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Microscopic meaning of grand potential resulting from combinatorial approach to a general system of particles

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We present an alternative approach to the problem of interacting fluids, which we believe may provide important insights into microscopic mechanisms that lead to the occurrence of phase transitions. The approach exploits enumerative properties and combinatorial meaning of Bell polynomials. We derive the exact formula for the probability of a general system of N particles at temperature T to consist of k weakly coupled clusters of various sizes. We also show that the grand potential of the system may be considered the exponential generating function for the number of internal states (thermodynamic probability) of these clusters. The microscopic interpretation of the grand potential is surprising, especially if one recalls that until now only the thermodynamic meaning of this free energy was known. We also derive an approximated expression for the density of states.

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I. INTRODUCTION AND MOTIVATION

This work springs from a fascination with the concepts of equilibrium, interaction, and collective behavior in physical systems. The analyzed systems are considered to be made up of separate clusters which are composed of particles (elements, units, etc.) interacting via short-range potentials. Exemplary systems where the assumptions apply are imperfect gases, for which the total interparticle potential energy is given by the sum of pair interactions characterized by a hard core and a weak attractive region. In this study we assume a particular type of interaction between clusters termed weak coupling. Weak coupling means that the only interaction between clusters is that provided by the migration of particles between them. For this reason, within the framework of statistical mechanics, the system can be actually described as consisting of disjoint, noninteracting, and independent clusters, i.e., the *perfect gas of clusters model*. A systematic method of dealing with such systems was first developed by Ursell [1], whose work was later extended by Mayer [2–7], who made the major advances in this field.

With this paper we start a new line of theoretical research on imperfect gases (or interacting fluids). Our approach originates in basic concepts of statistical physics (ensemble theory) [8] and enumerative combinatorics [9]. In particular, we derive an exact and general combinatorial formula for the probability of a system of N particles at temperature T consisting of k clusters of various sizes. To achieve the result we use the generating function for Bell polynomials [10]. To interpret it we exploit the combinatorial meaning of this function as given by the so-called exponential formula [11], which is the cornerstone of the art of counting in enumerative combinatorics.

To be definite, the exponential formula deals with the question of counting composite structures that are built out of a given set of building blocks [11] (in the exemplary case of imperfect gases, the term composite structure stands for the "microstate" of the system, while the term block means cluster). If you know how many blocks of each size there are, the formula tells you how many composite structures of each size can be built from those blocks. In short, the exponential formula states that the exponential generating function, $F(x)=\sum_{n=0}^{\infty}f_nx^n/n!$, for composite structures is the exponential of that for building blocks, $f(x)$, i.e., $F(x)=\exp[f(x)]$. With this statement in mind, the grand partition function in statistical physics [12], $\Xi(\beta,z)=\exp[-\beta\Phi(\beta,z)]$, which is also a kind of generating function for microscopic arrangements of the system investigated, gains an interesting interpretation as the generating function for composite states having a well-defined internal (clustered) structure. Furthermore, properties of this internal structure are encoded in another generating function, $\Phi(\beta,z)$, which appears to be the free energy of the system.

The outlined understanding of the grand partition function as given by the exponential formula is our result, but its theoretical basis partially refers to the cluster expansion method set out over 50 years ago in the works of Mayer [5,6]. Mayer's ideas were later developed by others [13,14], for example, by the distinguished physicist Uhlenbeck and his student Riddel, in whose thesis the exponential formula first appeared [15]. However, following initial interest among physicists, the idea of enumerative uses of generating functions was generalized and extended mainly by mathematicians (cf. [9,11]), and the physical origins of the concept have almost been forgotten.

