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Virial and high-density expansions for the Lee-Yang lattice gas

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On the basis of the recently established "hole-particle" symmetry of the lattice-gas Hamiltonian, the high-density equation of state has been derived in a form of pressure and density expansions in powers of activity. This equation is proposed as an alternative and complementary to the previously obtained pressure expansion in powers of density. For the well-known Lee-Yang lattice-gas model (a two-dimensional square lattice with a square-well interaction potential), the power coefficients (i.e., cluster and irreducible cluster integrals) up to the seventh order have been evaluated as accurate functions of temperature. The convergence of the expansions in powers of both density and activity to the exact Lee-Yang solution is investigated.

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I. INTRODUCTION

The lattice gas is a widely known statistical model, where the particles are restricted to occupy individual sites of a regular space lattice. This restriction makes the configuration phase space of a system discrete while the momentum phase space stays continuous. Therefore, all important statistical integrals over the configuration phase space turn into corresponding exact sums, and this feature simplifies their evaluation for some specific examples.

On the basis of the lattice-gas model, essential success has been achieved in the theoretical description of phase transitions. Namely, Lee and Yang [1,2] have proved a strong mathematical relation of the lattice-gas model to the well-known Ising model of ferromagnetism [3–5]. Using Onsager's solution for a two-dimensional ferromagnetic at a zero external field [6,7], they obtained the exact pressure and densities of the gas-liquid phase transition for a square-lattice gas [2], where any particle has a hard core and attracts other particles only in the four closest neighbor sites. The corresponding interaction model may be formally expressed in terms of the following square-well potential,

$$u(r) = \begin{cases} \infty & (r = 0), \\ -\varepsilon & (0 < r \leqslant 1), \\ 0 & (r > 1), \end{cases} \tag{1}$$

where ε is the attractive-well depth, and the distance r is a dimensionless integer (relative to a space period of the lattice).

Unfortunately, even for this simple two-dimensional model, there is still no accurate solution at lower or higher densities, and, for more complex lattice models, an exact solution is absent. Except for an extremely limited number of analytical studies, the problems concerning lattice gases are usually resolved numerically.

Some of those analytical approaches use the mean-field [4] or other [8–11] approximations. In addition, there are a number of accurate methods based on finite-size lattice statistics [12–15]. A group of other theoretical treatments are based on a general rigorously grounded expansion for pressure known as the virial equation of state [16], which can be applied to a lattice gas as well as any other model of matter at low-density states. The symmetrical high-density expansions were also derived for some specific lattice-gas models [2,17–19]. Recently, a similar but more general expansion in powers of density has been proposed [20] for lattice gases of various interaction models, arbitrary geometry, and dimensions.

In the present paper, the corresponding high-density expansion in powers of activity is derived on the basis of the "hole-particle" symmetry of the lattice-gas model, and the convergence to the Lee-Yang solution (the phase-transition parameters) is investigated for the low- and high-density expansions in powers of activity and density. In Sec. II, the existing expansions in powers of density are considered and the regions of their adequacy are discussed. The derivation of the high-density expansion in powers of activity is presented in Sec. III. Section IV includes the tasks related to the application of the expansions to the Lee-Yang lattice-gas model, e.g., the calculation of the power coefficients. The last section is devoted to discussing results and drawing conclusions.

II. EXPANSIONS IN POWERS OF DENSITY

The conventional form of the virial equation of state [21] is an expansion in powers of density $\rho = N/V$,

$$\frac{P}{k_B T} = \rho\left(1 - \sum_{k\geqslant 1}\frac{k}{k+1}\beta_k\rho^k\right), \tag{2}$$

where the power coefficients β_k's are the so-called irreducible cluster integrals. Equation (2) has a number of rigorous statistical derivations [16,22–25] based on the assumption of low density. Some studies [26–29] have demonstrated a strong theoretical restriction,

$$\sum_{k\geqslant 1} k\beta_k\rho^k < 1, \tag{3}$$

for the virial equation at subcritical temperatures. In addition, those studies indicated that the boundary of condition (3), i.e., the minimum density violating the condition, should be interpreted as a condensation point (in the sense of the saturated vapor point).

