PHYSICAL REVIEW E **102**, 042130 (2020)

Some universality in subcritical behavior of real substances and model fluids

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(Received 23 August 2020; revised 26 September 2020; accepted 13 October 2020; published 26 October 2020)

On the basis of the latest advances in Mayer's cluster-based approach, the reduced forms of the well-known virial expansions are derived in terms of scaled reducible and irreducible cluster integrals. This transformation minimizes the dependence on temperature and the effect of parameters specific for each thermodynamic system, thus making the resulting reduced expansions indeed universal on the quantitative level. In particular, the scaling of isotherms and saturation curves for various systems (the Lennard-Jones model, different lattice gases, and real substances with simple nonpolar molecules as well as complex polar ones) confirms the approximate universality of the proposed reduced variables for temperature, pressure, and density at subcritical gaseous states up to the saturation point. In addition, the temperature dependence of the correspondingly scaled second virial coefficients also appears similar for various systems.

DOI: 10.1103/PhysRevE.102.042130

I. INTRODUCTION

The search for some universal equation of state, which could describe the behavior of various substances in one qualitatively and quantitatively general manner, has a long history. The principle of corresponding states was first introduced by van der Waals and its approximate nature as well as serious restrictions on its applicability was the subject of subsequent studies: In fact, the corresponding-states behavior deviates significantly (see Fig. 1) for different classes of fluids, such as classical simple fluids with nonpolar molecules (inert gases, nitrogen, oxygen, etc.), simple polar fluids (water, short-chain alcohols), nonclassical fluids (low-temperature hydrogen and helium), and complex hydrocarbons, however, separately within a certain class, the scaling by critical parameters and some extensions of this approach work well enough [1–6]. Furthermore, the ideas of universality based on scale invariance and scaling transformations have played an important role in the statistical theory of second-order phase transitions and critical phenomena [7,8].

As to the statistical description of condensation phenomena (i.e., first-order phase transitions), some success has been achieved recently on the basis of Mayer's cluster expansion [13], which can be considered as qualitatively general, though, on the quantitative level, it yields different results for various substances. The studies of the long-known consequences of Mayer's approach [14–17] (virial expansions in terms of reducible and irreducible cluster integrals [13]—integrals specific for a certain interaction potential) as well as the relatively new equation of state [18–20] in terms of irreducible integrals have finally established a strict definition for the saturation point that is general for all classical fluids and even quantum systems [21,22]: The condensation begins exactly at the divergence point of the virial expansions in powers of activity (in terms of reducible cluster integrals) where the isothermal bulk modulus of the virial expansion in powers of density (in terms of irreducible integrals) vanishes.

Thus, theoretically, the saturation density and saturation activity are now both expressed in terms of Mayer's cluster integrals, but any practical quantitative application of such a theory to a certain fluid remains problematic due to technical difficulties of calculating the corresponding sets of cluster integrals—sets which, on the one hand, must include the integrals to very high orders (to guarantee the accuracy) and, on the other hand, significantly differ for various substances (because their microscopic and interaction parameters vary). In this situation, any possible findings in generalizing the behavior of cluster integrals for various systems and therefore simplifying the practical application of the theory could be very useful.

One step in this direction was made recently in Ref. [23]. There, a simple method to reproduce subcritical isotherms was proposed for real substances and model fluids up to their saturation point based on very limited theoretical or empirical information: Only the value of saturation activity and the set of several irreducible integrals of lowest orders can define the subcritical behavior of various systems with high accuracy.

Here, we logically follow up the above-mentioned studies of Mayer's cluster expansion and provide a possible explanation for the universality discovered in the latter work [23] by introducing another dimensionless form of virial expansions that should describe the subcritical behavior of absolutely different thermodynamic systems in a similar way even on a quantitative level. Namely, performed calculations indicate that the correspondingly scaled (in the proposed reduced variables) isotherms and saturation curves are very close for simple statistical models and a wide range of real fluids (with simple nonpolar molecules as well as complex polar ones).

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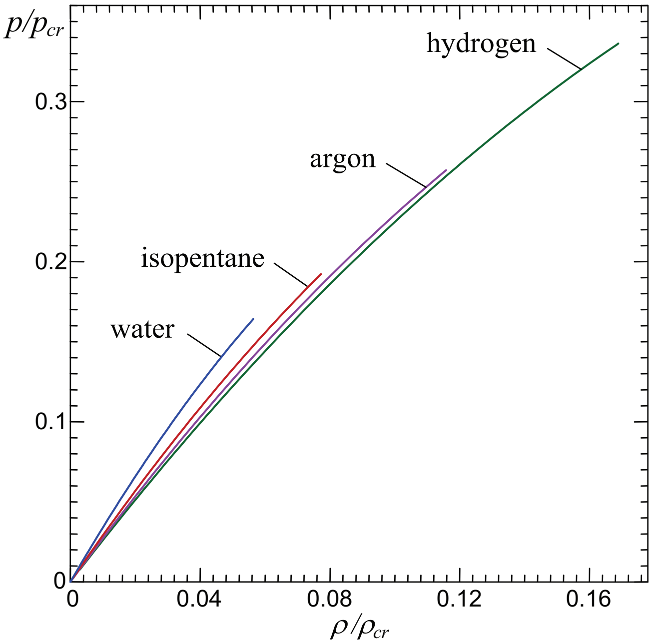

FIG. 1. Isotherms of various fluids (water [9], isopentane [10], argon [11], hydrogen [12]) at $T = 0.8T_{\rm cr}$ scaled by using the critical parameters.