This happens because Mayer's original approach to imperfect gases failed to match real systems. Foremost it failed in the description of the condensation effects in dense interacting gases for which it was originally developed. Mayer's theory of condensation is described in many textbooks of statistical mechanics (see, e.g., [16,17]). Originally, this theory was intended to express the exact equation of state of a real fluid, made up of interacting particles, as a series expansion in the density. To this end, Mayer proposed to decompose the partition function of a general system of interacting particles into the sum over all possible partitions of particles in independent clusters (the so-called diagrammatic expansion). He was convinced that the theory must describe the condensation density at which the macroscopic cluster first appears. However, Yang and Lee [18] proved that Mayer's theory is only exact in the limit of small particle densities and can be applied to neither dense gases nor liquids.

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Thus, is it worth coming back to this unsuccessful story? We believe it is worth it, especially since, given the present comprehension of different enumerative methods (including analytic combinatorics [19], which has emerged over the past few decades), one should be in a position to trace Mayer's failure and hopefully explain the controversy over rather subtle mathematical points involving the notion of the thermodynamic limit. Our preliminary studies indicate that Mayer's failure was in fact due to both (i) not very careful treatment of the infinite volume limit and (ii) the neglected excluded volume effect, similar to that described in the theory of polymer solutions [20]. It seems that, supported by our combinatorial approach, the delayed success of Mayer's approach is within grasp. It would be a great success for equilibrium statistical mechanics because although the alternative theory of equations of state and phase transitions initiated by Yang and Lee [18] makes possible a simple mathematical description of condensation phenomena, it still has (after more than six decades of research) the *disadvantage of being less detailed and physically rather obscure* (see [7], p. 123) compared with Mayer's approach.

Despite their connections with Mayer's theory, the ideas described in this paper were developed entirely independently. For that reason, the connections are not easily seen at first glance. In fact, for a long period of struggling with the exponential formula, Bell polynomials, etc., we were unaware of the previous contributions in the field. We were unaware that the *history* of the exponential formula started with Mayer's diagrammatic expansion, which now appears as a simple example of the formula itself. At present, after several months of rummaging through literature on the topic, we find our studies to be much more general than Mayer's approach and complementary to Markov models of systems in stochastic equilibrium studied by Whittle [21], which have now been independently developed within the framework of stochastic combinatorial processes [22,23].

The work reported in this paper is quite general and fairly abstract. Our results present a rigorous approach to a general system of interacting particles in the grand canonical ensemble, which works from the beginning with precisely defined states in infinite systems. In this respect, our approach is like the approach developed by Ruelle [24], which formulates statistical mechanics in the language of abstract algebras, similar to those used in field theories. Similar to what has been proposed by Ruelle, working from the start with systems of infinite spatial extent, we avoid the problem of starting with a finite system and then passing to the thermodynamic (infinite volume) limit [18]. Such a limit is necessary in the more conventional approaches in order to obtain precise definitions of extensive and intensive variables, i.e., for making thermodynamics independent of the shape and nature of boundaries of the system.

Our main result is that the grand potential may be considered as the exponential generating function for a number of internal states of clusters of different sizes. It puts the grand potential (also called the Landau free energy), $\Phi(\beta,z)$, in a new perspective. Until now the only macroscopic interpretation of this thermodynamic state function was known and considered (see Sec. 2F5 in Ref. [8]). We show that successive derivatives of this free energy have a definite microscopic mining. The ideas advanced in this paper (and in forthcoming presentations) reveal the meaning. This, in turn, may shed new light on the overall understanding of microscopic origins of phase transitions since they are traditionally classified according to the lowest-order derivative of the thermodynamic potential which changes discontinuously (or diverges) at the transition point (see Chaps. 3 and 7 in Ref. [8]). In subsequent presentations we will apply the methods here outlined to lattice gasses (the first such paper is already available on the arXiv preprint server [25]). We will also show how Mayer's approach and the virial expansion [7,16] of the equation of state for imperfect gases can be simply derived from our general results.

This paper is organized as follows. In Sec. II the main result of this paper, i.e., the exact combinatorial formula, is derived for the thermodynamic probability of a general system of N interacting particles which consists [or consisting] of weakly coupled clusters. Then, in Sec. III the properties of the formula are discussed, the general integral expression for the density of states is introduced, the hypothesis about the microscopic meaning of the grand potential is advanced, and the example of the ideal gas is worked out. Some general conclusions are given at the end of the paper.