Recently, Ushcats [20] has stated the "hole-particle" symmetry of the intermolecular interactions in the lattice-gas

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system. In accordance with his conclusions, the total interaction energy U of the system particles at any configuration is directly related to the interaction energy U' of the lattice holes,

$$U = Nu_0 - N'u_0 + U', \tag{4}$$

where u_0 is the potential energy of a particle in the close-packing state ($\rho = \rho_0$), when all its neighbor sites are occupied by other particles; $N' = N_0 - N$ is the number of holes; N_0 is the total number of sites in the lattice.

Mathematically, the energy U' is identical to U except that it is evaluated for the holes instead of particles, and thus the lattice holes can be treated as some pseudoparticles interacting similarly to the real particles. Relation (4) is especially convenient at dense states ($\rho \to \rho_0$), when the "hole density" ($\rho' = \rho_0 - \rho$) is low. Using the Mayer expansion [16] for the "hole partition function" at low values of the hole density, Ushcats derived the equation of state,

$$\frac{P}{k_BT} = \rho_0\left[\frac{u_0}{k_BT} + \ln\left(\frac{\rho_0}{\rho_0-\rho}\right) + \sum_{k\geqslant 1}\beta_k(\rho_0-\rho)^k\right] + (\rho_0-\rho)\left[1 - \sum_{k\geqslant 1}\frac{k}{k+1}\beta_k(\rho_0-\rho)^k\right], \tag{5}$$

symmetrical to Eq. (2) and applicable at dense states of a lattice gas. Its adequacy is theoretically limited by the condition

$$\sum_{k\geqslant 1} k\beta_k(\rho_0-\rho)^k < 1, \tag{6}$$

which is symmetrical to condition (3). As the boundary of condition (3) defines the saturated vapor point, the boundary of condition (6) defines the saturated liquid point. It should be noted that Eq. (5) contains the same irreducible integrals β_k's as those in Eq. (2).

Formally, both expansions (2) and (5) are exact at densities satisfying conditions (3) and (6), respectively, though, to be really accurate, they must contain an infinite set of irreducible integrals that is technically almost impossible at present. The evaluation of high-order irreducible integrals is usually a difficult computational problem even for the simplest models of molecular interaction, and, in practice, we may only use truncated (and hence approximated) expansions. Strictly saying, when the virial expansion is truncated at some finite order, we can never be sure of its accuracy even if this order is very high.

III. EXPANSIONS IN POWERS OF ACTIVITY

To improve our confidence in the results, experimental data or another solution of the same problem may be used for comparison. In particular, we can consider the pressure expansion in powers of activity [16] instead of Eq. (2) at low-density regimes.

In the classical Gibbs statistics, the pressure is related to the grand partition function Ξ,

$$PV = k_BT \ln \Xi, \tag{7}$$

and the particle number density is defined by the derivative of pressure with respect to the chemical potential

$$\rho = \left(\frac{\partial P}{\partial \mu}\right)_T. \tag{8}$$

Performing the integration over the momentum phase space separately, we can write the grand partition function as follows,

$$\Xi = \sum_{N=0}^{N_0}\frac{Q_N}{N!}z^N, \tag{9}$$

where $z = \lambda^{-3}\exp\left(\frac{\mu}{k_BT}\right)$ is the activity, and

$$Q_N = \int_{V^{(N)}} \exp\left(-\frac{U}{k_BT}\right)d\mathbf{r}^{(N)} \tag{10}$$

is the so-called configuration integral.

In the first half of the last century, Mayer and Goeppert Mayer [16] introduced the cluster expansion of the configuration integral

$$Q_N = N!\sum_{\{m_n\}}\prod_{n=1}^{N}\frac{(Vb_n)^{m_n}}{m_n!}, \tag{11}$$

where the summation is for all possible sets $\{m_j\}$ of N positive integers, such as $\sum_{n=1}^{N} nm_n = N$, and b_n is called the nth-order cluster integral. Any cluster integral b_n is expressed in terms of the irreducible integrals [see Eqs. (2) and (5)],

$$b_n = n^{-2}\sum_{\{j_k\}}\prod_{k=1}^{n-1}\frac{(n\beta_k)^{j_k}}{j_k!}, \tag{12}$$

where all possible integer sets $\{j_k\}$ must satisfy the condition $\sum_{k=1}^{n-1} kj_k = n-1$.

