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Divergence of activity expansions: Is it actually a problem?

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For realistic interaction models, which include both molecular attraction and repulsion (e.g., Lennard-Jones, modified Lennard-Jones, Morse, and square-well potentials), the asymptotic behavior of the virial expansions for pressure and density in powers of activity has been studied taking power terms of high orders into account on the basis of the known finite-order irreducible integrals as well as the recent approximations of infinite irreducible series. Even in the divergence region (at subcritical temperatures), this behavior stays thermodynamically adequate (in contrast to the behavior of the virial equation of state with the same set of irreducible integrals) and corresponds to the beginning of the first-order phase transition: the divergence yields the jump (discontinuity) in density at constant pressure and chemical potential. In general, it provides a statistical explanation of the condensation phenomenon, but for liquid or solid states, the physically proper description (which can turn the infinite discontinuity into a finite jump of density) still needs further study of high-order cluster integrals and, especially, their real dependence on the system volume (density).

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I. INTRODUCTION

Analytical studies of first-order phase transitions have a long history. For statistical mechanics, this problem has turned out to be particularly challenging. There are only two specific statistical examples of the condensation phenomenon: the Lee-Yang solution for a two-dimensional lattice gas [1,2] (a discrete model with a realistic interaction potential, i.e., the potential, which includes both repulsion and attraction), and the van der Waals–Maxwell equation of state [3,4] (a mean-field model). Unfortunately, more general statistical approaches, based on the local particle-distribution functions [5] as well as various approximations for the system partition function or its expansions in powers of a small parameter [6], could not describe the condensation even qualitatively.

In particular, the well-known problem of statistical mechanics is the divergence of the virial series in powers of activity and density. Mayer's cluster expansion [7] transforms the partition function to a complex sum of integrals. Additional summation at the thermodynamic limit ($N \to \infty$; $V \to \infty$) for the corresponding grand partition function yields the equation of state,

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

where the quantity

$$z = \lambda^{-3} \exp\left(\frac{\mu}{k_B T}\right)$$

is the activity (or, sometimes, fugacity) related to the chemical potential μ and de Broglie wavelength $\lambda = h/\sqrt{2\pi m k_B T}$, and $\{b_n\}$ are the so-called reducible cluster integrals defined in accordance to the actual interaction potential (see their detailed definition in Mayer's book [7]).

It should be noted that Eq. (1), is an exact representation of the grand partition function (its logarithm as the series for pressure and the derivative of the logarithm as the series for density) in terms of the cluster integrals and activity, provided that the set $\{b_n\}$ is also exact and completely known. In the case of a more general (and complex) definition of the cluster integrals $\{b_n\}$, Eq. (1) remains formally correct even for nonadditive interactions and multicomponent systems [7].

From this point of view, a possible divergence of the infinite series for pressure and density in Eq. (1) at some real finite value of activity can hardly be interpreted as the true behavior of the grand partition function: the divergence in the negative direction corresponds to the vanishing of the partition function, and the divergence in the positive direction corresponds to the divergence of the partition function itself, but both these options have no physical meaning.

The general mathematical properties of this divergence (or, conversely, the corresponding convergence conditions) have been studied for decades [5,8–12]. However, the actual behavior of the pressure and density series at the vicinity of the divergence point remains almost unknown due to the difficulty of evaluating the complete (or a large enough) set $\{b_n\}$ for a certain interaction model.

It is shown here that the real nature of such mathematical divergence in Eq. (1), for realistic models of matter at subcritical temperatures does not actually contradict thermodynamic laws and has an obvious statistical meaning, which directly indicates the beginning of the condensation process. Moreover, the nonphysical behavior of Eq. (1), in very dense states (liquid or solid states beyond the condensation region) can also be clearly explained as the result of some simplifications in evaluating the macroscopic (thermodynamic size) cluster integrals.

Even in dense states of a fluid, each reducible integral b_n for a microscopic cluster of n molecules ($n \ll N$) in a macroscopic system ($N \to \infty$) can exactly be expressed (for a single-component system with the interaction energy independent of the internal exited states of molecules) in terms

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of the irreducible integrals $\{\beta_k\}$ [7],

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

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

$$\sum_{k=1}^{n-1} k\, j_k = n - 1. \tag{2a}$$

Each irreducible cluster integral β_k in Eq. (2) is directly related to the corresponding virial coefficient, i.e., the power coefficient of the well-known pressure expansion in powers of density (virial equation of state, VEOS) [7]. There is great experience accumulated in calculation of virial coefficients that in principle allows evaluation of the reducible integrals $\{b_n\}$, but the direct use of relation (2) [along with condition (2a)] can hardly be implemented in practice for high-order integrals.