II. THEORETICAL BACKGROUND

A direct consequence of Mayer's cluster expansion for the grand partition function (i.e., at the thermodynamic limit) is the well-known pair of virial expansions for pressure and particle-number density [13,24],

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

in powers of *activity*

$$z = \lambda^{-3} \exp\left(\frac{\mu}{k_BT}\right), \tag{2}$$

where μ is the chemical potential and $\lambda = h/\sqrt{2\pi m k_B T}$ is the de Broglie wavelength. In contrast to the conventional modern interpretation of dimensionless activity, Mayer's activity in Eqs. (1) and (2) means the particle-number density of the ideal gas with the same chemical potential at the same temperature.

The power coefficients in Eq. (1) are the so-called *reducible cluster integrals* and, at the thermodynamic limit, they form the correspondingly huge (almost infinite) set $\{b_n(T, V)\}$, which is strictly defined by the interaction potential in the considered thermodynamic system: Each b_n in this set is the integral of a certain complex function (the function of interaction potential and temperature) over the configuration phase space of n molecules (and hence it depends on temperature and system volume).

Theoretically, Mayer's expansion and Eq. (1) (hereafter, we denote this parametrical virial equation of state in terms of activity as VEOSA) have no restriction on applicability. Under some modifications in the structure of cluster integrals $\{b_n\}$, they must be valid for any multicomponent system with an arbitrarily complex nonpairwise interaction potential, though practical computations of high-order integrals remain technically problematic even for the simplest statistical models of single-component fluids.

In order to additionally simplify the calculations of cluster integrals, they are usually treated as volume independent (i.e., the actual integration limits over the system volume are replaced by infinite limits). This simplification makes the VEOSA absolutely inapplicable in condensed states of matter, but its effect on the VEOSA adequacy remains negligible at any density below the boiling point [25]. In addition, the mentioned infinite limits of integration allow defining any reducible cluster integral $b_n(T)$ in terms of more simple *irreducible cluster integrals* $\{\beta_k(T)\}$ of orders from $k = 1$ to $k = n - 1$,

$$b_n = n^{-2} \sum_{\{j_k\}} \prod_{k=1}^{n-1} \frac{(n\beta_k)^{j_k}}{j_k!}, \tag{3}$$

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

$$\sum_{k=1}^{n-1} k j_k = n - 1. \tag{4}$$

This relationship between the $\{b_n\}$ and $\{\beta_k\}$ sets allows Mayer's transformation of Eq. (1) (VEOSA) into a simpler (and therefore more famous) form [13]: the virial expansion for pressure in powers of density,

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

which is usually called the virial equation of state (VEOS).

It is important to note that Mayer's transformation of VEOSA (1) into VEOS (5) has an additional restriction on its validity (besides the above-mentioned simplification of infinite integration limits): VEOS (5) adequately represents the behavior of Mayer's expansion only at densities below a specific value ρ_S, which corresponds to the point where the isothermal bulk modulus of the VEOS vanishes,

$$\sum_{k\geqslant 1} k\beta_k \rho_S^k = 1. \tag{6}$$

Later and more rigorous approaches to Mayer's expansion in terms of irreducible integrals [18,20,24] have no restriction on density (except that the simplification of infinite integration limits becomes invalid in condensed states [25]) and indicate the strict constancy of pressure beyond the ρ_S point.

On the one hand, this fact turns Eq. (6) into a general theoretical condition for the saturation density ρ_S, but, on the other hand, its practical quantitative usage unfortunately yields results of unsatisfactory accuracy: Though irreducible integrals are simpler than the reducible ones, their calculation remains technically limited by relatively low orders, even for the simplest models of matter [26–32]. In order to be accurate enough, Eq. (6) must include the $\{\beta_k\}$ set with irreducible integrals of orders up to hundreds or thousands, which is technically impossible at the moment, and even the modern approximations for such large sets [33,34] still yield results quantitatively far from perfect.

Some success has been achieved here by studying the divergence behavior of VEOSA (1) [15,16,35,36]. The matter is that even a limited set of irreducible integrals (i.e., the $\{\beta_k\}$ set truncated at some low order, $k_{\max}$) always defines the infinite set of corresponding reducible integrals $\{b_n\}$ in Eqs. (3) and (4): Actually, each correct b_n must be constructed of a full set of irreducible integrals, $\{\beta_1, \beta_2, \dots, \beta_{n-1}\}$, however, it has a certain nonzero value even for a truncated initial set, $\{\beta_1, \beta_2, \dots, \beta_{k_{\max}}, 0, 0, 0, \dots\}$. Therefore, such an infinite activity series in VEOSA (1) may diverge at some activity z_S, even in cases when the corresponding VEOS (5) is truncated and always converging.

The exact relation between the VEOSA convergence radius z_S and saturation density in Eq. (6), ρ_S, was presented in Mayer's transformation of VEOSA (1) into VEOS (5) [13,15],

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

Thus, the constancy of pressure beyond the ρ_S point is due to the VEOSA divergence [15,16] exactly at the $z_S(\rho_S)$ value of activity (the jump of density at some constant chemical potential is a sign of the first-order phase transition) at subcritical temperatures [when Eq. (6) has at least one real positive root ρ_S, and hence Eq. (7) for $z_S(\rho_S)$ is also valid].