The cluster expansion (11) allows us to rewrite the grand partition function (9) at the thermodynamic limit ($N_0 \to \infty$),

$$\Xi = \exp\left(V\sum_{n=1}^{\infty} b_n z^n\right),$$

and Eqs. (7) and (8) yield the expansions for pressure and density in powers of activity:

$$\begin{aligned}\frac{P}{k_BT} &= \sum_{n\geqslant 1} b_n z^n\\ \rho &= \sum_{n\geqslant 1} nb_n z^n,\end{aligned} \tag{13}$$

which may be considered as a parametric equation of state alternative to the virial expansion in powers of density [Eq. (2)]. It is also known as the virial expansion in powers of activity (fugacity) but rarely used in comparison to Eq. (2) because of its relative complexity.

In accordance with the conclusions of Ref. [16] and the results of some recent studies [29], the infinite activity expansion (13) diverges at the density violating condition (3), and thus this condition should theoretically limit the adequacy of Eq. (13) as well as Eq. (2).

In order to obtain the symmetrical high-density expansion in powers of activity, the configuration integral (10) may be transformed to the integral over the configuration phase space of holes on the basis of relation (4),

$$\frac{Q_N}{N!}\rho_0^N = \frac{Q'_{N'}}{N'!}\rho_0^{N'} \exp\left[-\frac{u_0}{k_B T}(N - N')\right].$$

Therefore, the grand partition function in Eq. (9) acquires the form

$$\Xi = \left[\frac{\rho_0}{x}\exp\left(\frac{u_0}{k_B T}\right)\right]^{N_0} \sum_{N'=0}^{N_0} \frac{Q'_{N'}}{N'!} x^{N'}, \tag{14}$$

where

$$x = \frac{\rho_0^2}{z}\exp\left(2\frac{u_0}{k_B T}\right) \tag{15}$$

is reciprocal of activity, and

$$Q'_{N'} = \int \exp\left(-\frac{U'}{k_B T}\right) d\mathbf{r}^{(N')}$$

is the "hole configuration integral."

On the basis of the cluster expansion (11) for that configuration integral at low values of the hole density $\rho' = \rho_0 - \rho$, we may rewrite the grand partition function in Eq. (14) at the thermodynamic limit in terms of the cluster integrals and powers of the variable x defined in Eq. (15),

$$\Xi = \left(\frac{\rho_0}{x}\right)^{N_0} \exp\left(\frac{N_0 u_0}{k_B T}\right) \exp\left(V\sum_{n=1}^{\infty} b_n x^n\right).$$

Using Eq. (7) and evaluating the derivative in Eq. (8),

$$\rho = \left(\frac{\partial P}{\partial \mu}\right)_T = \left[\frac{\partial (P/k_B T)}{\partial (\ln z)}\right]_T = -x\left[\frac{\partial (P/k_B T)}{\partial x}\right]_T,$$

we finally establish the high-density equation of state

$$\begin{aligned} \frac{P}{k_B T} &= \rho_0\left(\frac{u_0}{k_B T} + \ln\frac{\rho_0}{x}\right) + \sum_{n\geqslant 1} b_n x^n \\ \rho &= \rho_0 - \sum_{n\geqslant 1} n b_n x^n \end{aligned} \tag{16}$$

as an expansion in powers of activity [or inverse activity—see the relation of z to x in Eq. (15)].

Equation (16) contains the infinite set of the cluster integrals b_n's completely identical to those in the low-density virial equation (13), and its adequacy must symmetrically be limited at high-density regimes by condition (6), guaranteeing the convergence of the corresponding series in powers of x.

IV. EVALUATION OF THE POWER COEFFICIENTS

The problem of calculating the irreducible integrals (or virial coefficients) has a long history. The multidimensional numerical integration involves great technical difficulties for the high-order integrals. The quadrature methods have allowed the computation of the virial coefficients to the fifth order [30,31]. The modern Mayer sampling Monte Carlo integration [32] and its modifications [33,34] have essentially improved the situation [35].

