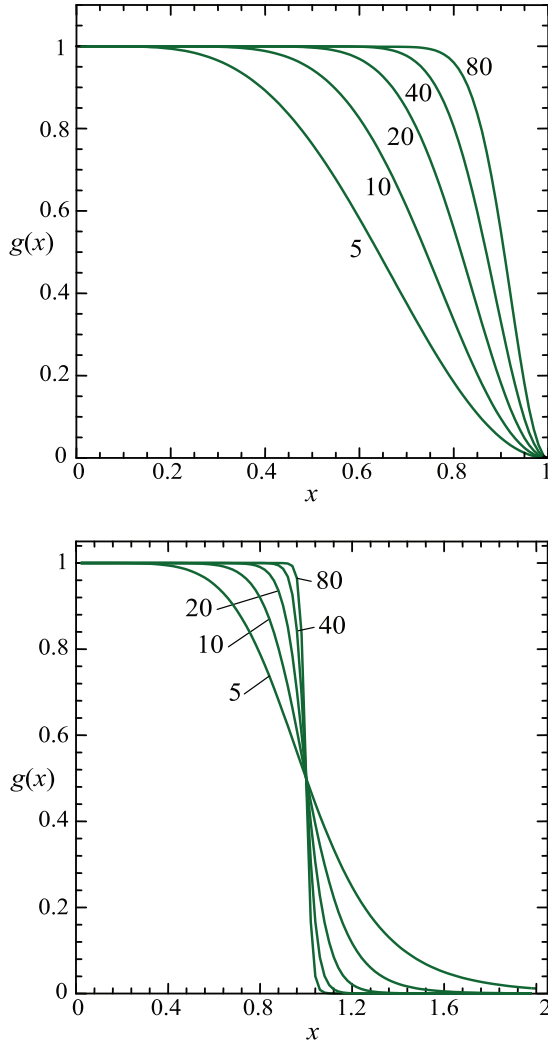
FIG. 3. Approximating functions (11) (top) and (12) (bottom) for different power factors, i (the numbers in the figure).

FIG. 4. Isotherms of Eq. (8) for the finite ($N = 4000$) Lennard-Jones system ($T = 1.0\varepsilon/k_B$), where the reducible cluster integrals, $\{b_n\}$, are volume dependent according to Eq. (9) with approximating functions (11) (solid line) and (12) (dotted line). The approximation parameter in Eq. (10), $\rho_0 = 0.25\sigma^{-3}$ (vertical dotted line). Constant reducible cluster integrals, $\{b_n^0\}$, are calculated accordingly to Ref. [15] on the basis of two different approximations for high-order irreducible integrals: [20] (a) and [32] (b).

by using both approximations of the g function [see Eqs. (11) and (12)] in a wide range of their parameters [i and v_0, see Eq. (10)].

The results of such computations are qualitatively similar: On all the isotherms of Eq. (8), the pressure constancy turns into its increasing at some density (which should have the meaning of the boiling-point density) higher than the ρ_0 (see Fig. 4) that well agrees with the all suppositions made above. In fact, the varying of the interaction models and the parameters of approximations affects this behavior quantitatively: Only the boiling-point location and the slope of the isotherms beyond this density actually differ in various computations.

It is important to note that the behavior of functions (11) and (12) may seem very similar though it fundamentally differs in an important aspect (see Fig. 3) when their parameter, i, is somehow related to the cluster order, n: function (11) vanishes exactly at $x = 1$ for all orders (i.e., all the cluster integrals vanish when their specific volume reaches the same value, v_0), but function (12) vanishes at different x for different orders (i.e., different cluster integrals vanish at different specific volumes). Potentially, such discrepancies
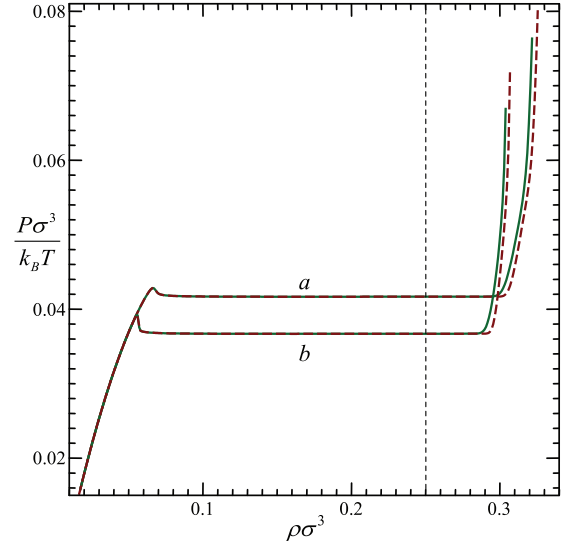
could affect the behavior of isotherms in essence. However, the actual difference of that behavior remains quantitative rather than qualitative (see the difference between the solid and dashed lines in Fig. 4).

