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Statistical Entropy of a Lattice-Gas Model: Multiparticle Correlation Expansion

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A formula expressing the statistical entropy of a lattice-gas model as a multiparticle correlation expansion is derived in the grand-canonical and in the canonical ensembles. The differences from the analogous expansion in the continuum case are elucidated. The Ising model in one dimension is discussed as a case study.

KEY WORDS: Statistical entropy; multiparticle correlations; cumulant expansion; lattice gases; Ising model.

I. INTRODUCTION

The history of the interplay between entropy and correlations dates back to 1952, when H. S. Green expressed the entropy of a simple fluid as a multiparticle correlation expansion in the canonical ensemble.(1) Each term in the series is associated with an integer power of the density and involves the logarithm of the reduced n-body distribution function ($n = 2, 3, \ldots, N$, for a system of N particles). In 1955 Richardson, apparently unaware of Green's result, wrote a cumulant expansion for the free energy, later recognized as the canonical entropy functional.(2) Then, Nettleton and M. S. Green obtained a similar expansion for the entropy of an ensemble of open systems, where new fluctuation integrals appear besides the logarithmic terms.(3) In particular, the "two-body entropy" reads:

$$S_2 = -\tfrac{1}{2}\mathcal{N}\rho \int d\mathbf{r}\; g(r) \ln g(r) + \tfrac{1}{2}\mathcal{N}\rho \int d\mathbf{r}(g(r)-1) \tag{1.1}$$

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where $\mathcal{N}$ is the average particle number and $g(r)$ is the radial distribution function.

Later on, Morita and Hiroike established Eq. (1.1) in the framework of a variational formulation of equilibrium statistical mechanics,[4] while De Dominicis carried out a generalization of this approach to the quantum case.[5] A formal analysis of the "fine structure" of the entropy in the grand-canonical ensemble was then performed also by Yvon who, by using the cumulant method, pushed the explicit calculation of partial entropies up to terms arising from correlations between quartets of particles.[6] A different route was subsequently exploited by Raveché, who resorted to a generating-function formalism involving activity derivatives of correlation functionals,[7] while Baxter showed how the convolution hypernetted-chain and the Percus–Yevick approximations can be derived in the entropy-functional scheme.[8] A similar strategy, exploiting the possibility of generating approximate integral equations through a truncated entropy functional for continuum and lattice-gas systems, was outlined also by Percus.[9]

However, it is only very recently that the multiparticle correlation expansion for the statistical entropy has found renewed interest on the computational side. First, Wallace corrected some minor errors in the original formulation of H. S. Green.[10] Then, Baranyai and Evans commented further on this, emphasizing for the first time the ensemble invariance of the entropy expansion.[11] Moreover, their numerical estimate of the three-body term at liquid densities indicates that the entropy series is rapidly convergent. Later Hernando, in 1990, extended Raveché's treatment in the grand-canonical ensemble to mixtures of many molecular species.[12] In the meanwhile, the entropy series appears also in connection with the application of the cluster variation methodology, originally proposed by Kikuchi,[13] to the theory of fluids. Schlijper and Harris carried out the minimisation of a truncated entropy functional to derive approximate fluid theories.[14]

The pair entropy has been evaluated for a number of systems.[15–19] In some cases, the three-body term has been calculated as well.[20–23] We note here that all of these calculations aim at obtaining a semi-quantitative estimate of the total entropy at moderate densities and/or temperatures through a truncated expansion which has to neglect *a fortiori* all terms beyond the second or, more rarely, the third one. However, as originally shown in refs. 24 and 25, such a residue, despite its minor quantitative relevance in the overall entropic balance, is rich of information on the statistical thermodynamics of the system and, in particular, on the interplay between phase transitions and high-order spatial correlations. Indeed, it turns out that the "residual multiparticle entropy" ΔS, a quantity defined as the difference between the excess entropy and the two-body term (1.1), whose evaluation requires the knowledge of the pair distribution function only, can be used as a sort of "microscope" that is capable of unravelling hidden tendencies towards ordering of any kind.[24–36]

As yet, the problem of finding an entropy expansion for a lattice-gas system in the thermodynamic limit, analogous to that valid for continuous systems, has not, to our knowledge, been posed. In the present paper, we solve this problem both in the canonical and in the grand-canonical ensembles, confirming the ensemble invariance of the final expression and further showing that new features appear in the entropy series of a lattice system.

