Cluster properties of the one-dimensional lattice gas: The microscopic meaning of grand potential

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(Received 30 October 2012; published 21 February 2013)

Using a concrete example, we demonstrate how the combinatorial approach to a general system of particles, which was introduced in detail in an earlier paper [Fronczak, Phys. Rev. E **86**, 041139 (2012)], works and where this approach provides a genuine extension of results obtained through more traditional methods of statistical mechanics. We study the cluster properties of a one-dimensional lattice gas with nearest-neighbor interactions. Three cases (the infinite temperature limit, the range of finite temperatures, and the zero temperature limit) are discussed separately, yielding interesting results and providing alternative proof of known results. In particular, the closed-form expression for the grand partition function in the zero temperature limit is obtained, which results in the nonanalytic behavior of the grand potential, in accordance with the Yang-Lee theory.

DOI: 10.1103/PhysRevE.87.022131 PACS number(s): 05.20.Gg, 02.10.Ox

I. INTRODUCTION

In our recent paper [1] (hereafter referred to as paper I), we started a line of theoretical research on imperfect gases and interacting fluids. We exploited concepts of enumerative combinatorics to deal with equilibrium systems in the infinite volume limit. The approach provides precise mathematical techniques relevant for studying phase transitions. In particular, we showed that the *perfect gas of clusters model* [2] underlying various cluster/droplet theories of phase transitions (see, e.g., [3] and references therein) emerges naturally from our approach. In the model, an imperfect fluid, which is made up of interacting particles, is considered an ideal gas of clusters at thermodynamic and chemical equilibrium. There is no potential energy of interaction between the clusters, and the clusters do not compete with each other for volume. The main conclusion drawn from the earlier paper was that the grand potential (the Landau free energy) of such a clustered system of interacting particles may be considered as the exponential generating function for the number of internal states (thermodynamic probability) of these clusters.

In this paper, we use the combinatorial approach described in paper I to analyze the properties of a one-dimensional lattice gas with nearest-neighbor interactions. The aim of this paper is twofold. First, we show in a specific case how our approach to interacting fluids works and where our approach provides a genuine extension of the results obtainable with more traditional methods. Second, we demonstrate with the first concrete example that the approach may provide important insights into the microscopic mechanisms that lead to phase transitions. Although phase transitions in the traditional sense are proved not to exist in the one-dimensional lattice gas investigated in this paper, the behavior at $T=0$ K seems to have direct bearing on the problem. To show this, we focus on the relation between thermodynamics and the cluster properties of lattice gas. The general question of this relation has been raised by various theories of phase transitions, in which geometric interpretation of the liquid-gas transition was shown to consist of the sudden formation of the macroscopic cluster. In the following, using an example of one-dimensional lattice gas, we show that our approach is well suited for handling such problems.

The outline of the paper is as follows. In Sec. II, we briefly review the results of paper I. Section III is devoted to a detailed description of the one-dimensional lattice gas model and its equivalence with the chain of Ising spins in the external magnetic field. In Sec. IV, methods described in Sec. II are used to study cluster properties of the lattice gas. The paper is concluded in Sec. V.

II. MICROSCOPIC MEANING OF GRAND POTENTIAL

A. Combinatorial approach to a general system of particles

In paper I, we considered a general system of interacting particles. The thermodynamic state of the system was given by the temperature T and the chemical potential per molecule, μ. Assuming that the classical treatment is adequate, we used the grand canonical ensemble to describe the open system in the infinite volume limit, $V\to\infty$. We showed that the grand partition function

$$\Xi(\beta,z)=\sum_{N=0}^{\infty}z^NZ(\beta,N)=1+\sum_{N=1}^{\infty}z^NZ(\beta,N) \quad (1)$$

$$=1+\sum_{N=1}^{\infty}z^N\int_0^{\infty}e^{-\beta E}g(E,N)dE, \quad (2)$$

where $\beta=(k_BT)^{-1}$, $z=e^{\beta\mu}$, $Z(\beta,N)$ is the canonical partition function of the system with N particles, $Z(\beta,0)=1$ represents the so-called vacuum state, and $g(E,N)$ stands for the density of states, can be written as

$$\Xi(\beta,z)=\exp[-\beta\ \Phi(\beta,z)] \quad (3)$$

$$=\exp\left[-\beta\sum_{m=1}^{\infty}\frac{z^m}{m!}\phi_m(\beta)\right] \quad (4)$$

$$=1+\sum_{N=1}^{\infty}\frac{z^N}{N!}\,B_N[\{w_n(\beta)\}] \quad (5)$$

$$=1+\sum_{N=1}^{\infty}\frac{z^N}{N!}\sum_{k=1}^{N}B_{N,k}[\{w_n(\beta)\}], \quad (6)$$