II. DERIVATION OF THE MAIN RESULT

In this paper, we limit ourselves to the simplest possible case: a system composed of identical monoatomic molecules without internal degrees of freedom. The thermodynamic state of the system is given by the temperature T and the chemical potential per molecule μ. We assume that the classical treatment is adequate and use the formalism of the grand canonical ensemble (see Sec. 7G in Ref. [8]) to describe the open system in the infinite volume limit.

To derive the main result, we write the grand partition function (GPF) of a general system of particles in two ways. First, we use a slightly modified textbook approach which exploits the definition of the density of states function (DOS) as the number of states whose energies lie in some narrow range between E and $E+dE$. Second, we make use of the generating function for partial Bell polynomials [10], which has a very nice combinatorial interpretation given by the exponential formula [11]. Then, we compare both expressions. For reasons of clarity the GPF is denoted, respectively, by Ξ_1 and Ξ_2 in the two approaches.

In the infinite volume limit the grand partition function $\Xi_1(\beta,z)$ of a general system of particles is defined as the sum of Boltzmann exponential factors $e^{-\beta(E-\mu N)}$ over all microscopic realizations (microstates) Ω of the system,

$$\Xi_1(\beta,z)=\sum_{\Omega}e^{-\beta[E(\Omega)-\mu N(\Omega)]}=1+\sum_{N=1}^{\infty}z^N Z(\beta,N), \quad (1)$$

where $\beta=(k_BT)^{-1},\mu,E$ and N have their usual meanings [26], the parameter $z=e^{\beta\mu}$ is called fugacity (or activity), and

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

stands for the canonical partition function (PF). Inserting Eq. (2) into Eq. (1) and then multiplying the resulting expression by the sum over the probability distribution $f(k,E)$ that the considered system with energy E consists of k weakly coupled (i.e., statistically independent disjoint groups of particles),

$$\sum_{k=1}^{N} f(k,E) = h(E) \equiv 1, \qquad (3)$$

one gets

$$\Xi_1(\beta,z) = 1 + \sum_{N=1}^{\infty} z^N \int_0^{\infty} g(E,N) e^{-\beta E} \left(\sum_{k=1}^{N} f(k,E) \right) dE \qquad (4)$$

$$= 1 + \sum_{N=1}^{\infty} z^N \int_0^{\infty} \sum_{k=1}^{N} f(k,E) g(E,N) e^{-\beta E} dE. \qquad (5)$$

To proceed further we have to assume that [27] (i) the sum in Eq. (3) is identically equal to one almost everywhere, that is, except on a set of measure zero, and (ii) the unknown function $f(k,E)$, multiplied by the probability $g(E,N)e^{-\beta E}$ that the energy of the considered system of N particles lies in a narrow range between E and $E + dE$, is an essentially bounded function of E. In line with these two assumptions, the grand partition function Ξ_1 can be rewritten as

$$\Xi_1(\beta,z) = 1 + \sum_{N=1}^{\infty} z^N \sum_{k=1}^{N} \int_0^{\infty} f(k,E) g(E,N) e^{-\beta E} dE. \qquad (6)$$

The grand partition function $\Xi_2(\beta,z)$ may also be written in the following way:

$$\Xi_2(\beta,z) = e^{-\beta\Phi(\beta,z)} = \exp\left[-\beta \sum_{m=0}^{\infty} \frac{z^m}{m!} \phi_m(\beta) \right], \qquad (7)$$

where $\Phi(\beta,z)$ is the grand thermodynamic potential, derivatives of which, $\phi_m(\beta)$, are denoted by

$$\phi_m(\beta) = \left. \frac{\partial^m \Phi(\beta,z)}{\partial z^m} \right|_{z=0}, \qquad (8)$$