The paper is organized as follows. After defining grand-canonical distribution functions on a lattice (Section 2), we derive the novel entropy expansion in Section 3, closely following Hernando's treatment. In Section 4, our result is checked against the Ising lattice gas in one dimension. Then, we move to the canonical ensemble where we first sketch a new derivation of the entropy formula for a continuous system (Section 5). In particular, we prove that the entropy expansion retains its grand-canonical form for any particle number. Conversely, in treating the lattice-gas case (Section 6), we find an expansion similar to the grand-canonical one only after the thermodynamic limit has been taken. Finally, Section 7 is devoted to concluding remarks.

II. DISTRIBUTION FUNCTIONS ON A LATTICE

We consider a lattice-gas model, namely a system of particles living on a regular lattice (of arbitrary dimensionality) with N sites. In the grand-canonical ensemble, the partition function of the system reads

$$\Xi = 1 + \sum_{n=1}^{N} e^{\beta\mu n} Z_n \tag{2.1}$$

where β is the inverse temperature, μ is the chemical potential, and Z_n is the (canonical) partition function of a n-particle system. The latter is given as a (constrained) sum of Boltzmann factors,

$$Z_n = \sum_{\{c\}}^{(n)} e^{-\beta\mathscr{H}[c]} \tag{2.2}$$

in the occupation-number representation where particles are considered as being *indistinguishable*. For the sake of clarity we ignore multiple site occupancy, i.e., $c_i = 0, 1$. In Eq. (2.2), the superscript is there to recall the number of occupied lattice sites, namely $\sum_{i=1}^{N} c_i = n$. The system Hamiltonian can be cast into the following general form:

$$\mathscr{H}[c] = \sum_i U_i^{(1)} c_i + \sum_{i<j} U_{ij}^{(2)} c_i c_j + \sum_{i<j<k} U_{ijk}^{(3)} c_i c_j c_k + \cdots \tag{2.3}$$

with arbitrary one-body, two-body, etc., interactions between particles. At equilibrium, the probability of having just n particles in the lattice is $P_n = e^{\beta\mu n} Z_n / \Xi$, while $P_0 = 1/\Xi$ is the chance to have an empty lattice.

We define

$$\langle A[c] \rangle^{(n)} = \frac{\sum_{\{c\}}^{(n)} A[c]\, e^{-\beta \mathscr{H}[c]}}{Z_n} \tag{2.4}$$

as the (canonical) average of A in a n-particle system, while

$$\langle A[c] \rangle = \frac{A[0] + \sum_{n=1}^{N} e^{\beta\mu n} Z_n \langle A[c] \rangle^{(n)}}{\Xi} \tag{2.5}$$

is the average of the same quantity in the grand-canonical ensemble.