On the other hand, it should additionally be emphasized that the v_0 parameter itself [and, hence, its usage in the x variable, see Eq. (10)] is just a *rough simplification*. At present, there is no strictly grounded equation to evaluate this "phenomenological" parameter explicitly: For instance, the choice of $\rho_0 = 1/v_0$ in Fig. 4 mentioned above is rather intended to improve the visibility of the results (which should be considered as only qualitative in any case) and is not grounded on accurate numerical data. Actually, the v_0 (and the corresponding density ρ_0) must be temperature dependent, and this dependence can principally differ for various clusters. Moreover, the actual dependence of the x variable on the system volume may fundamentally differ from that in Eq. (10).

For example, the real form of the binodal (the liquid branch of all the known binodals, $\rho_L(T)$, is an essentially nonlinear decreasing function of temperature) can be reproduced only if the v_0 is a correspondingly increasing function of temperature. Again, this dependence can even be explained qualitatively. As mentioned before, each reducible integral is a very complex combination of various "connected" irreducible ones (see detailed description of reducible diagrams in Mayer's book [7]). They may be connected as some "stars," "chains," or their combinations. Figure 5 demonstrates the weights of various irreducible integrals in a certain reducible one at different temperatures [each weight, $w_b(k)$, is evaluated by comparison of the b_n values calculated with the actual β_k and vanishing β_k]. Diagrams of different types cannot be distinguished explicitly there, but some important conclusions may be drawn
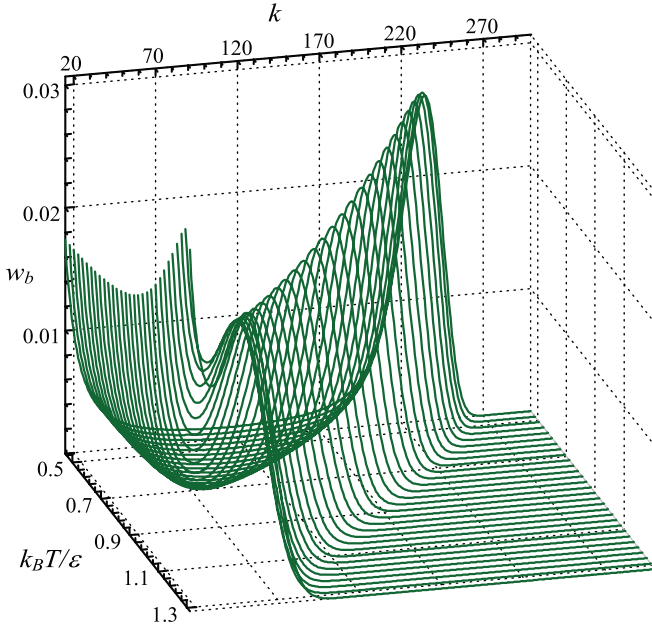
FIG. 5. Relative weight, $w_b(k) = |b_n - b_n^-(k)|/b_n$, of the irreducible integral, β_k, in the reducible one, b_{300} [$b_n^-(k)$ is the b_n calculated under assumption that $\beta_k = 0$], for various orders and temperatures. Cluster integrals are calculated by using the existing techniques [15,20] for the Lennard-Jones fluid.

from this figure. The high-order irreducible integrals cannot form relatively long "chains": At low temperatures, the contribution of the high-order irreducible integrals is dominant, and the resulting reducible integral rather depends on volume as it is supposed in Eq. (10). On the contrary, the low-order irreducible integrals can form "chains" large enough that are much more "sensitive" to any changes of the integration volume: At higher temperatures, the prevailing contribution of the low-order irreducible components makes the reducible integral more sensitive to the system compression that means the corresponding increasing of v_0 or even makes Eq. (10) inadequate in principle.