with

$$\phi_0(\beta) = 0, \qquad (9)$$

which results from a simple comparison of Eqs. (1) and (7) for $z = 0$. Now, taking advantage of the generating function for partial Bell polynomials $B_{N,k}(\{\phi_n\})$, which are the polynomials with an infinite number of variables $\{\phi_n\} = \phi_1, \phi_2, \phi_3 \ldots$, defined by the formal double series expansion [10]

$$G(t,u) = \exp\left[u \sum_{m=1}^{\infty} \phi_m \frac{t^m}{m!} \right] \qquad (10)$$

$$= 1 + \sum_{N=1}^{\infty} \frac{t^N}{N!} \sum_{k=1}^{N} u^k B_{N,k}(\{\phi_n\}), \qquad (11)$$

Eq. (7) can be rewritten as

$$\Xi_2(\beta,z) = 1 + \sum_{N=1}^{\infty} \frac{z^N}{N!} \sum_{k=1}^{N} (-\beta)^k B_{N,k}(\{\phi_n(\beta)\}), \qquad (12)$$

where $B_{N,k}(\{\phi_n\}) = B_{N,k}(\phi_1, \phi_2, \ldots, \phi_{N-k+1})$ represent the so-called partial (or incomplete) Bell polynomials, which are defined as

$$B_{N,k}(\{\phi_n\}) = N! \sum \prod_{n=1}^{N-k+1} \frac{1}{c_n!} \left(\frac{\phi_n}{n!} \right)^{c_n}, \qquad (13)$$

where the summation takes place over all integers $c_n \geqslant 0$, such that $\sum_n c_n = k$ and $\sum_n n c_n = N$.

Finally, comparing Eqs. (6) and (12), one can readily obtain the following expression for the canonical partition function:

$$Z(\beta,N) = \sum_{k=1}^{N} \int_0^{\infty} f(k,E) g(E,N) e^{-\beta E} dE \qquad (14)$$

$$= \sum_{k=1}^{N} \frac{(-\beta)^k}{N!} B_{N,k}(\{\phi_n(\beta)\}). \qquad (15)$$

Then, given the combinatorial meaning of Bell polynomials (see Sec. III A) and also having in mind the physical meaning of the probability $f(k,E)$, one can find that the equality of the two series, Eqs. (14) and (15), implies equality of their terms (see Sec. III B), i.e.,

$$\int_0^{\infty} f(k,E) g(E,N) e^{-\beta E} dE = \frac{(-\beta)^k}{N!} B_{N,k}(\{\phi_n(\beta)\}). \qquad (16)$$

Using the properties of Bell polynomials (see p. 135 in Ref. [10]),

$$a^k b^N B_{N,k}(\{\phi_n\}) = B_{N,k}(\{a b^n \phi_n\}), \qquad (17)$$

Eq. (16) can be simplified to

$$\int_0^{\infty} f(k,E) g(E,N) e^{-\beta E} dE = \frac{1}{N!} B_{N,k}(\{w_n(\beta)\}), \qquad (18)$$

where the coefficients of Bell polynomials,

$$w_n(\beta) = -\beta \phi_n(\beta), \qquad (19)$$

must all be non-negative,

$$\forall_{n \geqslant 1} \quad w_n(\beta) \geqslant 0, \qquad (20)$$

in order to assure non-negativity of the left-hand side of Eq. (18), which has the meaning of a probability.

Equation (18) for the integral transform of $g(E,N)e^{-\beta E} dE$, with the kernel function given by $f(k,E)$, is the main result of this paper. The formula describes the probability that a general system of N particles at temperature $T = (k_B \beta)^{-1}$, regardless of its energy, consists of k weakly coupled clusters. Furthermore, it provides a neat probabilistic description of microscopic arrangements (in terms of independent clusters) of the system investigated.

In the next section, a few points about Eq. (18) are picked up. In particular, a strictly microscopic interpretation of the grand thermodynamic potential is discussed and a general combinatorial formula for the density of states is derived. The case of an ideal gas is considered as an example.