In an ideal-gas system, i.e., $\mathscr{H}[c] = 0$, we have $Z_n^{(\mathrm{id})} = \binom{N}{n}$, whence $\Xi^{(\mathrm{id})} = (1 + e^{\beta\mu})^N$, $\langle c_k \rangle_{(\mathrm{id})}^{(n)} = n/N$, and $\langle c_k \rangle^{(\mathrm{id})} = e^{\beta\mu}/(1 + e^{\beta\mu})$. The latter expression coincides with $(1/N)(\partial \ln \Xi^{(\mathrm{id})}/\partial \beta\mu)$, the density ρ, a result that is not limited to the ideal-gas system, provided homogeneity holds, i.e., as far as $U_i^{(1)} = u^{(1)}$, $U_{ij}^{(2)} = u_{i-j}^{(2)}$, $U_{ijk}^{(3)} = u_{i-j,\, i-k,\, j-k}^{(3)}$, and so on. For such a system, $\mathscr{H}[c]$ is invariant under translations $i \to i' = \mathscr{R}[i]$. Any such a cyclic substitution into the sum (2.4) for $A[c] = c_k$ leaves each Boltzmann factor unchanged, but not c_k itself which transforms into $c_{k'}$, leading to $\langle c_k \rangle^{(n)} = \langle c_{k'} \rangle^{(n)}$, i.e., translational invariance. Then $\langle c_k \rangle^{(n)} = (1/N) \times \langle \sum_i c_i \rangle^{(n)} = (n/N)$ and $\langle c_k \rangle = (1/N)(\partial \ln \Xi/\partial \beta\mu) = \rho$. More generally, the p-body density $\langle c_{k_1} \cdots c_{k_p} \rangle$ (defined only for $k_r \neq k_s$, when $r \neq s$) in a n-particle ideal-gas system (with $n \geqslant p$) equals

$$\langle c_{k_1} \cdots c_{k_p} \rangle_{(\mathrm{id})}^{(n)} = \frac{n(n-1) \cdots (n-p+1)}{N(N-1) \cdots (N-p+1)} \tag{2.6}$$

In particular, for $p = 2$, we have:

$$\langle c_k c_l \rangle^{(\mathrm{id})} = \frac{\sum_{n=2}^{N} e^{\beta\mu n} Z_n^{(\mathrm{id})} \langle c_k c_l \rangle_{(\mathrm{id})}^{(n)}}{\Xi^{(\mathrm{id})}} = \rho^2 \tag{2.7}$$

Upon defining the two-body distribution function g_{kl} (for $k \neq l$) as:

$$g_{kl} = \frac{\langle c_k c_l \rangle}{\rho^2} \tag{2.8}$$

we obtain $g_{kl}^{(\mathrm{id})} = 1$. The above definition of the pair distribution function is suggested by the general identity (where n_c is the current particle number $\sum_i c_i$ and $\Delta n_c = n_c - \langle n_c \rangle$):

$$\frac{\langle \Delta n_c^2 \rangle}{\langle n_c \rangle} = 1 + \rho \left(\frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i} \frac{\langle c_i c_j \rangle}{\rho^2} - N \right) \tag{2.9}$$

which closely resembles the fluctuation expression for a continuous system:

$$\frac{\langle \Delta n_c^2 \rangle}{\langle n_c \rangle} = 1 + \frac{\rho}{V} \int d\mathbf{r}\, d\mathbf{r}' (g_2(\mathbf{r}, \mathbf{r}') - 1) \tag{2.10}$$

We now seek an expression for the grand-canonical density functions of a lattice system in terms of probability densities. Upon extracting just one term from the sum, the M-body density ($M \leqslant N$) can be written as:

$$n_M(i^M) \equiv \langle c_{i_1} \cdots c_{i_M} \rangle$$
$$= \frac{e^{\beta\mu M} Z_M}{\Xi} \langle c_{i_1} \cdots c_{i_M} \rangle^{(M)} + \sum_{n=M+1}^{N} \frac{e^{\beta\mu n} Z_n}{\Xi} \langle c_{i_1} \cdots c_{i_M} \rangle^{(n)} \tag{2.11}$$

(the last term missing when $M = N$). There is only one state contributing to $\langle c_{i_1} \cdots c_{i_M} \rangle^{(M)}$, i.e., $c_{i_1} = \cdots = c_{i_M} = 1$, whereas $c_k = 0$ for $k \neq i_1, ..., i_M$. We call $U_M(i^M)$ the value corresponding to $\mathscr{H}[c]$. Here, $i^M = (i_1, ..., i_M)$. $U_M(i^M)$ represents the interaction energy of M particles sitting at i^M when no other particles are present. Hence:

$$\langle c_{i_1} \cdots c_{i_M} \rangle^{(M)} = \frac{e^{-\beta U_M(i^M)}}{Z_M} \tag{2.12}$$