In case of a lattice gas, the numerical integration turns into the exact but laborious summation over a huge (for high-order integrals) number of discrete configurations. An additional problem arises, when the need for generating the correct set of irreducible graphs makes the integration algorithm too complex. The number of different irreducible graphs increases approximately as $2^{N(N-1)/2}/N!$ for the integral order N.

TABLE I. Irreducible cluster integrals β_k of various orders k's for the two-dimensional square-well potential (1).

k	$k\beta_k\rho_0^k$
1	$4f - 1$
2	$-12f^2 - 1$
3	$12f^4 + 40f^3 + 12f^2 - 1$
4	$-160f^5 - 220f^4 - 80f^3 - 1$
5	$60f^7 + 1380f^6 + 1704f^5 + 600f^4 + 40f^3 - 1$
6	$-1428f^8 - 10584f^7 - 13440f^6 - 5376f^5 - 588f^4 - 1$

An effective algorithm to evaluate the whole irreducible integral has been recently proposed by Wheatley [36]. The algorithm is actually based on Mayer's cluster expansion, i.e., Eqs. (11) and (12). At its first stage, the cluster integrand of b_N is evaluated by the direct calculation of the Q_N integrand and the other lower-order integrands ($b_{n<N}$) in a recursive procedure equivalent to Eq. (11). At the final, more laborious, stage of Wheatley's algorithm, the searched irreducible integrand $\beta_{k=N-1}$ is calculated on the basis of another recursive procedure equivalent to Eq. (12), which uses the b_N and lower-order irreducible integrands ($\beta_{k<N-1}$).

In fact, there is no need to perform the last step of Wheatley's algorithm at each configuration point. Only the Nth-order cluster integrand should be calculated [the first stage of the algorithm based on Eq. (11)] at all the points of the configuration phase space of N particles (in the present study, we actually used an even more simple procedure, calculating the Q_N and all possible $Q_{n<N}$ instead of $b_{n<N}$ at each point). The summation of the data over the entire configuration phase space yields the proper cluster integral b_N, and then the corresponding irreducible integral β_{N-1} can be directly evaluated on the basis of Eq. (12) by using the precalculated integrals of lower orders. This reinterpretation of Wheatley's algorithm essentially simplifies the calculations (at least in cases of a discrete exact summation).

TABLE II. Cluster integrals b_n of various orders n's for the two-dimensional square-well potential (1).

n	$n!b_n\rho_0^{n-1}$
1	1
2	$4f - 1$
3	$36f^2 - 24f + 2$
4	$24f^4 + 528f^3 - 600f^2 + 144f - 6$
5	$960f^5 + 9960f^4 - 17760f^3 + 7680f^2 - 960f + 24$
6	$1440f^7 + 38880f^6 + 224640f^5 - 598320f^4 + 402240f^3$ $-93600f^2 + 7200f - 120$
7	$110880f^8 + 1572480f^7 + 5453280f^6 - 22639680f^5$ $+21666960f^4 - 7922880f^3 + 1159200f^2 - 60480f + 720$

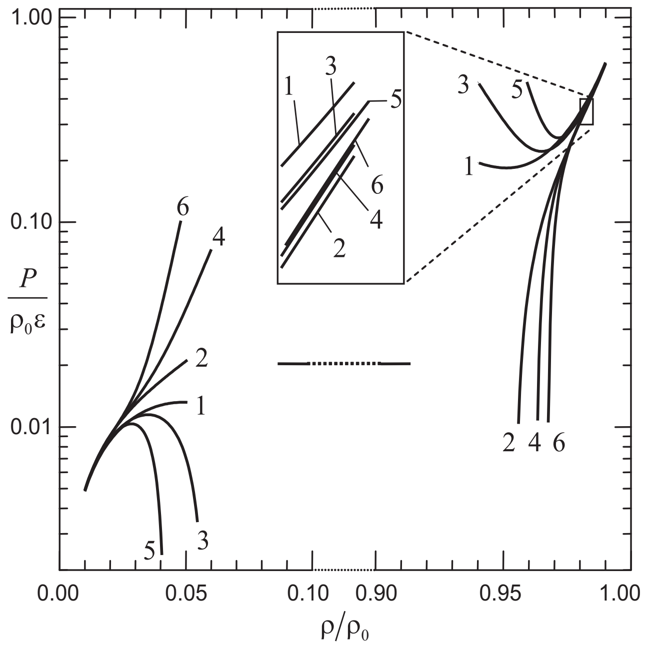

FIG. 1. The isotherms ($k_BT/\varepsilon = 0.54$) of Eq. (2) (left) and Eq. (5) (right) numbered in correspondence to the equation order. The horizontal line shows the Lee-Yang phase-transition region.