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where the coefficients $w_n(\beta)$ are given by the partial derivatives of the grand thermodynamic potential, $\Phi(\beta,z)$,

$$w_n(\beta) = -\beta\phi_n(\beta) = -\beta\left.\frac{\partial^n\Phi}{\partial z^n}\right|_{z=0}, \quad (7)$$

while $B_{N,k}(\{w_n\}) = B_{N,k}(w_1,w_2,\ldots,w_{N-k+1})$, and $B_N(\{w_n\}) = \sum_{k=1}^{N} B_{N,k}(\{w_n\})$ [with $B_0(\{w_n\}) := 0$] represent the incomplete and complete Bell polynomials, respectively.

The partial Bell polynomials in Eq. (6) are defined as

$$B_{N,k}[\{w_n(\beta)\}] = N!\sum\prod_{n=1}^{N-k+1}\frac{1}{c_n!}\left(\frac{w_n(\beta)}{n!}\right)^{c_n}, \quad (8)$$

where the summation takes place over all non-negative integers $c_n \geqslant 0$, such that the constraints $\sum_n c_n = k$ and $\sum_n nc_n = N$ hold. Given a combinatorial meaning of the Bell polynomials, we showed in paper I that when the coefficients $w_n(\beta)$ are all non-negative,

$$\forall_{n\geqslant 1}\; w_n(\beta) \geqslant 0, \quad (9)$$

the equality of the two series, given by Eqs. (2) and (6), give rise to the following formula:

$$\int_0^\infty f(k,E)g(E,N)e^{-\beta E}dE = \frac{1}{N!}B_{N,k}[\{w_n(\beta)\}], \quad (10)$$

where $f(k,E)$ is the probability that the system with energy E consists of k independent clusters. In addition, we showed that Eq. (10) describes the probability that a general system of N interacting particles at temperature T, regardless of its energy, consists of k clusters. It has been argued that the formula provides an alternative and strictly microscopic understanding of the grand thermodynamic potential, as the exponential generating function for the numbers of internal states, $w_n(\beta)$, of n clusters,

$$\Phi(\beta,z) = -\frac{1}{\beta}\ln\Xi(\beta,z) \quad (11)$$

$$= -\frac{1}{\beta}\sum_{n=1}^{\infty}\frac{w_n(\beta)}{n!}z^n. \quad (12)$$

Finally, in the earlier paper, we noted that comparing Eqs. (1) and (5) leads to a neat expression for the canonical partition function:

$$Z(\beta,N) = \frac{1}{N!}B_N[\{w_n(\beta)\}] \quad (13)$$

$$= \frac{1}{N!}\sum_{k=1}^{N}B_{N,k}[\{w_n(\beta)\}]. \quad (14)$$

The expression is valid regardless of whether the conditions for the perfect gas of clusters model, given by Eq. (9), are satisfied.

B. Perfect gas of clusters model

The microscopic meaning of the grand potential described in paper I directly relates to the perfect gas of clusters model (which is known from the classical theory of simple fluids [3]). In the model, we deal with a collection of noninteracting clusters, without knowing how we can build them as disjoint sets of interacting particles. In the infinite volume limit $V\to\infty$, the pressure, the density, and the cluster size distribution (the mean number of clusters of size n) are given by, respectively,

$$P = \frac{1}{\beta V}\sum_{n=1}^{\infty}Z_n(\beta,V)z^n, \quad (15)$$

$$\rho = \frac{1}{V}\sum_{n=1}^{\infty}nZ_n(\beta,V)z^n, \quad (16)$$

and

$$N_n(\beta,V) = Z_n(\beta,V)z^n, \quad (17)$$

where $Z_n(\beta,V)$ stands for the partition function that characterizes clusters of size n.