III. DISCUSSION OF EQ. (18)

A. Bell polynomials

The essential difficulty with Eq. (18) arises from the interpretation of Bell polynomials $B_{N,k}(\{w_n\})$, which are described by Eq. (13). For this reason, we begin by elucidating their combinatorial meaning [11,22].

Suppose that N particles labeled by elements of the set $[N]=\{1,2,\dots,N\}$ are partitioned into clusters in such a way that each particle belongs to a unique cluster. Obviously, for each composition of $[N]$ into k disjoint nonempty clusters (subsets, blocks, etc.) of $n_i>0$ elements each, there are exactly

$$\binom{N}{n_1,n_2,\dots,n_k}=\frac{N!}{n_1!n_2!\cdots n_k!} \tag{21}$$

such compositions (partitions, distributions, etc.), where $n_1+n_2+\dots+n_k=N$. Suppose further that each cluster of size n in such a composition can be in any one of w_n different internal states. Then, the number of configurations of the system of N particles with k clusters is given by

$$N!\prod_{n=1}^{N-k+1}\left(\frac{w_n}{n!}\right)^{c_n}, \tag{22}$$

where $c_n\geqslant 0$ stands for the number of clusters of size n, the largest cluster size is $N-k+1$, and

$$\sum_{n=1}^{N-k+1}c_n=k,\qquad \sum_{n=1}^{N-k+1}nc_n=N. \tag{23}$$

Equation (22) describes a system of N distinguishable particles with k clusters. If one assumes that the considered particles are indistinguishable and also that clusters of the same size are indistinguishable, the number of configurations (compositions) becomes

$$\prod_{n=1}^{N-k+1}\frac{1}{c_n!}\left(\frac{w_n}{n!}\right)^{c_n}, \tag{24}$$

which corresponds to Eq. (22) divided by $N!\prod_n c_n!$. Finally, summing Eq. (24) over all integers $c_n\geqslant 0$ specified by Eqs. (23), one gets the right-hand side of our main result, Eq. (18).

B. How Eq. (15) implies Eq. (18)

A pivotal role in our reasoning is played by the probability distribution $f(k,E)$ that the considered system of N particles with energy E consists of k noninteracting, disjoint, and statistically independent clusters. In the simplest case of $N=1$, Eq. (15) is equivalent to Eq. (18), i.e.,

$$\int_0^{\infty}f(1,E)g(E,1)e^{-\beta E}dE=B_{1,1}(\{w_n(\beta)\})=w_1(\beta). \tag{25}$$

In other words, the above expression describes the probability of a system which consists of only one particle. Obviously, in this case the particle itself is the only cluster of size $n=1$, and its number of internal states is $w_1(\beta)$.

In the case of $N=2$, Eq. (15) can be written in the following way:

$$\begin{aligned}\int_0^{\infty}f(1,E)g(E,2)e^{-\beta E}dE&+\int_0^{\infty}f(2,E)g(E,2)e^{-\beta E}dE\\ &=\frac{1}{2}B_{2,1}(\{w_n(\beta)\})+\frac{1}{2}B_{2,2}(\{w_n(\beta)\})\\ &=w_2(\beta)+w_1(\beta)^2.\end{aligned} \tag{26}$$

In accordance with Eq. (25), the second terms in each row of the above three-line expression represent the thermodynamic probability of two, $k=2$, disjoint and statistically independent clusters of size $n=1$, i.e.,

$$\begin{aligned}w_1(\beta)^2&=\frac{1}{2}B_{2,2}(\{w_n(\beta)\})=\left(\int_0^{\infty}f(1,E)g(E,1)e^{-\beta E}dE\right)^2\\ &=\int_0^{\infty}f(2,E)g(E,2)e^{-\beta E}dE,\end{aligned} \tag{27}$$

where we have exploited a useful feature of the grand canonical ensemble that, for noninteracting particles, the grand partition function factorizes into a product of grand partition functions for each single particle.