More generally, for $n > M$ it follows:

$$\langle c_{i_1} \cdots c_{i_M} \rangle^{(n)} = \frac{1}{(n-M)!} \sum_{\substack{i'_1, ..., i'_{n-M} = 1 \\ (i'_p, \neq i'_q,\, i'_p \neq i_r)}}^{N} \frac{e^{-\beta U_n(i^M, i'^{n-M})}}{Z_n} \tag{2.13}$$

where the factorial corrects for multiple counting of $(n-M)$-tuples, and there are $(N-M)!/(N-n)!$ terms in the sum. Finally, the canonical partition function can be re-written as:

$$Z_n = \frac{1}{n!} \sum_{\substack{i_1, \ldots, i_n = 1 \\ (i_p \neq i_q)}}^{N} e^{-\beta U_n(i^n)} = \sum_{i_1 < \cdots < i_n} e^{-\beta U_n(i^n)} \tag{2.14}$$

Now, take the lattice probability density as:

$$P_n(i^n) = \frac{e^{\beta\mu n} e^{-\beta U_n(i^n)}}{\Xi} \tag{2.15}$$

$P_n(i^n)$ represents the probability of finding n particles in the lattice at the sites specified by i^n. Note that a normalization condition holds:

$$P_0 + \sum_{n=1}^{N} \sum_{i_1 < < i_n} P_n(i^n) = 1 \tag{2.16}$$

Using Eqs. (2.12)–(2.15), the M-body density (2.11) can be written as:

$$\begin{aligned} n_M(i^M) &\equiv \rho^M G_M(i^M) \\ &= P_M(i^M) + \sum_{S=1}^{N-M} \frac{1}{S!} \sum_{\substack{i'_1, \ldots, i'_S = 1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}}^{N} P_{M+S}(i^M, i'^S) \end{aligned} \tag{2.17}$$

The above formula holds even for $M=0$ if we take $n_0 = G_0 = 1$. Quite generally, it defines the M-body distribution function $G_M(i^M)$ in the grand-canonical ensemble. We note that Eq. (2.17) can be cast into the more compact form:

$$n_M(i^M) = e^B P_M(i^M) \tag{2.18}$$

where

$$B = \sum_{\substack{j=1 \\ (j \neq i_1, \ldots, i_M)}}^{N} b_j^+ \tag{2.19}$$

and b_i^+ is an operator which adds one particle at site i. We enforce single site occupancy by requiring that $(b_i^+)^2 = 0$; moreover, $b_i^+ b_j^+ = b_j^+ b_i^+$, when

$i \neq j$, due to the indistinguishability of the particles. Since $e^{-B}e^{B}=1$, Eq. (2.18) can be inverted to give:

$$P_M(i^M) = \rho^M G_M(i^M) + \sum_{S=1}^{N-M} \frac{(-1)^S}{S!} \rho^{M+S} \sum_{\substack{i'_1,\dots,i'_S=1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}}^{N} G_{M+S}(i^M, i'^S) \tag{2.20}$$

This expression is crucial for obtaining a multiparticle expansion for the entropy. In particular,

$$P_0 = \frac{1}{\Xi} = 1 + \sum_{S=1}^{N} \frac{(-1)^S}{S!} \rho^S \sum_{\substack{i_1,\dots,i_S=1 \\ (i_p \neq i_q)}}^{N} G_S(i^S) \tag{2.21}$$

provides an expansion for Ξ^{-1}.

III. ENTROPY EXPANSION IN THE GRAND-CANONICAL ENSEMBLE

The inverse temperature β and (minus) the reduced chemical potential $-\beta\mu$ are the control parameters in the grand-canonical ensemble representation. Here, the Massieu function reads

$$\frac{1}{k_B} S[\beta, -\beta\mu] = \frac{S}{k_B} - \beta U + \beta\mu\mathcal{N} = \ln \Xi \tag{3.1}$$

where it is assumed that entropy S, energy U, and particle number $\mathcal{N}$ all depend upon β and $-\beta\mu$. In particular, the ideal-gas entropy equals:

$$\frac{S^{(\mathrm{id})}}{Nk_B} = -\rho \ln \rho - (1-\rho) \ln(1-\rho) \tag{3.2}$$

with $\rho = \mathcal{N}^{(\mathrm{id})}/N$. This form for the entropy is to be contrasted with the simpler form ($\ln \rho$) which holds in the continuum.