The relation between our results and the classical gas of clusters model [2] can be seen by first rewriting Eq. (15) in the following equivalent form:

$$\Phi(\beta,z) = -PV = -\frac{1}{\beta}\sum_{n=1}^{\infty}Z_n(\beta,V)z^n, \quad (18)$$

and then comparing Eq. (18) with the expression for the grand thermodynamic potential, given by Eq. (12), which raises the microscopic meaning of $\Phi(\beta,z)$. The comparison shows that the conditions given by Eq. (9) make our approach to a general system of interacting particles equivalent to the perfect gas of clusters model with

$$\lim_{V\to\infty}Z_n(\beta,V) = \frac{w_n(\beta)}{n!}. \quad (19)$$

III. ONE-DIMENSIONAL LATTICE GAS: SURVEY OF KNOWN RESULTS

Let us consider a one-dimensional periodic lattice that consists of V sites (in the model, V represents volume) and a collection of N particles. The particles occupy sites of the lattice with the restriction that not more than one particle can occupy a given lattice site and only particles on the nearest-neighbor sites interact. If we introduce the variable σ_i for each lattice site i, such that $\sigma_i = +1$ if the site is occupied and $\sigma_i = 0$ otherwise, then the total energy for a given configuration of particles $\{\sigma_i\}$ is

$$E_G(\{\sigma_i\}) = -\varepsilon\sum_{i=1}^{V}\sigma_i\sigma_{i+1}, \quad (20)$$

where $-\varepsilon$ is the interaction energy between two neighboring particles, the periodicity of the lattice is imposed by assuming that $\sigma_{V+1} = \sigma_1$, and

$$\sum_{i=1}^{V}\sigma_i = N. \quad (21)$$

To apply the general method described in Sec. II to investigate one-dimensional lattice gas, the first task is to find the grand partition function in the infinite volume limit, $V\to\infty$,

$$\Xi_G(\beta,V,z) = 1 + \sum_{N=1}^{V}z^N Z_G(\beta,V,N) \quad (22)$$

$$= 1 + \sum_{N=1}^{V}z^N\sum_{\{\sigma_i\}^*}e^{-\beta E_G(\{\sigma_i\})} \quad (23)$$

$$= \sum_{\{\sigma_i\}}\exp\left[\beta\varepsilon\sum_{i=1}^{V}\sigma_i\sigma_{i+1} + \beta\mu\sum_{i=1}^{V}\sigma_i\right], \quad (24)$$

where $Z_G(\beta,V,N)$ in Eq. (22) is the canonical partition function for this gas and the starred configurations $\{\sigma_i\}^*$ in the second sum of Eq. (23) are those for which the condition given by Eq. (21) holds. We exploit the mathematical equivalence between the grand partition function for lattice gas and the canonical partition function for the Ising model in the external magnetic field [4].

The one-dimensional Ising model consists of a chain of V spins, $s_i = \pm 1$, with the interaction energy in a given configuration $\{s_i\}$ given by

$$E_I(\{s_i\}) = -J\sum_{i=1}^{V} s_i s_{i+1} - H\sum_{i=1}^{V} s_i, \tag{25}$$

where J is the coupling constant between nearest neighbors, H is the external magnetic field, and $s_{V+1} = s_1$. The canonical partition function for the model can be written as

$$Z_I(\beta,V,H) = \sum_{\{s_i\}} e^{-\beta E_I(\{s_i\})} \tag{26}$$

$$= \sum_{\{s_i\}} \exp\left[\beta J\sum_{i=1}^{V} s_i s_{i+1} + \beta H\sum_{i=1}^{V} s_i\right]. \tag{27}$$