It should additionally be noted that all the presented considerations about the volume and temperature dependencies of cluster integrals are rather *phenomenological suppositions* and have no strict quantitative ground at the moment. Any more or less accurate values of high-order cluster integrals remain unknown even for the most used models of matter and even in cases when these integrals are treated as constant (i.e., integrated over infinite limits). For example, the high-order virial coefficients (irreducible cluster integrals) of the Lennard-Jones fluid can now be approximated on the basis of two different approaches [20,32] that yields quantitatively different results: The saturation parameters based on one approximation [32] essentially diverge from those based on the other [20] (see the corresponding isotherms, a and b, in Fig. 4), and both approximations yields some discrepancies with the existing data of numerical simulations (which, in turn, are also not absolutely converging). Unfortunately, we are still far away from an accurate quantitative theoretical description of the first-order phase transitions in certain realistic models of matter. On the other hand, the statistical

derivation of Eq. (8) is absolutely rigorous and contains neither simplification nor approximation. Any possible inaccuracy of the mentioned equation of state may appear only due to inaccurate practical evaluation of $\{b_n(V)\}$ functions. Despite some quantitative discrepancies, the behavior of this equation stays *qualitatively* adequate (see the finite jump of density at constant pressure in Fig. 4) and unchanged for various interaction models when different approximations are used in order to define the constant cluster integrals, $\{b_n^0\}$, and reproduce their volume dependence, $\{b_n(V)\}$.

V. CONCLUSIONS

Despite the recent considerable achievements of classical statistics in description of the gas-liquid phase transition on the basis of the cluster-based (Mayer's) approach, the applicability of this approach has still remained extremely limited at condensed states of fluids. The origins of these restrictions are in the volume independence of the corresponding cluster integrals due to the well-known simplification of their integration limits, when the actual configuration phase space of a studied system is substituted by the infinite space at the thermodynamic limit.

The key results of the present study may be grouped into the following items:

(i) the simplification of the infinite integration limits is sufficient only for microscopic clusters of thermodynamic systems and can be used in dilute regimes where the principal contribution to the partition function indeed belongs to the low-order cluster integrals (see Fig. 2); however, this simplification is incorrect for macroscopic (very large) clusters and therefore should not be used in dense (condensed) regimes of fluids when the contribution of the corresponding high-order cluster integrals to the partition function becomes essential;

(ii) as the irreducible cluster integrals can properly be defined only in absolutely infinite volumes (they are similar parts of different reducible cluster integrals over absolutely unlimited configuration phase-space), Mayer's cluster expansion of the partition function can adequately describe the balance between attraction and repulsion (during the phase transition) exclusively in terms of the volume-dependent (or density-dependent) reducible cluster integrals;

(iii) on the basis of such cluster expansion, the recursive equation of state has been derived for finite closed systems, and this equation include the reducible cluster integrals as explicit functions of the system volume [see Eqs. (7) and (8)].

It is also important to note that all the mentioned issues have remained unexplored in physics until now. Although the derived equation of state should theoretically be correct in all possible regimes of fluids (in contrast to the previously used equations), its accurate practical usage unfortunately remains hardly possible due to the absence of the reliable and complete information on the high-order cluster integrals and, especially, their actual volume dependence even for the simplest realistic interaction models.

In order to study the adequacy of Eq. (8) at least qualitatively, a number of rough approximations are proposed for the volume dependence of reducible integrals on the basis of a supposition that the positive value of the subcritical high-order integrals should reduce under the system compression and

vanish at some small specific volume per particle for the corresponding cluster.

The computations based on these approximations have reproduced the isotherms that are qualitatively similar to the subcritical isotherms of real substances: The jump of density at constant pressure ends at some dense state, which can be interpreted as a boiling point, and further compression leads to the increasing of pressure that may correspond to the condensed (liquid) regimes of fluids.

Of course, the computations mentioned above do not pretend to accuracy as to the actual behavior of the studied model systems (such as the Morse or Lennard-Jones fluids) at condensed states. At the current stage of our knowledge about the cluster integrals, the proposed approximations are too rough to be used in *quantitative theoretical description of the condensation phenomenon*. In fact, these approximations (and all their parameters as well) do not even have a strict theoretical ground—they are based only on the logical suppositions about the real behavior of the high-order cluster integrals.

The performed computations demonstrate the possibilities of Eq. (8) on the qualitative level—its ability to describe the behavior of fluids continuously from dilute to condensed regimes including the phase transition region.

In essence, the actual reasons for the nonphysical behavior of Mayer's cluster expansion at dense states can already be considered as completely known, and the present study clearly establishes the directions to resolve this problem. There is much laborious research ahead, and the main efforts should be focused on the evaluation of reducible cluster integrals and especially their dependence on the real integration limits.

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