Of course, the incompleteness of the known $\{\beta_k\}$ sets (in the practice of calculations even for the widely used statistical models, they are usually truncated at low orders, as it is stated above) greatly affects the accuracy of the resulting z_S and $\{b_n\}$. On the other hand, the direct mathematical relation [37] between the convergence radius of some power series and its power coefficients directly relates the asymptotics of high-order reducible integrals to the VEOSA convergence radius z_S,

$$\lim_{n\to\infty}(n^2 b_n) = z_S^{-(n-1)}. \tag{8}$$

This relation (8), which was additionally proved for various models in Ref. [16], has finally allowed a correction of high-order cluster integrals in cases when the actual value of saturation activity is known: The incorrect reducible integrals [i.e., defined in Eqs. (3) and (4) on the basis of some truncated $\{\beta_k\}$ set] may be scaled [23,36] so that they would correspond to the true saturation activity instead of the incorrect one [i.e., defined in Eqs. (6) and (7) on the basis of the same truncated $\{\beta_k\}$ set].

III. A UNIVERSAL REDUCED FORM OF VIRIAL EXPANSIONS

The above-mentioned approach to correct the set of reducible integrals cardinally improved the accuracy of VEOSA (1) for some model systems with theoretically defined values of saturation activity [36] as well as other fluids (model and absolutely real ones) with experimentally established values of $z_S(T)$ [23]. Moreover, this approach can be further generalized by scaling the virial expansions themselves in a manner that they would yield quantitatively similar results for various systems.

A possible way to transform VEOSA (1) is to make its variable (activity) dimensionless by using the constant (at a certain temperature) value of saturation activity (which is additionally the convergence radius z_S),

$$x = \frac{z}{z_S}. \tag{9}$$

In turn, this transformation of the VEOSA variable requires the corresponding transformation of its power coefficients $\{b_n\}$. In order to make them dimensionless, let us introduce a *scaled reducible integral* of the nth order,

$$a_n = b_n z_S^{n-1}. \tag{10}$$

Therefore, VEOSA (1) takes the following form of a dimensionless power series for dimensionless pressure and density in powers of the reduced activity x [see Eq. (9)],

$$\left.\begin{aligned} w &= \tfrac{P}{z_S k_B T} = \sum_{n=1}^{\infty} a_n x^n, \\ y &= \tfrac{\rho}{z_S} = \sum_{n=1}^{\infty} n a_n x^n. \end{aligned}\right\} \tag{11}$$

It is important to note that the first-order reducible integral (which is always equal to identity) remains untransformed with regard for Eq. (10),

$$a_1 \equiv b_1 \equiv 1,$$

and this fact makes Eq. (11) [let us hereafter denote this reduced form of VEOSA (1) as RVEOSA] absolutely identical for all ideal gases or real substances in dilute regimes ($b_{n>1} \equiv 0$ for any substance without molecular interactions).

In addition, the asymptotic behavior of scaled reducible integrals $\{a_n\}$ must also be identical for all possible systems at subcritical temperatures,

$$\lim_{n\to\infty}(n^2 a_n) = 1,$$

in accordance with Eqs. (8) and (10), and hence the RVEOSA convergence radius (the scaled activity of phase transition),

$$x_S \equiv 1,$$

at any subcritical temperature regardless of the actual microscopic properties of the considered macroscopic systems.

All these features should significantly reduce the dependence of RVEOSA (11) (and therefore the dependence of reduced pressure, $w = \frac{P}{z_S k_B T}$, and reduced density, $y = \frac{\rho}{z_S}$) on the temperature and chemical composition of systems in subcritical regimes: The first power coefficient (a_1) and high-power coefficients ($a_{n\gg 1}$) in both series of the RVEOSA are certainly constant, so only the remaining low-order coefficients may indeed depend on the temperature and interaction parameters.

Moreover, the proposed transformation of VEOSA (1) into RVEOSA (11) automatically leads to the transformation of VEOS (5) into the following relation between the reduced density y and reduced pressure w,

$$w = \frac{P}{z_S k_B T} = y\left(1 - \sum_{k\geqslant 1}\frac{k}{k+1}\alpha_k y^k\right), \tag{12}$$

where the scaling of each irreducible integral,

$$\alpha_k = \beta_k z_S^k, \tag{13}$$

exactly corresponds to the scaling of any reducible integral in Eq. (10) [see Eq. (3) taking condition (4) into account]. A logical abbreviation for Eq. (12) (as a reduced form of the VEOS) is RVEOS, and any α_k in Eq. (13) may be called a *scaled irreducible integral* of the kth order.

It should be remembered that RVEOS (12) is theoretically adequate only at regimes beneath the point y_S where its isothermal bulk modulus vanishes [see Eq. (6)],

$$\sum_{k\geqslant 1} k\alpha_k y_S^k = 1,$$

and the same point must be considered as the *reduced saturation density*.