To show that Eqs. (24) and (27) are in fact equivalent, we merely have to note that the variable σ_i can be obtained from the variables s_i by writing

$$\sigma_i = \frac{s_i + 1}{2}. \tag{28}$$

By substituting (28) into (24), we get

$$\Xi_G(\beta,V,z) = e^{\beta C_G V} Z_I(\beta,V,H_G), \tag{29}$$

where

$$C_G = \frac{\varepsilon}{4} + \frac{\mu}{2}, \tag{30}$$

and

$$Z_I(\beta,V,H_G) = \sum_{\{s_i\}} \exp\left[\beta J_G\sum_{i=1}^{V} s_i s_{i+1} + \beta H_G\sum_{i=1}^{V} s_i\right] \tag{31}$$

is the Ising partition function, given by Eq. (27), with

$$J_G = \frac{\varepsilon}{4}, \quad H_G = \frac{\varepsilon + \mu}{2}. \tag{32}$$

Now, putting into Eq. (29) the well-known exact formula for the partition function of the closed Ising chain of V spins in the external magnetic field [5,6],

$$Z_I(\beta,V,H_G) = \lambda_+(\beta,H_G)^V + \lambda_-(\beta,H_G)^V \tag{33}$$

$$\overset{V\to\infty}{\simeq} \lambda_+(\beta,H_G)^V, \tag{34}$$

where

$$\lambda_\pm(\beta,H_G) = e^{\beta J_G}[\cosh(\beta H_G) \pm \sqrt{\sinh^2(\beta H_G) + e^{-4\beta J_G}}], \tag{35}$$

the grand partition function for one-dimensional lattice gas with nearest-neighbor interactions becomes, for $V \to \infty$,

$$\Xi_G(x,V,z) = [x\sqrt{z}\,\lambda_+(x,z)]^V, \tag{36}$$

where

$$x = e^{\beta\varepsilon/4}, \quad z = e^{\beta\mu}, \tag{37}$$

and

$$\lambda_\pm(x,z) = \frac{x^3\sqrt{z}}{2} + \frac{1}{2x\sqrt{z}} \pm \sqrt{\frac{x^6 z}{4} + \frac{1}{4x^2 z} + \frac{1}{x^2} - \frac{x^2}{2}} \tag{38}$$

corresponds to Eq. (35) but is written in the new variables x and z. Finally, inserting Eq. (36) into Eq. (11), we get the free energy of a one-dimensional lattice gas with nearest-neighbor interactions in the infinite volume limit,

$$\Phi_G(x,V,z) = -\frac{V}{\beta}\ln[x\sqrt{z}\,\lambda_+(x,z)]. \tag{39}$$

In Sec. IV, the results from this section are used to analyze cluster properties of the lattice gas model.

IV. CLUSTERS IN LATTICE-GAS MODEL

In this section, the combinatorial approach described in Sec. II is used to study the properties of the one-dimensional lattice gas model. In what follows, three cases (the infinite temperature, the range of finite temperatures, and the zero temperature limit) are discussed separately.

A. Infinite temperature limit

In the infinite temperature limit, we have

$$\lim_{T\to\infty}\beta = 0. \tag{40}$$

Therefore, since $\varepsilon = \text{const}$, one gets [see Eq. (37)]

$$\lim_{T\to\infty} x = 1, \tag{41}$$

and the expression for the grand partition function, given by Eq. (36), is simplified to

$$\Xi_G(x,V,z) = (1+z)^V. \tag{42}$$

Accordingly, the grand potential becomes

$$\Phi_G(x,V,z) = -\frac{V}{\beta}\ln(1+z). \tag{43}$$

Successive derivatives ϕ_n of the grand potential regarding z and evaluated at $z = 0$, given by Eq. (7), give the following closed-form expression for the Bell polynomial coefficients:

$$w_n(\beta) = V(n-1)!(-1)^{n-1}. \tag{44}$$

From the last expression, it is obvious that the parameters do not satisfy the conditions under which the gas is the ideal gas of clusters; cf. Eq. (9). By definition, lattice gas clusters are sets of neighboring particles. There is no energy of interaction between such clusters; cf. Eq. (20). However, due to the excluded volume effect, lattice gas clusters in some sense interact with each other, even if there is no direct interaction between the particles. The effect originates in the cluster-counting problem, and consists of the fact that two clusters of a given size once defined cannot approach close enough to one another to be counted, under the definition, as a single cluster. Consequently, only at small densities can lattice gas be considered a perfect gas of clusters.