In addition, the simplicity of the square-well interaction potential in Eq. (1) removes the need for independent calculations for different temperatures. The two-particle integrand may only have the following three different values: -1 (the absolute repulsion); $f = \exp\left(\frac{\varepsilon}{k_BT}\right) - 1$ (Mayer's function for the attractive well); 0 (there is no interaction at larger distances). This feature allows the explicit evaluation of the integrals in the functional form, $b_n(f)$ and $\beta_k(f)$.

As a result, accurate temperature dependences (as a power series of Mayer's function f) have been obtained for the irreducible integrals to the sixth order (Table I) and cluster integrals to the corresponding seventh order (Table II) in the case of the two-dimensional square-well interaction model [see Eq. (1)].

In Fig. 1, the calculated isotherms are shown for the virial (2) and high-density (5) equations of state (expansions in powers of density) truncated at various orders. In turn, Fig. 2 demonstrates the isotherms of Eqs. (13) and (16) (expansions in powers of activity).

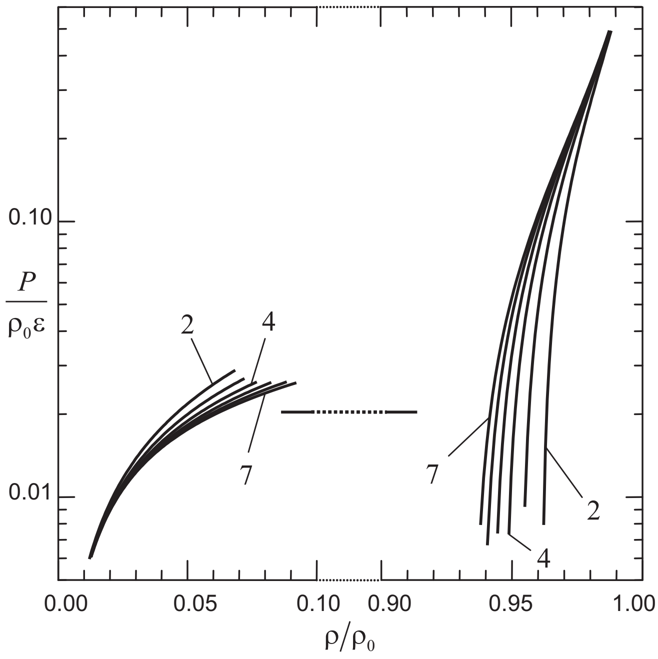

FIG. 2. The isotherms ($k_BT/\varepsilon = 0.54$) of Eq. (13) (left) and Eq. (16) (right) numbered in correspondence to the equation order. The horizontal line shows the Lee-Yang phase-transition region.

V. DISCUSSION AND SUMMARY

In the previous study [20], the high-density equation of state (5) was derived, and its combination with the low-density virial equation (2) was proposed as a general solution for the lattice gas (and therefore the Ising) problem. Formally, this solution is exact, but, in practice, its accuracy is limited because the set of power coefficients that can actually be evaluated is also very limited. In the present study, we propose another general high-density expansion in Eq. (16) that can be used together with the low-density expansion in Eq. (13) as an alternative and complementary solution.

Unfortunately, using any finite-order series, we cannot surely state the convergence or divergence for the expansions in powers of density as well as activity. Qualitatively, both types of expansions seem to converge to the exact Lee-Yang solution, but the nature and rates of their convergence differ fundamentally. As the order of Eqs. (13) and (16) increases, the activity expansions converge gradually and monotonically (Fig. 2). In contrast to the cluster integrals, the irreducible integrals oscillate in sign (see Table I), and the behavior of the corresponding alternating series in powers of density is more complex (Fig. 1). At first sight, the density expansions may even seem to be diverging, but, actually, their behavior is typical for other converging alternating series. For example, a finite-order expansion for the exponent of a negative argument behaves very similarly though it definitely converges for the infinite order. To roughly check the convergence, we should look at the middle region of the isotherms rather than their ends. There, the higher-order isotherms become closer to each other (see Fig. 1), and when the order increases, this region of convergence moves toward the Lee-Yang solution.