Therefore, since two particles, $N=2$, may be placed in either two clusters of size $n=1$ or a single cluster of size $n=2$, the first terms in Eqs. (26) should stand for the thermodynamic probability of the second realizability; i.e., they must describe the number of microstates of the system with the only a cluster of size $n=2$,

$$\int_0^{\infty}f(1,E)g(E,2)e^{-\beta E}dE=\frac{1}{2}B_{2,1}(\{w_n(\beta)\})=w_2(\beta). \tag{28}$$

Similar to what has been said about the right-hand side of Eq. (25), it is clear the right-hand side of the above equation, $w_2(\beta)$, is the number of internal states of a single cluster of size $n=2$. Analogously, one can show that Eq. (18) is true for all $k\geqslant 3$.

C. Microscopic interpretation of the grand thermodynamic potential

From the previous section it is clear that the right-hand side of Eq. (18) represents the number of microscopic arrangements of a system of N particles at temperature T which consists of k clusters of various sizes. The number of internal states $w_n(\beta)$ of a cluster of size n is, up to a multiplicative constant, $-\beta$, which is proportional to the nth derivative of the grand potential $\phi_n(\beta)$ [cf. Eq. (19)].

The understanding of the grand potential as the exponential generating function,

$$\Phi(z,\beta)=\sum_{n=1}^{\infty}\frac{z^n}{n!}\phi_n(\beta), \tag{29}$$

for the number of internal states of n clusters (i.e., groups of n interacting particles) is a result of our study. It offers a microscopic interpretation of this well-known thermodynamic function.

It is also interesting to note that from the microscopic interpretation of the grand potential, very general implications for the stability requirements on the Landau free energy of the system of weakly coupled clusters arise. In general, the classical stability theory (see Chap. 2H in Ref. [8] and Chaps. 12–14 in Ref. [28]) places certain conditions on the sign of the second derivatives of the thermodynamic potentials of the system investigated. However, given our derivations, it seems necessary to expand the Gibbs stability requirements to higher derivatives. To be definite, from the non-negative definiteness of the coefficients, $w_n(\beta)$, of Bell polynomials [see Eq. (20)], one gets the following conditions:

$$\forall_{n\geqslant 1}\quad \phi_n(\beta)\leqslant 0. \tag{30}$$

One can speculate that the requirements may have connections to higher order phase transitions (similar to the way the classical stability theory, which exploits second order derivatives, is used to characterize critical phenomena). The analogy will be further elaborated in our future presentations.

D. The case of the classical ideal gas

In this section, we apply our formalism to the classical ideal gas. In this case, the grand partition function can be written as [cf. Eq. (1)]

$$\Xi_G(\beta,z)=1+\sum_{N=1}^{\infty}\frac{z^N}{N!}[Z_1(\beta)]^N=e^{zZ_1(\beta)}, \tag{31}$$

where

$$Z_1(\beta)=\frac{V}{\lambda(\beta)^3}=V\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \tag{32}$$

is the partition function of a single particle, $\lambda(\beta)$ stands for the de Broglie wavelength, V is volume, and h is the Planck's constant.

Using Eq. (7), one finds that the grand potential of the gas is a linear function of the parameter z,

$$\Phi_G(\beta,z)=-\frac{Z_1(\beta)}{\beta}z, \tag{33}$$

and the coefficients of the Bell polynomial in Eq. (18) are equal,

$$w_1(\beta)=Z_1(\beta),\quad \forall_{n\geqslant 2}\ w_n(\beta)=0. \tag{34}$$

From Eqs. (34) it follows that the only possible cluster decomposition of a general system of N particles described by the linear grand potential is the one in which each particle is located in a separate cluster. In fact, in the considered case of the ideal gas, where particles do not interact with each other, this result is the only reasonable one. Furthermore, since the number of internal states of a single particle is $Z_1(\beta)=V\lambda(\beta)^{-3}$ and the particles are statistically independent, one finds that the thermodynamic probability of the system as a whole is $Z_1(\beta)^N=w_1(\beta)^N=B_{N,N}(\{w_n(\beta)\})$, which agrees with Eq. (18).