Nevertheless, the case of one-dimensional lattice gas in the infinite temperature limit allows us to validate our combinatorial approach directly. By inserting the coefficients $\{w_n(\beta)\}$, given by Eq. (44), into the expression for the canonical partition function, given by Eq. (14), after some algebra, we get

$$Z_G(\beta,V,N) = \sum_{k=1}^{N} \frac{V^k(-1)^{N-k}}{N!} B_{N,k}(\{(n-1)!\}) \tag{45}$$

$$= \sum_{k=1}^{N} \frac{V^k(-1)^{N-k}}{N!} |s(N,k)| = \binom{V}{N}, \tag{46}$$

where $|s(N,k)|$ represents the signless (or unsigned) Stirling number of the first kind, $\binom{V}{N}$ stands for the binomial coefficient, and several basic combinatorial identities have been used, including properties of Bell polynomials ([7], pp. 133–137),

$$B_{N,k}(\{ab^n x_n\}) = a^k b^N B_{N,k}(\{x_n\}), \tag{47}$$

and

$$B_{N,k}(\{(n-1)!\}) = |s(N,k)|, \tag{48}$$

and identities involving Stirling numbers of the first kind [8], i.e., the relation between signed and unsigned Stirling numbers,

$$|s(N,k)| = (-1)^{N-k} s(N,k), \tag{49}$$

and its generating function,

$$\binom{V}{N} = \sum_{k=1}^{N} \frac{V^k}{N!} s(N,k). \tag{50}$$

The result, given by Eq. (46),

$$Z_G(\beta,V,N) = \binom{V}{N}, \tag{51}$$

is exactly the expected one. In the infinite temperature limit, all accessible microstates are equally probable. Therefore, the canonical partition function is just the number of microstates allowed, i.e., the number of ways to choose positions for N particles from the available V positions.

B. Finite temperatures

In the range of finite temperatures, for

$$0 < \beta < \infty, \quad 1 < x < \infty, \tag{52}$$

and for small particle densities,

$$\lim_{V\to\infty} \frac{N}{V} \ll 1, \tag{53}$$

we can directly test Eq. (10), which describes the probability that the gas of N particles, regardless of its energy, consists of k clusters. The expression holds exactly only for the ideal gas of clusters. In this case, however, although in general lattice gas does not satisfy the conditions specified by Eq. (9), given the small particle densities, the coefficients $w_n(\beta)$ are non-negative for a reasonable range of cluster sizes n. In addition, Eq. (10) seems to provide good approximation for cluster statistics.

The coefficients $w_n(\beta)$ of the Bell polynomials in Eq. (10),

$$w_1(\beta) = V, \tag{54}$$

$$w_2(\beta) = V(2x^4 - 3), \tag{55}$$

$$w_3(\beta) = V(6x^8 - 12x^4 + 10), \tag{56}$$

$$\dots$$

$$w_n(\beta) = V(n!x^{4(n-1)} - \dots), \tag{57}$$

and the polynomials can be easily calculated using MATHEMATICA (partial Bell polynomials are implemented in MATHEMATICA 9.0 as BellY). The normalized probability distribution $P(k)$ for the number of clusters k, that is, the right-hand side of Eq. (10) divided by Eq. (13),

$$P(k) = \frac{B_{N,k}(\{w_n(\beta)\})}{B_N(\{w_n(\beta)\})}, \tag{58}$$

is shown in Fig. 1 with Monte Carlo simulations of the one-dimensional conserved-order-parameter Ising model [9], which is often used to study the properties of lattice gases.

In the figure, we see that for $N,V = \text{const}$, the average number of clusters, and thus, the average cluster size, strongly depends on the temperature. At lower temperatures (for higher values of β), particles try to stay in clusters. Configurations $\{\sigma_i\}$ with a smaller number of large clusters are more likely to be observed than configurations with a large number of small clusters that are typical of higher temperatures.

C. Zero temperature limit

1. Nonanalyticity of the grand partition function

Van Hove's theorem [10,11] states that the limiting free energy, given by Eq. (12), characterizing one-dimensional gases with short-range interactions (such as the one considered in this study) is an analytic function for all real positive values of T. This statement excludes phase transitions for $T > 0$ K.