A similar scaling for more rigorous equations in terms of irreducible integrals [18,20,24] does not change the form of the RVEOS except that the reduced pressure w must be constant beyond the y_S point. Unfortunately, the accuracy of the y_S density in the last equation is directly related to the accuracy and completeness of the corresponding $\{\alpha_k\}$ set, and computations of high-order scaled irreducible integrals seem no simpler technically than the computations of nonscaled ones, $\{\beta_k\}$. In contrast to the reducible integrals (scaled or not), the asymptotics of high-order irreducible ones remains unexplored, though Eq. (7) takes a somewhat simpler form for the scaled $\{\alpha_k\}$ set,

$$y_S \exp\left(-\sum_{k\geqslant 1} \beta_k y_S^k\right) = 1.$$

IV. THE “HOLE-PARTICLE” SYMMETRY OF LATTICE GASES

A statistical model of matter, which is widely used in the theory of phase transitions, is the so-called *lattice gas*. There, the particles are restricted to occupy individual sites of a regular space lattice that makes the configuration phase space of a system discrete, and therefore all the corresponding statistical integrals turn into some exact sums. A special interest in this model was due to its formal mathematical relation to the Ising problem [38–40]: By using Onsager's solution for a two-dimensional ferromagnetic at a zero external field [41,42], Lee and Yang [43,44] obtained the exact parameters of the gas-liquid phase transition for a lattice gas, where each particle has a hard core and attracts other particles only in the four closest neighbor sites of the two-dimensional square lattice.

Later, the “hole-particle” symmetry [45] (when empty cells can statistically be treated as some particles) has allowed deriving the following virial expansions for dense regimes of various lattice gases with a hard core [45,46]: the expansion “symmetrical” to VEOS (5) (hereafter referred to as SVEOS),

$$\frac{P}{k_BT} = \rho_0\left(\frac{u_0}{k_BT} + \ln\left(\frac{\rho_0}{\rho'}\right) + \sum_{k\geqslant 1} \beta_k \rho'^k\right) + \rho'\left[1 - \sum_{k\geqslant 1} \frac{k}{k+1}\beta_k \rho'^k\right], \tag{14}$$

in powers of the “hole number density,”

$$\rho' = \rho_0 - \rho,$$

and expansions “symmetrical” to the VEOSA (1) (hereafter referred to as SVEOSA),

$$\left.\begin{aligned} \tfrac{P}{k_BT} &= \rho_0\left(\tfrac{u_0}{k_BT} + \ln\tfrac{\rho_0}{\eta}\right) + \sum_{n\geqslant 1} b_n \eta^n, \\ \rho &= \rho_0 - \sum_{n\geqslant 1} n b_n \eta^n, \end{aligned}\right\} \tag{15}$$

in powers of the “reciprocal activity,”

$$\eta = \frac{\rho_0^2}{z}\exp\left(2\frac{u_0}{k_BT}\right), \tag{16}$$

where u_0 is the potential energy per particle in the close-packing state and ρ_0 is the particle number density in the same close-packing state.

Recently, an exact analytical expression has been derived for the phase-transition activity of lattice gases [17],

$$z_S = \rho_0 \exp\left(\frac{u_0}{k_BT}\right), \tag{17}$$

and this expression is especially important in this paper because it concretizes RVEOSA (11) and RVEOS (12) for lattice gases and allows transforming of SVEOSA (15) and SVEOS (14) into the following simpler reduced forms (SRVEOSA and SRVEOS, respectively),

$$\left.\begin{aligned} w &= \frac{P\exp\left(-\frac{u_0}{k_BT}\right)}{\rho_0 k_BT} = \sum_{n=1}^{\infty} a_n x'^n - \exp\left(-\tfrac{u_0}{k_BT}\right)\ln x', \\ y' &= \left(1 - \tfrac{\rho}{\rho_0}\right)\exp\left(-\tfrac{u_0}{k_BT}\right) = \sum_{n=1}^{\infty} n a_n x'^n, \end{aligned}\right\} \tag{18}$$

$$w = y'\left(1 - \sum_{k\geqslant 1}\frac{k}{k+1}\alpha_k y'^k\right) + \exp\left(-\frac{u_0}{k_BT}\right)\left(\sum_{k\geqslant 1}\beta_k y'^k - \ln y'\right), \tag{19}$$

where

$$x' = \frac{1}{x}$$

is the reduced reciprocal activity [see Eq. (16)].

An essential feature of SRVEOSA (18) and SRVEOS (19), which cardinally distinguishes them from RVEOSA (11) and RVEOS (12), is that they *must yield certainly different results for various lattice gases* due to the presence of the exponential function at their right-hand sides—a function which explicitly involves the model parameter u_0. Thus, although similar “symmetrical” high-density expansions are now absent for continuous models of matter or real substances, the example of lattice gases obviously indicates that, as proposed in Sec. III, the scaling of pressure and density into the reduced parameters w and y *can indeed be general only at subcritical gaseous states up to the saturation point*: The mentioned scaling should certainly yield different results for different systems in condensed (liquid or solid) regimes.

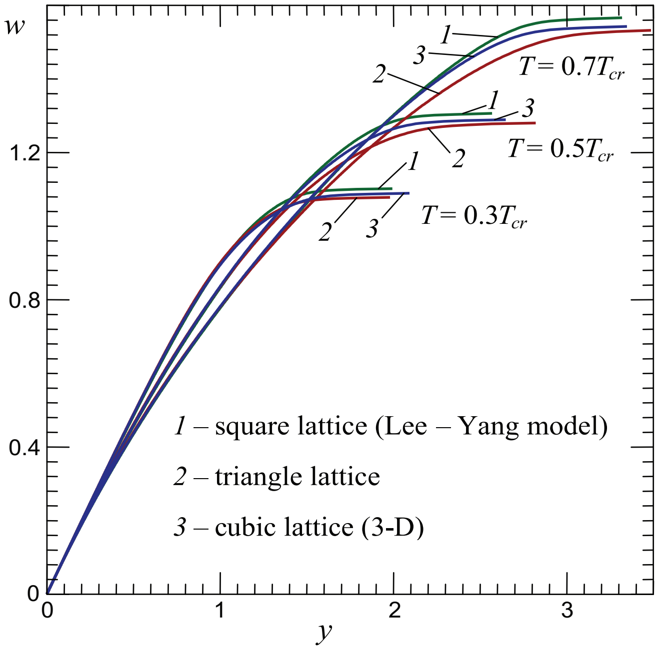

FIG. 2. Isotherms of RVEOSA (11) in reduced variables $w(y)$ for various lattice gases at different temperatures (in units of the critical one, $T_{\rm cr}$).