On the other hand, Eqs. (2) and (2a) may be transformed to much more effective and convenient expressions,

$$b_n = \frac{A_{n,n-1}}{n^2}, \tag{3}$$

where

$$A_{n,i} = n \sum_{k=1}^{i} \frac{k}{i} \beta_k A_{n,i-k}, \quad A_{n,0} = 1.$$

Although this recursive algorithm cannot be considered absolutely new (it may be found, in somewhat different forms, in a number of studies [13–17]), it has not yet been used to investigate the large series of Eq. (1).

For any known set of irreducible integrals $\{\beta_k\}$, Eq. (3) allows the evaluation of the corresponding reducible integrals $\{b_n\}$ to an arbitrary large order, which, in turn, provides the opportunity to study the true behavior of Eq. (1) (in fact, the behavior of the grand partition function, where the molecular interactions are accurately or approximately defined by the full or truncated set of irreducible integrals $\{\beta_k\}$), and check the adequacy of the VEOS with the corresponding (full or truncated) set of virial coefficients.

Such calculations were performed by using the different sets of virial coefficients known for various realistic interaction models (e.g., Lennard-Jones [20–22], modified Lennard-Jones [23,24], Morse [25], and square-well [26] potentials). In all these cases, the subcritical isotherms of Eq. (1) (with the activity series truncated at very high orders), demonstrate a similar behavior (see Fig. 1): once the isothermal bulk modulus vanishes at some density ρ_C, it stays constant at any higher density, i.e.,

$$\left(\frac{\partial P}{\partial \rho}\right)_{\rho \geqslant \rho_C} \equiv 0.$$

This behavior fundamentally differs from that of the VEOS isotherms, which can have a negative bulk modulus (thermodynamically forbidden) and an interval similar to the "van der Waals loop" (for set $\{\beta_k\}$ truncated at low orders).

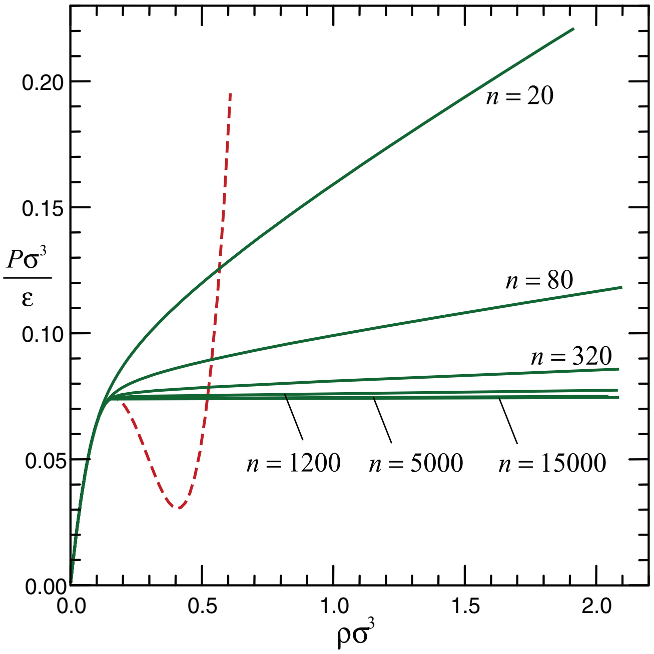

FIG. 1. Isotherms of Eq. (1) truncated at different orders n (solid lines) and one isotherm of the VEOS (dotted line). Virial coefficients in the VEOS and reducible integrals in Eq. (1) are calculated on the basis of the first three irreducible integrals $\{\beta_1, \beta_2, \beta_3\}$ for the Lennard-Jones model [18,19] at subcritical temperature $T = 1.28\varepsilon/k_B$ (ε and σ are the parameters of the Lennard-Jones model).

Mayer's derivation of the VEOS is limited by the convergence condition of the series $\sum n^2 b_n z^n$ [7,27–29],

$$z \leqslant z_C = \rho_C \exp\left(-\sum_{k\geqslant 1} \beta_k \rho_C^k\right), \tag{4}$$

where ρ_C is defined in the equation

$$\sum_{k\geqslant 1} k\beta_k \rho_C^k = 1 \tag{5}$$

as the density (mentioned above), where the isothermal bulk modulus of the VEOS or Eq. (1), vanishes (up to this density, there is no difference between these equations). Thus, the VEOS as a conventional and more convenient "substitute" for Eq. (1), can be adequate only in the region where Eq. (1), converges (i.e., at any density lower than ρ_C), which puts the issue of the activity series convergence at the forefront (in contrast to the convergence of the VEOS itself).