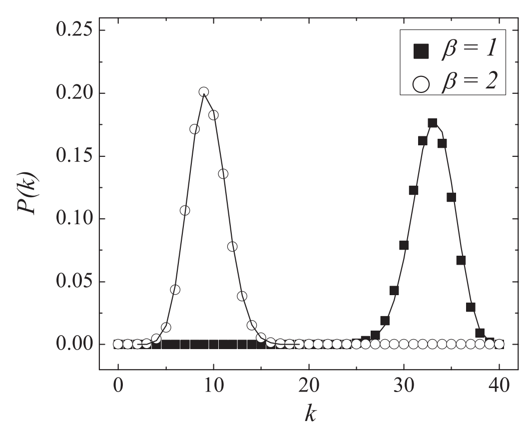

FIG. 1. Comparison of probability distributions for the number of clusters k in the one-dimensional lattice gas obtained from Monte Carlo simulations of $N = 40$ particles on $V = 8000$ sites (scattered points) and theoretical distributions $P(k)$ given by Eq. (58) (solid lines). Numerical simulations were conducted using the Metropolis algorithm with the coupling energy between two neighboring particles $\varepsilon = 4$ [cf. Eq. (20)] and for two different values of the inverse temperature, $\beta = 1$ and 2.

The theorem, however, does not say anything about the analyticity of the free energy at $T = 0$ K. In fact, the grand potential given by Eq. (39) is nonanalytic at $T = 0$ K,

$$\lim_{T\to 0K} \beta = \infty, \quad (59)$$

and

$$\lim_{T\to 0K} x = \infty. \quad (60)$$

Obviously, this nonanalyticity is of the same mathematical nature as the one observed in the free energy of the one-dimensional Ising model at zero temperature, when the magnetic field H goes to zero.

At low temperatures, $T \to 0$ K, we find that Eq. (35) becomes [6]

$$\begin{aligned}\lambda_\pm(\beta,H_G) &= e^{\beta J_G}\{\cosh(\beta H_G)\\ &\quad \pm|\sinh(\beta H_G)|[1 + O(e^{-4\beta J_G})]\}\\ &\simeq e^{\beta(J_G\pm|H_G|)}. \end{aligned}\quad (61)$$

Rewriting the last expression in the variables x and z [cf. Eq. (37)], after some algebra we get

$$\lambda_\pm(x,z) = xe^{\pm|\ln(x^2\sqrt{z})|}. \quad (62)$$

Correspondingly, the resulting grand partition function for $V \to \infty$, given by Eq. (36), can be written as follows:

$$\Xi_G(x,V,z) = (e^{\ln(x^2\sqrt{z})+|\ln(x^2\sqrt{z})|})^V. \quad (63)$$

The expression reveals nonanalytic behavior at

$$\lim_{T\to 0K} x^4 z = 1, \quad (64)$$

since

$$\lim_{x^4z\to 1^-} \Xi_G(x,V,z) = 1, \quad (65)$$

while

$$\lim_{x^4z\to 1^+} \Xi_G(x,V,z) = x^{4V}z^V. \quad (66)$$

2. Cluster properties

The nonanalytic behavior of the grand partition function just described has a very clear and convincing interpretation in terms of our combinatorial approach. Comparing Eqs. (65) and (66) with Eq. (1), we get the following expressions for the canonical partition functions:

$$\lim_{x^4z\to 1^-} Z_G(\beta,V,N) = \delta_{N,0}, \quad (67)$$

and

$$\lim_{x^4z\to 1^+} Z_G(\beta,V,N) = x^{4N}\delta_{N,V}, \quad (68)$$

where $\delta_{i,j}$ is the Kronecker delta.

The last two expressions show that in the case of the zero temperature limit, the one-dimensional lattice gas with nearest-neighbor interactions can be observed in only two particle configurations. The first configuration,

$$\forall_{1\leqslant i\leqslant V}\ \sigma_i = 0, \quad (69)$$

is consistent with Eqs. (65) and (67) and describes a system with no particles (the vacuum state). The second configuration,

$$\forall_{1\leqslant i\leqslant V}\ \sigma_i = 1, \quad (70)$$

results from Eqs. (66) and (68), and corresponds to the spanning cluster of size V.