V. UNIVERSALITY OF SUBCRITICAL ISOTHERMS FOR REAL AND MODEL GASES

In order to check how the scaled virial expansions behave for essentially different lattice gases, the corresponding calculations have been performed for the following three models: a two-dimensional square lattice where each particle attracts the others only in the four closest neighbor sites (the Lee-Yang model [43]); a two-dimensional triangle lattice where the attraction is only for six neighbors at the hexagon vertices; and a three-dimensional cubic lattice where only the six closest neighbors are attracted. In all three cases, the calculations were based on the $\{\beta_k\}$ set including the first three irreducible integrals, $\{\beta_1, \beta_2, \beta_3\}$, known for each model as analytical functions of temperature [36,46]. First, this $\{\beta_k\}$ set was scaled into the corresponding $\{\alpha_k\}$ by using Eq. (13) and the z_S from Eq. (17), and then the scaled reducible integrals $\{a_n\}$ were calculated up to the order $n_{\rm max} = 10\,000$ by using the method proposed in Ref. [36] to guarantee the correct asymptotics of high-order integrals (the only difference from that method is that the convergence radius is always equal to the identity for the scaled virial series).

Some results of the described calculations are presented in Fig. 2. An important feature that can be seen in this figure is the *relatively* weak dependence on temperature: It should be noted that, within the presented temperature interval, the nonscaled values of pressure and density on the corresponding isotherms of nonscaled VEOSA (1) differ by several orders that, in turn, force the logarithmic scales to be used in analogous figures [35,36,46].

Another important aspect concerns the similarity of the results for various lattice-gas models. Although the temperature dependence becomes somewhat weaker (as it is stated above), it still cannot be neglected and, thus, the proposed approach requires a choice of some universal reduced temperature to make possible any comparison among the different models. A natural choice can be the temperature relative to the critical one because it agrees with the principle of corresponding states, and Fig. 2 indicates the validity of such a choice. Unfortunately, the exact critical temperature is known for the Lee-Yang model only, but approximate evaluations of critical temperatures for the other two models confirm the fact that the scaled isotherms of various lattice gases are quantitatively similar at similar values of the reduced temperature, $t = T/T_{\rm cr}$.

Of course, RVEOSA (11) does not differ from VEOSA (1) in essence, except that the former is technically much more convenient due to avoiding the computer operations with too small or big floating-point numbers: Even at the vicinity of the divergence point, its high-order terms are close to identity. Actually, exactly the same results can be obtained by using the VEOSA instead of the RVEOSA with the following scaling of the results to the corresponding reduced units, and similar considerations are valid for the pair of VEOS (5) and RVEOS (12).

Moreover, it has been shown recently [23] that the practical usage of VEOSA (1) can essentially be simplified when the saturation activity z_S is explicitly known: There is no need to calculate the actual huge set of reducible integrals $\{b_n\}$. Instead, only a dozen or two dozen of such integrals can be calculated on the basis of some known $\{\beta_k\}$ set, and the corresponding simplified VEOSA (1) would sufficiently well describe all the gaseous states ($z \leqslant z_S$) up to the saturation point ($z = z_S$). Beyond the saturation point the isotherms become flat, which corresponds to the divergence of true VEOSA (1). The same considerations are valid for RVEOSA (11): Its simplified option may involve only a few dozen scaled reducible integrals $\{a_n\}$ and would be applicable at all $x \leqslant 1$ [the actual divergence of true RVEOSA (11) at $x = 1$ means that all the high-order scaled reducible integrals are simply equal to identity].

Nevertheless, *the main advantage* that we see in the presented transformation of VEOSA (1) and VEOS (5) into RVEOSA (11) and RVEOS (12) is that the logic of this transformation has led us to the above-mentioned reduced units themselves. In fact, this logic means that *any adequate equation of state for gaseous subcritical regimes of any system must yield quantitatively similar results when they expressed in the following reduced temperature, pressure, and density*,

$$\left.\begin{aligned} t &= \frac{T}{T_{\rm cr}},\\ w &= \frac{P}{z_S k_B T} = \frac{P}{f_S},\\ y &= \frac{\rho}{z_S}. \end{aligned}\right\} \qquad (20)$$

There, f is the conventionally defined *fugacity* (i.e., the pressure of the corresponding ideal gas with the same chemical potential at the same temperature), and $f_S(T)$ is the value of this fugacity at the saturation point.