We search a general expression of the entropy in terms of multiparticle correlations, having Eq. (3.2) as the zeroth-order term. To this end, it is convenient to consider the following function:

$$F_M(i^M) = \frac{\Xi}{z^M} \rho^M G_M(i^M) \tag{3.3}$$

for $0 \leqslant M \leqslant N$ and $z = e^{\beta\mu}$. Using Eq. (2.17), we obtain, for $1 \leqslant M \leqslant N-1$:

$$F_M(i^M) = e^{-\beta U_M(i^M)} + \sum_{S=1}^{N-M} \frac{z^S}{S!} \sum_{\substack{i'_1, \ldots, i'_S = 1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}}^{N} e^{-\beta U_{M+S}(i^M, i'^S)} \tag{3.4}$$

Furthermore, we define:

$$F_0 = \Xi = 1 + \sum_{S=1}^{N} \frac{z^S}{S!} \sum_{\substack{i_1, \ldots, i_S = 1 \\ (i_p \neq i_q)}}^{N} e^{-\beta U_S(i^S)} \tag{3.5}$$

and $F_N(i^N) = e^{-\beta U_N(i^N)}$. Taken a linear operator $\Gamma^{(R)}$ (for $R \geqslant 0$) as:

$$\Gamma^{(R)} = z^R \frac{\partial^R}{\partial z^R} \tag{3.6}$$

we have, for $0 \leqslant M \leqslant N-1$ and $1 \leqslant R \leqslant N-M$:

$$\Gamma^{(R)} F_M(i^M) = \sum_{S=R}^{N-M} \frac{z^S}{(S-R)!} \sum_{\substack{i'_1, \ldots, i'_S = 1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}}^{N} e^{-\beta U_{U+S}(i^M, i'^S)} \tag{3.7}$$

whereas $\Gamma^{(R)} F_N(i^N) = 0$.

Then, for $0 \leqslant M \leqslant N$, we calculate

$$A_M(i^M) = \frac{1}{F_M(i^M)} \sum_{R=0}^{N-M} \frac{(-1)^R}{R!} \Gamma^{(R)} F_M(i^M) \tag{3.8}$$

(note that $A_N(i^N) = 1$, since $\Gamma^{(0)} F_N = F_N$). Using Eq. (3.6), we get (for $M < N$):

$$A_M(i^M) = 1 + \frac{z^M}{\Xi \rho^M G_M(i^M)} \sum_{R=1}^{N-M} \sum_{S=R}^{N-M} \frac{(-1)^R z^S}{R!\,(S-R)!} \times \sum_{\substack{i'_1, \ldots, i'_S = 1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}}^{N} e^{-\beta U_{M+S}(i^M, i'^S)} \tag{3.9}$$

The double sum can be further simplified after noting that:

$$\sum_{R=1}^{N-M} \sum_{S=R}^{N-M} \frac{(-1)^R z^S C_S}{R!\,(S-R)!} = \sum_{S=1}^{N-M} \left[\sum_{R=1}^{S} (-1)^R \binom{S}{R} \right] \frac{z^S}{S!} C_S$$
$$= -\sum_{S=1}^{N-M} \frac{z^S}{S!} C_S \tag{3.10}$$

which leads to:

$$A_M(i^M) = \frac{z^M e^{-\beta U_M(i^M)}}{\Xi \rho^M G_M(i^M)} \tag{3.11}$$

This result holds for all $M \leqslant N$. In particular, $A_0 = 1/\Xi$. Equation (3.11) can be used to calculate the entropy as follows. We first obtain:

$$-\beta U + \beta\mu\mathcal{N} - \ln \Xi = \overline{\ln A} + \mathcal{N} \ln \rho + \overline{\ln G} \tag{3.12}$$

where

$$\bar{B} \equiv P_0 B_0 + \sum_{n=1}^{N} \frac{1}{n!} \sum_{\substack{i_1,\ldots,i_n=1 \\ (i_p \neq i_q)}}^{N} P_n(i^n)\, B_n(i^n) \tag{3.13}$$

represents the grand-canonical average of a local quantity. Finally, Eqs. (3.1), (3.2), and (3.12) together give the entropy as:

$$\frac{S}{k_B} = \frac{S^{(\mathrm{id})}}{k_B} - \overline{\ln A} - \overline{\ln G} + N(1-\rho)\ln(1-\rho) \tag{3.14}$$

We note that the ideal-gas entropy appearing in Eq. (3.14) has the same form as in Eq. (3.2) but for a density ρ which is that of the interacting system. The entropy expansion is hidden inside Eq. (3.14). Now, we just need to expand the thermal averages in Eq. (3.14), by making use of the cumulant method.

Given a function:

$$f(\xi) = \sum_{m=1}^{\infty} \frac{\mu_m}{m!} \xi^m \tag{3.15}$$

which vanishes for $\xi = 0$, and taken:

$$g(\xi) = \ln(1 + f(\xi)) \tag{3.16}$$

it follows that $g(\xi)$ has a power-series expansion around $\xi=0$ in the form:

$$g(\xi)=\sum_{m=1}^{\infty}\frac{\kappa_m}{m!}\,\xi^m \tag{3.17}$$

with

$$\kappa_m=-m!\sum_{n_1,\ldots,n_m}(-1)^{\sum_{k=1}^{m}n_k}\left(\sum_{k=1}^{m}n_k-1\right)!\prod_{k=1}^{m}\frac{1}{n_k!}\left(\frac{\mu_k}{k!}\right)^{n_k} \tag{3.18}$$

The sum in Eq. (3.18) is over all m-tuples of non-negative integers under the condition $\sum_{k=1}^{m}kn_k=m$. The numbers κ_k are called cumulants. The inverse formula yields:

$$\mu_m=m!\sum_{n_1,\ldots,n_m}\prod_{k=1}^{m}\frac{1}{n_k!}\left(\frac{\kappa_k}{k!}\right)^{n_k} \tag{3.19}$$

with the same prescription as above for $n_1,\ldots,n_m$. Other useful formulae are:

$$\frac{d^m\ln F(x)}{dx^m}=-m!\sum_{n_1,\ldots,n_m}\left(\sum_{k=1}^{m}n_k-1\right)!\prod_{k=1}^{m}\frac{1}{n_k!}\left(\frac{-1}{k!\,F(x)}\frac{d^kF(x)}{dx^k}\right)^{n_k} \tag{3.20}$$

and, conversely,

$$\frac{d^mF(x)}{dx^m}=m!\,F(x)\sum_{n_1,\ldots,n_m}\prod_{k=1}^{m}\frac{1}{n_k!}\left(\frac{1}{k!}\frac{d^k\ln F(x)}{dx^k}\right)^{n_k} \tag{3.21}$$

Equations (3.20) and (3.21) are valid for any m-time differentiable function $F(x)$, with $\sum_{k=1}^{m}kn_k=m$.

With the help of Eq. (3.21), we get (for $0\leqslant M\leqslant N-1$):

$$A_M=1+\sum_{R=1}^{N-M}(-1)^R\sum_{n_1,\ldots,n_R}\prod_{k=1}^{R}\frac{1}{n_k!}\left(\frac{1}{k!}\,\Gamma^{(k)}\ln F_M\right)^{n_k} \tag{3.22}$$

with $\sum_{k=1}^{R}kn_k=R$. Taken $\kappa_R=(-1)^R\,\Gamma^{(R)}\ln F_M(i^M)$ and

$$g(\xi)=\sum_{R=1}^{N-M}\frac{\kappa_R}{R!}\,\xi^R \tag{3.23}$$

we find, using Eq. (3.19):

$$e^{g(\xi)} = 1 + \sum_{R=1}^{\infty} (-\xi)^R \sum_{n_1,\ldots,n_R} \prod_{k=1}^{R} \frac{1}{n_k!} \left(\frac{1}{k!} \Gamma^{(k)} \ln F_M \right)^{n_k} \tag{3.24}$$