To proceed with understanding the combinatorial approach described in Sec. II, we analyze Eqs. (67) and (68) with the help of the general formula for the canonical partition function, given by Eq. (14). Using the properties of Bell polynomials,

$$B_{N,k}(0,0,\ldots,0,x_j,0,\ldots) = \delta_{N,jk}\frac{(jk)!}{k!(j!)^k}x_j^k, \quad (71)$$

we can show that the case when x^4z approaches 1 from the left-hand side, given by Eq. (67), corresponds to

$$\forall_{n\geqslant 1}\ w_n(\beta) = 0, \quad (72)$$

while the case when x^4z approaches 1 from the right-hand side, given by Eq. (68), amounts to

$$\forall_{n\geqslant 1;n\neq V}\ w_n(\beta) = 0, \quad (73)$$

and

$$w_V(\beta) = V!\,x^{4V}. \quad (74)$$

Equations (72)–(74) show that the limiting behavior meets the conditions specified in Eq. (9). This validates our cluster-based combinatorial approach to a general system of interacting particles and emphasizes the potential usefulness of our theory for the theory of phase transitions.

3. Zeros of the grand partition function

In the zero temperature limit, for $x \to \infty$, Eq. (57) can be approximated by

$$\forall_{n\geqslant 1}\ w_n(\beta) = Vn!x^{4(n-1)}. \quad (75)$$

By inserting the last expression into Eq. (14) for the canonical partition function, we get

$$\begin{aligned} Z_G(x,V,N) &= \frac{1}{N!}\sum_{k=1}^{N} B_{N,k}(\{Vn!x^{4(n-1)}\}) \quad (76)\\ &= \frac{1}{N!}\sum_{k=1}^{N} V^k(x^4)^{(N-k)}B_{N,k}(\{n!\}) \quad (77)\\ &= \frac{1}{N!}\sum_{k=1}^{N} V^k(x^4)^{(N-k)}L(N,k), \quad (78)\end{aligned}$$

where Eq. (47) has been used, and where $L(N,k)$ represent Lah numbers, which are defined as follows:

$$L(N,k) = \binom{N-1}{k-1}\frac{N!}{k!} = B_{N,k}(\{n!\}). \quad (79)$$

Lah numbers have an interesting meaning in combinatorics. They count the number of ways a set of N elements can be partitioned into k nonempty linearly ordered subsets. The combinatorial meaning of $L(N,k)$ allows a direct understanding of the canonical partition function $Z_G(x,V,z)$, as given by Eq. (78). In short, Eq. (78) states that there are $L(N,k)$ particle configurations in which N particles can be arranged into k linear clusters. All such configurations have the same energy, given by Eq. (20), and, therefore, the same Boltzmann factor, $x^{4(N-k)}$. Finally, the factor V^k is due to cluster arrangement along the one-dimensional lattice, in which one assumes that every cluster may start at the same lattice site. Obviously, the arrangement factor does not take into account the excluded-volume effect. For this reason, it is only correct in the zero temperature limit.

Now, putting the canonical partition function given by Eq. (78) into the general formula for the grand partition function, given by Eq. (1), we get

$$\Xi_G(x,z) = 1 + \sum_{N=1}^{\infty}\sum_{k=1}^{N}\frac{(zx^4)^N}{N!}\left(\frac{V}{x^4}\right)^k L(N,k) \tag{80}$$

$$= \exp\left[\frac{Vz}{1-x^4z}\right], \tag{81}$$

where the infinite expansion involving Lah numbers has been used (see [7], p. 156, or [12], pp. 108-113),

$$\exp\left[\frac{tu}{1-t}\right] = 1 + \sum_{N=1}^{\infty}\sum_{k=1}^{N}\frac{t^N u^k}{k!}\binom{N-1}{k-1}. \tag{82}$$

The grand partition function $\Xi_G(x,z)$ applies to one-dimensional lattice gas in the thermodynamic limit. In Eq. (81), volume plays the role of an extensive factor of the grand potential, given by Eq. (11),

$$\Phi_G(x,z) = -\frac{z}{\beta(1-x^4z)}\,V, \tag{83}$$

rather than an independent variable. In addition, in the considered zero temperature limit, $x \to \infty$, the grand potential per unit volume, which defines pressure [Eq. (18)],

$$P = -\frac{z}{\beta(1-x^4z)}, \tag{84}$$

reveals a nonanalytic dependence on z at $x^4z \to 1$. The nonanalyticity translates into the root of the grand partition function, given by Eq. (81), for $z = 0$.