Another important issue concerns such a great difference between the expansions. In fact, the finite-order expansions in powers of density and activity would never be equivalent. They must coincide only for the infinite order. In accordance with Eq. (12), any cluster integral b_n consists of the irreducible ones of all lower orders ($\beta_{k<n}$). When we use the density expansions in Eqs. (2) and (5) truncated at some finite order k, we thus assume all the irreducible integrals of higher orders to vanish, but, for the corresponding activity series in Eqs. (13) and (16), it means that all the cluster integrals (even to infinite order) do not vanish. In this case, any higher-order cluster integral ($n > k + 1$) is just evaluated incorrectly because it includes the truncated set of irreducible integrals instead of the full set, but it does not vanish. Therefore, any truncated density expansion is always equivalent to the infinite activity expansion, where the set of cluster integrals is evaluated somewhat incorrectly. This infinite set may really be correct only for the infinite density expansion (the difference between the infinite expansions disappears).

It is hard to state surely which expansion is more accurate—the infinite but partially incorrect activity series (corresponding to the truncated density series) or the correct but truncated activity series (when the cluster integrals of higher orders are simply supposed to vanish). However, we may expect the exact solution somewhere between those two edge (and approximate in practice) solutions. We may also regard both solutions to be earnestly accurate in the regions where they coincide or differ slightly enough. Figure 3 indicates that these regions of accuracy expand for the low-density equations (2) and (13) as well as high-density equations (5) and (16) with the increasing of the equation order—their boundaries move toward the Lee-Yang solution at low temperatures and toward each other at high temperatures. It is also obvious that the accuracy of the seventh-order equations is still very limited.

Although the last sections of the paper concern only a particular example of the Lee-Yang model, the theoretical basis of the presented approach [i.e., the combinations of Eqs. (2) and (5) and Eqs. (13) and (16)] is general for lattice gases of arbitrary geometry and dimensions. The interaction model can also be much more complex than that in Eq. (1). It may include any finite attraction or repulsion at nonzero distances, and $u(\mathbf{r}_{ij})$ can even be anisotropic.

Further studies and additional information on the high-order cluster integrals for various lattice-gas models may help us to establish a certain regularity and evaluate the infinite virial series as it has recently been done for some continuous realistic models [37–39] that, in turn, would make the solutions really accurate in the future.

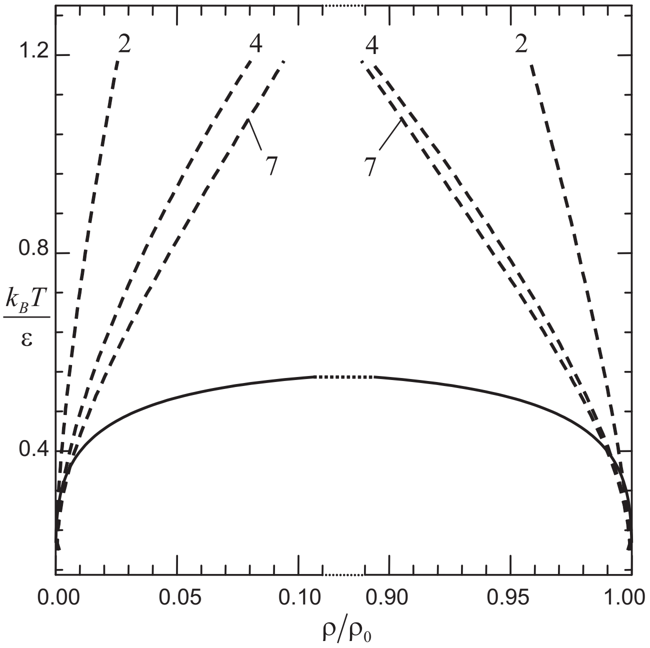

FIG. 3. The Lee-Yang coexistence curve (solid line) and loci of the 1% deviation between the expansions in powers of density and activity (dashed lines numbered in correspondence to the activity expansion order).

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