In accordance with the Cauchy-Hadamard theorem, the series for pressure and density in Eq. (1), are both diverging (and the results of calculations additionally confirm that behavior) at the divergence point of the series $\sum n^2 b_n z^n$ [the activity z_C defined in Eq. (4) or the density ρ_C defined in Eq. (5)]. However, the coefficient n in the series for the density makes it increase much more rapidly than the pressure in the vicinity of z_C. At the thermodynamic limit ($n \to \infty$), such divergence of Eq. (1), causes a jump (discontinuity) of the density under constant values of pressure and activity (chemical potential), which corresponds to the thermodynamic signs of the first-order phase transition.

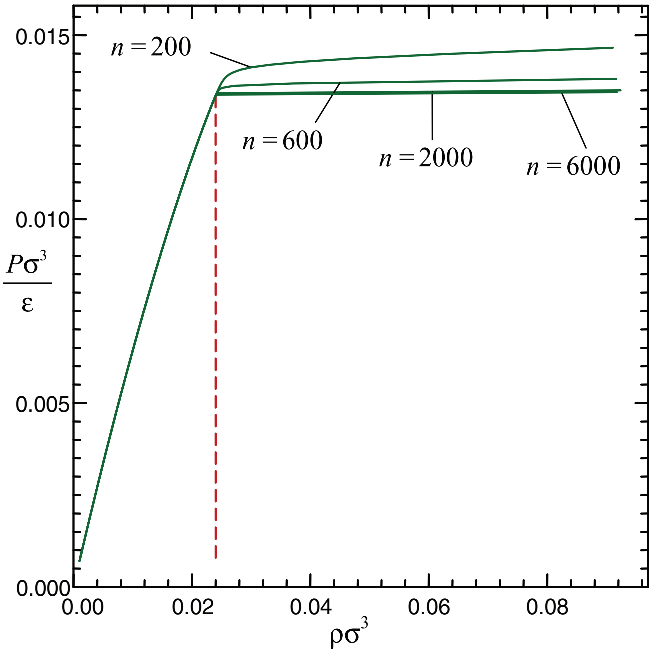

FIG. 2. Isotherms of Eq. (1) truncated at different orders n (solid lines) and one isotherm of the VEOS truncated at order $i = 6000$ (dotted line). Virial coefficients in the VEOS and reducible integrals in Eq. (1) are calculated on the basis of the extrapolation [30] for the modified Lennard-Jones model [31,32] at subcritical temperature $T = 0.7\varepsilon/k_B$.

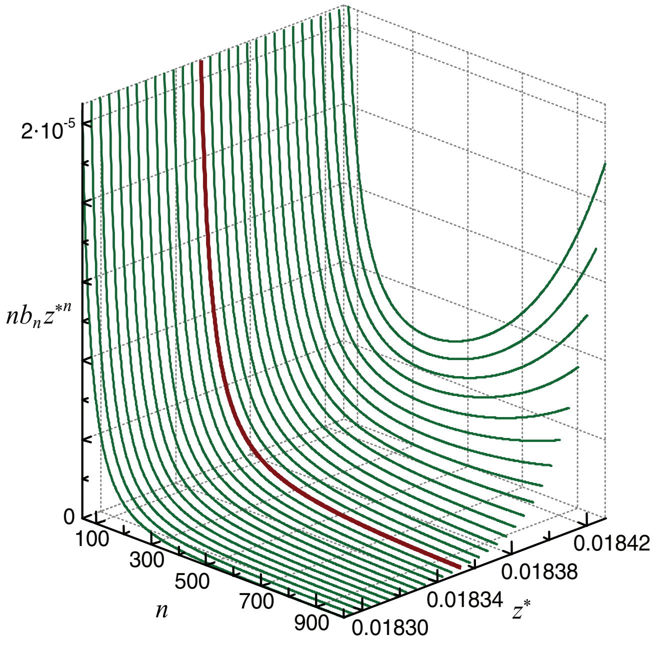

FIG. 3. Contributions to the density series of Eq. (1) for terms $(nb_n z^{*n})$ of various orders n at different activities ($z^* = z\sigma^3$). The bold red line corresponds to the divergence activity z_C defined in Eq. (4). Reducible integrals in the series and z_C are calculated on the basis of the first six irreducible integrals $\{\beta_1,\beta_2,\beta_3,\beta_4,\beta_5,\beta_6\}$ for the Morse model (the parameter of that model $\alpha\sigma = 4.0$) [36] at subcritical temperature $T = 0.8\varepsilon/k_B$.