The significance of the zeros of the grand partition function was first pointed out by Yang and Lee [13], who showed that a phase transition in the sense of a nonanalytic dependence of P on z for physical (real and positive) values of z can occur only when $\Xi_G(x,z) = 0$. In the one-dimensional lattice gas with nearest-neighbor interactions analyzed in this study, the only root of the grand partition function is for $z = 0$; it does not occur on the positive z axis. Therefore, one claims that phase transitions in the traditional sense do not exist in this gas, although its behavior in the zero temperature limit has direct bearing on the problem of phase transitions.

4. *Supplementary remark*

Equation (83) can be derived most easily by inserting Eq. (75) in Eq. (12) and assuming that $x^4z < 1$:

$$\Phi_G(x,z) = -\frac{V}{\beta x^4}\sum_{n=1}^{\infty}(x^4z)^n = -\frac{z}{\beta(1-x^4z)}\,V. \tag{85}$$

There is a problem with proceeding in this way, however. Conflicting with our previous results, the expression obtained is not justified for $x^4z > 1$. There is no such problem if we use our combinatorial approach (described in Sec. II) because it is based on a *formal power series* [7,14].

In mathematics, formal power series are a generalization of polynomials as formal objects. A formal power series is an object that just records a sequence of coefficients. One may think of such a series as a power series in which one ignores questions of convergence. However, formal power series still allow us to use much of the analytical machinery of a *normal* power series, especially in settings that do not have natural notions of convergence. We believe that this perspective makes our combinatorial approach to equilibrium statistical mechanics peculiarly well suited for handling problems with convergence, which are often encountered in the theory of phase transitions.

V. SUMMARY

The aim of this paper was to demonstrate, with a concrete example, how our general combinatorial approach to interacting fluids works. To this end, a one-dimensional lattice gas with nearest-neighbor interactions was considered. Exploiting the mathematical equivalence between the grand partition function for the gas and the canonical partition function for the one-dimensional Ising model in the external magnetic field, cluster properties of the former were explored. Three cases (the infinite temperature limit, the range of finite temperatures, and the zero temperature limit) were discussed separately. In particular, in the range of finite temperature and for small particle densities, the normalized probability distribution for the number of clusters was found, and the nonanalytic behavior of the grand potential in the zero temperature limit, which has direct bearing on phase transitions, was analyzed. Our investigation of the zero temperature limit for the gas has allowed us to remark on the formal power series method behind our approach, which, we believe, makes the approach peculiarly well suited for handling problems covered by the theory of phase transitions.

In this study, our main purpose was to validate the general results of our earlier paper. Apart from this purpose, however, we have made interesting additions to the still-developing theory of one-dimensional lattice gases (see, e.g., [15–18]), which has proven useful in studying many natural phenomena in nanophysics, surface science, and biophysics (see, e.g., [19–22]).

ACKNOWLEDGMENTS

I am indebted to Piotr Fronczak for the help in performing Monte Carlo simulations, the results of which are shown in Fig. 1. The work was supported by internal funds of the Faculty of Physics at Warsaw University of Technology and by the Ministry of Science and Higher Education in Poland (national three-year scholarship for outstanding young scientists).

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[2] To justify the name of the model (i.e., perfect gas of clusters), one just needs to write Eq. (15) as a function of the cluster size distribution, i.e., with the help of Eq. (17), namely, $\beta PV = \sum_{n=1}^{\infty} N_n(\beta,V)$. The last formula clearly shows that in the limit of infinite volume, the imperfect gas or fluid can be seen as

composed of $\sum_{n=1}^{\infty} N_n(\beta,V)$ noninteracting and independent clusters.
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