E. The integral transform for the density of states

Although in Eq. (18) the kernel function $f(k,E)$, which describes the probability of the considered system of N particles consisting of k weakly coupled clusters, depends on the system itself [29], $f(k,E)$ given explicitly may also provide valuable information about the system. For example, let the kernel function be the Poisson distribution in the number of clusters,

$$f(k,E)\simeq P(k;\langle k\rangle)=\frac{e^{-\langle k\rangle}\langle k\rangle^k}{k!}, \tag{35}$$

where $k=E/q$, $\langle k\rangle=\langle E\rangle/q$, and q stands for an energy quanta, such that [30]

$$\sum_{k=1}^{N}P(k;\langle k\rangle)\simeq\sum_{k=0}^{\infty}P(k;\langle k\rangle)=1. \tag{36}$$

Inserting Eq. (35) into Eq. (18), one gets the following integral formula for the density of states:

$$\mathbb{P}\left[g(E,N)e^{-\beta E};\frac{E}{q},k\right]=\frac{1}{N!}B_{N,k}(\{-\beta\phi_n(\beta)\}), \tag{37}$$

where the symbolic notation $\mathbb{P}[\cdots]$ represents the Poisson transform, which is defined as [31,32]

$$\mathbb{P}[f(x);x,k]=\int_0^{\infty}\frac{e^{-x}x^k}{k!}f(x)dx=F(k). \tag{38}$$

To elucidate how Eq. (37) can be used to describe the energy distribution in the system composed of N interacting particles, one should start with some remarks about the Poisson transform. Thus, when working with this transform, it is important to understand how it acts on an arbitrary function. In some sense, it is reasonable to say that the transform $F(k)$ is a kind of weighted moving average of the original function $f(x)$. Compared with the simple moving average, in which the unweighted mean over some range of neighboring values is taken into account, in the Poisson transform the averaging is performed over the whole domain, $x\in\langle 0,\infty)$, of the original function $f(x)$, with the weights given by the Poisson distribution with the moving mean value, which is equal to x. For this reason, due to the properties of the Poisson distribution, the averaging is actually done over the nearest neighborhood of x. The transform $F(k)=\mathbb{P}[f(x);x,k]$ looks like a smooth (or fuzzy) image of the original function $f(x)$, and it is often reasonable to assume that [33] $F(k)\simeq f(x)|_{x=k}$.

Therefore, simplifying, one could say that the left-hand side of Eq. (37) represents a smoothed thermodynamic probability,

$$g(E,N)e^{-\beta E}|_{E=kq}\simeq\frac{1}{N!}B_{N,k}(\{w_n(\beta)\}), \tag{39}$$

from which one gets the approximated general combinatorial formula for the density of states,

$$g(E,N)|_{E=kq}\simeq\frac{e^{\beta qk}}{N!}B_{N,k}(\{-\beta\phi_n(\beta)\}), \tag{40}$$

where q may be interpreted as the resolution parameter for the energy distribution.

Equation (40) gives a simple way to calculate the DOS when the grand partition function is known. The partial and complete Bell polynomials are implemented in MATHEMATICA 8.0 (Wolfram, Inc.). Their computation is not at all expensive. The most time-consuming task is calculating the coefficients of the Bell polynomials, i.e., derivatives, $\phi_n(\beta)$, of the grand potential.

IV. SUMMARY AND CONCLUDING REMARKS

In this paper we have derived an exact combinatorial formula for the probability that a general system of N particles at temperature T consists of k weakly coupled clusters of various sizes. We have also found that the grand potential (i.e., the Landau free energy) may be considered as the exponential generating function for the number of internal states of these clusters. Finally, we have derived an approximated expression for the density of states.

We believe that this approach, when applied to systems such as lattice gases (see [25]), will provide important insights into the mechanisms that lead to the occurrence of phase transitions. We also believe that the approach is the correct starting point for a future theory of higher order phase transitions.

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