In order to check whether the proposed scaling for temperature, pressure, and density in Eq. (20) indeed yields similar results for substantially different statistical models and real substances, we have simply scaled the existing theoretical and empirical dependences. In particular, Fig. 3 demonstrates

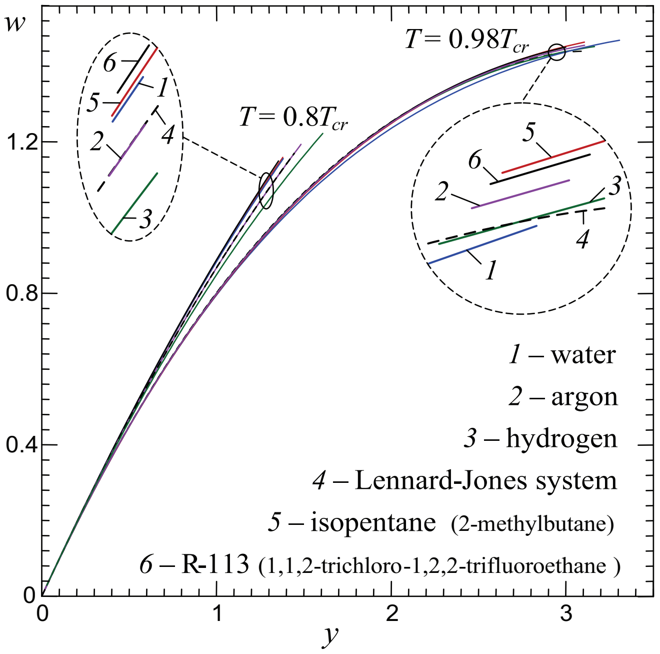

FIG. 3. Isotherms of various substances in reduced variables $w(y)$.

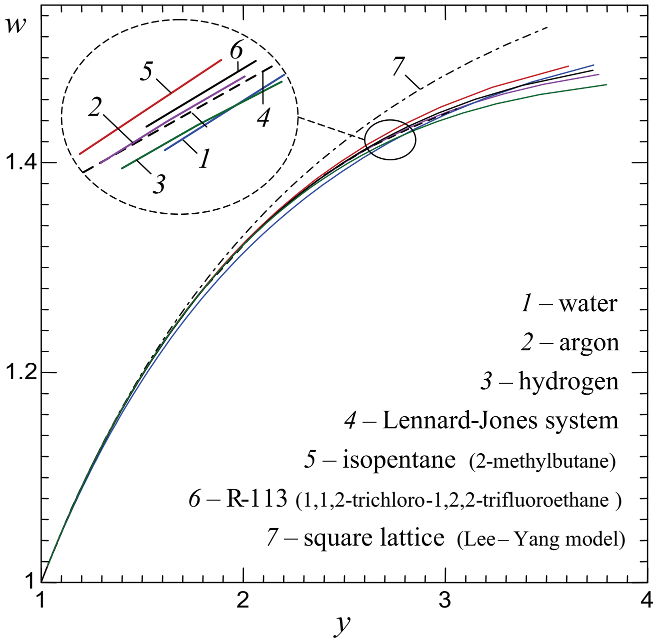

FIG. 4. Saturation curves of various substances in reduced units $w(y)$.

the scaled isotherms of various real substances whose experimental data are available from the National Institute of Standards and Technology (NIST): water [9] (an essentially polar fluid), isopentane [10], refrigerant-113 [47] (complex hydrocarbons), argon [11] (a simple nonpolar fluid), and hydrogen [12] (a fluid which can hardly be considered as classical). In Fig. 3, there are also isotherms of the most widely used statistical model of matter (the Lennard-Jones fluid [48,49]), whose data are known from numerical simulations [50]. The scaling essentially reduces the temperature dependence (for example, the nonscaled saturation parameters of isopentane vary by six to seven orders within the temperature interval from its triple point to the critical one). At similar values of reduced temperature, $t = T/T_{\text{cr}}$, all the isotherms in Fig. 3 are expectedly close to each other, in contrast to the isotherms presented in Fig. 1 which are scaled in accordance with the principle of corresponding states. For the same systems, Fig. 4 demonstrates the similarity of their saturation curves in reduced variables $w(y)$, defined by Eq. (20) (for comparison, the scaled theoretical saturation curve of the Lee-Yang lattice gas [43] is also presented in this figure). It is quite expected that the deviations among different saturation curves increase at the vicinity of the critical point where the role of high-order virial coefficients becomes important.

Although the discrete statistical model of lattice gases fundamentally differs from any factual conception on the structure of real substances (and hence the results obtained for this model agree with the others at a somewhat lower level), the overall similarity observed for absolutely different systems directly indicates a certain universality of the proposed reduced variables in Eq. (20).

Returning to the Mayer cluster-based approach, this observed similarity indicates that not only the asymptotics of high-order Mayer's cluster integrals, $\{b_n(T/T_{\text{cr}})\}$, is universal [as it is guaranteed by their scaling into the $\{a_n(T/T_{\text{cr}})\}$ set in Eq. (10)], but also the low-order integrals should behave similarly for various thermodynamic systems when they are scaled properly.

Of course, real molecular interactions can hardly be considered as exactly pairwise additive (especially for some real fluids, whose data are presented in Figs. 3 and 4). However, any possible nonadditivity of the actual interaction potential imposes no fundamental restriction on the applicability of Mayer's cluster expansion in general and the proposed scaling in particular. As it was already stated in Sec. II, the nonadditivity can only complicate the structure of reducible cluster integrals [namely, Eq. (3) must be modified essentially in order to account for this nonadditivity], but there are some techniques [51], even saving the conventional terminology as to the "irreducible integrals" (though the definition of such "nonadditive" irreducible integrals and corresponding virial coefficients naturally becomes more complex).