For a number of realistic interaction models an extrapolation of the virial coefficients was proposed [25,30], which allows the evaluation of the reducible integrals $\{b_n\}$ on the basis of the infinite set of irreducible ones $\{\beta_k\}$ (i.e., allows the calculation of each b_n with regard to all its irreducible parts up to the order $k = n - 1$). It makes the isotherms of Eq. (1), qualitatively similar to the real isotherms in the vicinity of the condensation point ρ_C (as a dry saturated point): the tangent of the isotherms has a discontinuity there (see Fig. 2). Recently, another extrapolation has been proposed for the virial coefficients of the Lennard-Jones model [33]. Although it quantitatively yields somewhat different results, the qualitative behavior of the corresponding theoretical isotherms remains the same.

It is important to note that the observed behavior of Eq. (1), agrees exactly with that of equations (not based on the VEOS) where the dependence on activity is excluded: in terms of reducible cluster integrals [13] (for finite systems) and irreducible integrals [27–29,34,35] (for finite as well as thermodynamic systems).

However, in contrast to these equations, the present approach provides an obvious statistical interpretation of the condensation phenomenon. The divergence of a series always means the principal increase in its high-order terms. In dilute states ($z < z_C$; $\rho < \rho_C$), the value of different terms ($nb_n z^n$) is a monotonically decreasing function of the order n (see Fig. 3) and, hence, the determinative contribution to the partition function (logarithm of the grand partition function and its derivative) belongs to the smallest (microscopic) clusters. When the activity exceeds the z_C defined in Eq. (4) [and the density exceeds the ρ_C defined in Eq. (5)], the contribution function becomes increasing for high orders (in Fig. 3, this function is shown for large but finite orders). For the grand partition function of a real thermodynamic system ($N \to \infty$), the contribution of the largest clusters ($n \to \infty$) rapidly becomes essential exactly at the point z_C that causes the discontinuity of density in Eq. (1), beyond the ρ_C. Therefore, the condensation begins when the statistical weight of high-order cluster integrals turns to an increasing function of the order.

Moreover, if the reducible integrals for the largest (macroscopic) clusters stay constant (similarly to the microscopic ones), the density discontinuity is essential (to infinity) and the condensation process cannot stop (pressure and activity also stay constant even when $\rho \to \infty$).

Actually, the constancy of reducible integrals [their definition by Eqs. (2) and (2a) for the infinite macroscopic volume] can only be adequate for the microscopic clusters (and, therefore, in dilute states, when $\rho < \rho_C$). For the macroscopic clusters, whose contribution cannot be neglected when condensation begins ($\rho \geqslant \rho_C$), any changes in the system volume automatically mean considerable changes in the integration limits; each high-order cluster integral must be a certain function of the volume (or density). This makes the relation between the reducible and the irreducible integrals [i.e., Eqs. (2) and (2a) or Eq. (3)] incorrect for large clusters in the condensation region, and furthermore, the definition of irreducible integrals becomes irrelevant there: any β_k of a microscopic cluster stays volume independent, while the corresponding β_k (of the same order k) belonging to a macroscopic cluster must depend on the volume.

The compression first affects the long-distance positive (i.e., attractive) part of the integrands (products of Mayer's functions [7]), and it, in turn, must reduce the value of the high-order cluster integrals or even change their sign. Only these changes of the power coefficients in Eq. (1) can transform the essential (infinite) discontinuity of the density into a jump (finite) discontinuity (i.e., stop the condensation at some high density—the boiling point) and cause the increasing pressure (as well as activity) in denser states (liquid or solid) in a certain balance of molecular attraction and repulsion.

Of course, the presented analysis cannot be considered a complete statistical theory of condensation. It just demonstrates a possible general way to describe the physical phenomenon of condensation based on statistical mechanics. The most important conclusion is that the cluster-based statistical approach, in general, and Eq. (1), in particular, stay absolutely adequate in all states of matter—from gaseous to liquid (or solid), including the phase-transition region—and any nonphysical features of their behavior can only be due to some simplifications or approximations used for the evaluation of the corresponding cluster integrals [namely, all the equations obtained before in terms of the irreducible integrals or virial coefficients [27–29,34,35] use such simplification of the infinite volume in Eq. (2)].

Thus, the construction of a rigorous statistical theory for first-order phase transitions should be focused on the equations in terms of the reducible cluster integrals (instead of the equations in terms of the irreducible ones, which cannot describe the boiling point in principle). This theory also needs further thorough studies to provide accurate data on high-order reducible integrals and, especially, their real dependence on the volume or density.

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