As it has been shown recently [23], at temperatures below the critical one, the main contribution to virial expansions belongs to the second virial coefficient $B_2 = -\beta_1/2$ (where β_1 is the first-order irreducible integral), up to the saturation point, and the role of other virial coefficients (i.e., the irreducible integrals of higher orders) becomes leading only at the saturation point itself. Therefore, at least the second virial coefficient should behave similarly for various systems when it is scaled into the corresponding dimensionless form $A_2 = -\alpha_1/2$ [where α_1 is the scaled first-order irreducible integral—see Eq. (13)], and Fig. 5 demonstrates the explicit similarity of the $A_2(T/T_{cr})$ dependences for various systems, whose data are presented in Figs. 3 and 4 and are based on the above-mentioned sources.

This fact can partially explain the universality found in Ref. [23] that only two quantities (the saturation activity z_S and second virial coefficient B_2) define the subcritical

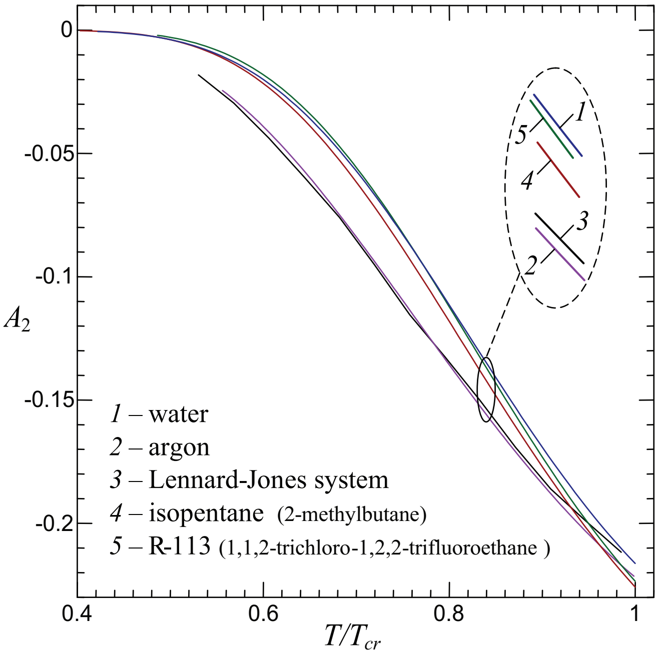

FIG. 5. The scaled second virial coefficient ($A_2 = -\alpha_1/2$) of various substances.

behavior of various systems with high accuracy. Moreover, the present study indicates that only one of the mentioned quantities appears sufficient to approximately describe the subcritical behavior of various gases up to their saturation point because the other quantity is automatically defined by the observed and approximately universal $A_2(T/T_{\text{cr}}) = B_2 z_S$ dependence.

From this point of view, the second virial coefficient may be considered as some base quantity which mainly defines the curvature of subcritical isotherms (their deviation from the ideal-gas isotherms), but it also defines the saturation parameters (and therefore the high-order virial coefficients at temperatures below the critical one) in some complex and still unexplored manner that is a potentially important issue of molecular physics and statistical mechanics.

VI. CONCLUSIONS

Based on the latest achievements of Mayer's cluster-based approach, the reduced forms of the well-known virial expansions have been derived [see RVEOSA (11) and RVEOS (12)] in terms of the correspondingly scaled reducible and irreducible cluster integrals [see Eqs. (10) and (13), respectively].

The main goal of such a transformation was to minimize the effect of parameters specific for each thermodynamic system, thus making the resulting reduced expansions quantitatively universal. In particular, the proposed scaling makes the convergence radius of reduced virial expansions equal to the identity and independent on temperature or microscopic parameters of different systems that guarantees the similarity of the condensation processes in those systems whereas saving the universal behavior of the original virial expansions in dilute regimes (the ideal-gas regimes).

The example of lattice-gas models, where the symmetrical high-density virial expansions are valid for condensed states, has allowed establishing a serious restriction on the considered universality: The above-mentioned scaling may yield similar results for different systems in gaseous subcritical regimes only, and, at condensed states of matter, the results should be specific for each system.

The performed scaling of isotherms and saturation curves for various systems (the Lennard-Jones model, different lattice gases, and real substances with simple nonpolar molecules as well as complex polar ones) has confirmed the approximate universality of the proposed reduced variables for temperature, pressure, and density [see Eq. (20)] at subcritical gaseous states up to the saturation point.

Moreover, the universal behavior of the correspondingly scaled second virial coefficients has been observed for various systems that additionally expands a range of possible practical applications of the proposed scaling.

ACKNOWLEDGMENT

The work was funded by the Ministry of Education and Science of Ukraine (Grant No. 0120U102051).

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[1] K. S. Pitzer, J. Chem. Phys. **7**, 583 (1939).
[2] E. A. Guggenheim, J. Chem. Phys. **13**, 253 (1945).
[3] M. G. Noro and D. Frenkel, J. Chem. Phys. **113**, 2941 (2000).
[4] P. Orea, A. Romero-Martínez, E. Basurto, C. A. Vargas, and G. Odriozola, J. Chem. Phys. **143**, 024504 (2015).
[5] V. C. Weiss, J. Chem. Phys. **144**, 234502 (2016).
[6] M. Fugel and V. C. Weiss, J. Chem. Phys. **146**, 064505 (2017).
[7] J. Cardy, *Scaling and Renormalization in Statistical Physics*, Cambridge Lecture Notes in Physics (Cambridge University Press, Cambridge, U.K., 1996).
[8] L. P. Kadanoff, *Statistical Physics: Statics, Dynamics and Renormalization* (World Scientific, Singapore, 2000).
[9] W. Wagner and A. Pruss, J. Phys. Chem. Ref. Data **31**, 387 (2002).
[10] E. W. Lemmon and R. Span, J. Chem. Eng. Data **51**, 785 (2006).
[11] C. Tegeler, R. Span, and W. Wagner, J. Phys. Chem. Ref. Data **28**, 779 (1999).
[12] J. W. Leachman, R. T. Jacobsen, S. G. Penoncello, and E. W. Lemmon, J. Phys. Chem. Ref. Data **38**, 721 (2009).
[13] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1977).
[14] M. V. Ushcats, Phys. Rev. E **87**, 042111 (2013).
[15] M. V. Ushcats, L. A. Bulavin, V. M. Sysoev, and S. Y. Ushcats, Phys. Rev. E **96**, 062115 (2017).
[16] S. Ushcats, M. Ushcats, L. Bulavin, O. Svechnikova, and I. Mykheliev, Pramana **91**, 31 (2018).
[17] M. V. Ushcats, L. A. Bulavin, and S. Y. Ushcats, Phys. Rev. E **98**, 042127 (2018).
[18] M. V. Ushcats, Phys. Rev. Lett. **109**, 040601 (2012).
[19] M. V. Ushcats, J. Chem. Phys. **138**, 094309 (2013).

[20] V. M. Bannur, Physica A **419**, 675 (2015).
[21] T. P. Suresh and K. M. Udayanandan, Turk. J. Phys. **42**, 668 (2018).
[22] T. P. Suresh and K. M. Udayanandan, Pramana **94**, 26 (2020).
[23] M. V. Ushcats and L. A. Bulavin, Phys. Rev. E **101**, 062128 (2020).
[24] M. V. Ushcats, L. A. Bulavin, V. M. Sysoev, V. Y. Bardik, and A. N. Alekseev, J. Mol. Liq. **224**, 694 (2016).
[25] M. V. Ushcats, S. Y. Ushcats, L. A. Bulavin, and V. M. Sysoev, Phys. Rev. E **98**, 032135 (2018).
[26] J. K. Singh and D. A. Kofke, Phys. Rev. Lett. **92**, 220601 (2004).
[27] M. V. Ushcats, Ukr. J. Phys. **59**, 172 (2014).
[28] M. V. Ushcats, Ukr. J. Phys. **59**, 737 (2014).
[29] M. V. Ushcats, J. Chem. Phys. **140**, 234309 (2014).
[30] M. V. Ushcats, S. J. Ushcats, and A. A. Mochalov, Ukr. J. Phys. **61**, 160 (2016).
[31] R. J. Wheatley, Phys. Rev. Lett. **110**, 200601 (2013).
[32] C. Feng, A. J. Schultz, V. Chaudhary, and D. A. Kofke, J. Chem. Phys. **143**, 044504 (2015).
[33] M. V. Ushcats, J. Chem. Phys. **141**, 101103 (2014).
[34] A. J. Schultz and D. A. Kofke, Fluid Phase Equilib. **409**, 12 (2016).
[35] M. V. Ushcats, L. A. Bulavin, V. M. Sysoev, and S. Y. Ushcats, Ukr. J. Phys. **62**, 533 (2017).
[36] S. Ushcats, M. Ushcats, V. Sysoev, and D. Gavryushenko, Ukr. J. Phys. **63**, 1066 (2018).
[37] J. Hadamard, J. Math. Pures Appl. **8**, 101 (1892).
[38] E. Ising, Z. Phys. **31**, 253 (1925).
[39] R. Baxter, *Exactly Solved Models in Statistical Mechanics*, Dover Books on Physics (Dover, New York, 2007).
[40] A. Isihara, *Statistical Physics* (Academic, New York, 1971).
[41] B. Kaufman, Phys. Rev. **76**, 1232 (1949).
[42] L. Onsager, Phys. Rev. **65**, 117 (1944).
[43] C. N. Yang, Phys. Rev. **85**, 808 (1952).
[44] T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).
[45] M. V. Ushcats, Phys. Rev. E **91**, 052144 (2015).
[46] M. V. Ushcats, L. A. Bulavin, V. M. Sysoev, and S. J. Ushcats, Phys. Rev. E **94**, 012143 (2016).
[47] W. Wagner, A. Pruß, and V. Marx, *Neue Zustandsgleichungen für R12, R22, R11 und R113: Beschreibung des thermodynamischen Zustandsverhaltens bei Temperaturen bis 525 K und Drücken bis 200 MPa, Reihe 19, Wärmetechnik/Kältetechnik, Fortschritt-Berichte VDI*, Vol. 57 (VDI-Verlag, Düsseldorf, 1992).
[48] J. Lennard-Jones, Proc. R. Soc. London, Ser. A **106**, 441 (1924).
[49] J. Lennard-Jones, Proc. R. Soc. London, Ser. A **106**, 463 (1924).
[50] A. Lotfi, J. Vrabec, and J. Fischer, Mol. Phys. **76**, 1319 (1992).
[51] R. Hellmann and E. Bich, J. Chem. Phys. **135**, 084117 (2011).