Finally, comparing Eq. (3.22) with Eq. (3.24), we obtain, *in the thermodynamic limit*:

$$A_M(i^M) = e^{g(1)} = \exp\left(\sum_{R=1}^{\infty} \frac{(-1)^R}{R!} \Gamma^{(R)} \ln F_M(i^M) \right) \tag{3.25}$$

where it has been assumed that the radius of convergence of the power series in Eq. (3.24) is greater than 1. Finally, plugging Eq. (3.25) into Eq. (3.14), we get the "excess entropy" as

$$\frac{S^{(\mathrm{ex})}}{k_B} \equiv \frac{S - S^{(\mathrm{id})}}{k_B} = -\overline{\ln G} - \sum_{R>0} \frac{(-1)^R}{R!} \overline{\Gamma^{(R)} \ln F} + N(1-\rho)\ln(1-\rho) \tag{3.26}$$

We now need to calculate $\Gamma^{(R)} \ln F_M$ for $0 \leqslant M \leqslant N-1$ and $1 \leqslant R \leqslant N-M$. Using Eq. (3.20), we obtain:

$$\Gamma^{(R)} \ln F_M = -R! \sum_{n_1,\ldots,n_R} \left(\sum_{k=1}^{R} n_k - 1 \right)! \prod_{k=1}^{R} \frac{1}{n_k!} \left(\frac{-z^k}{k!\, F_M} \frac{\partial^k F_M}{\partial z^k} \right)^{n_k} \tag{3.27}$$

The last derivative can be expressed in terms of correlations, using Eqs. (3.7) and (2.17), as:

$$\frac{z^k}{F_M} \frac{\partial^k F_M}{\partial z^k} = \rho^k \sum_{\substack{i'_1,\ldots,i'_k=1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}} \frac{G_{M+k}(i^M, i^k)}{G_M(i^M)} \tag{3.28}$$

Since $\Gamma^{(R)} \ln F_N = 0$, we finally get:

$$\begin{aligned}
\overline{\Gamma^{(R)} \ln F} = {} & \frac{1}{\Xi} \Gamma^{(R)} \ln \Xi + \sum_{n=1}^{N-1} \frac{1}{n!} \sum_{\substack{i_1,\ldots,i_n=1 \\ (i_r \neq i_s)}}^{N} (-R!) \\
& \times \left[\rho^{n+R} G_n(i^n) + \sum_{S=1}^{N-n} \frac{(-1)^S}{S!} \rho^{n+S+R} \sum_{\substack{i'_1,\ldots,i'_S=1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}}^{N} G_{n+S}(i^n, i'^S) \right] \\
& \times \sum_{n_1,\ldots,n_R} \left(\sum_{k=1}^{R} n_k - 1 \right)! \prod_{k=1}^{R} \frac{1}{n_k!} \left(\frac{-1}{k!} \sum_{\substack{i'_1,\ldots,i'_k=1 \\ (i'_p \neq i'_q,\, i'_p \neq i_r)}}^{N} \frac{G_{n+k}(i^n, i'^k)}{G_n(i^n)} \right)^{n_k}
\end{aligned} \tag{3.29}$$

The last unknown term in the entropy expansion is $\sum_{R>0}[(-1)^R/R!]\times\Gamma^{(R)}\ln\Xi$ which must be expressed in terms of the G's. Recalling that $F_0=\Xi$ and using Eqs. (3.27) and (3.28), we get:

$$\sum_{R>0}\frac{(-1)^R}{R!}\Gamma^{(R)}\ln\Xi=-\sum_{R>0}(-\rho)^R\sum_{n_1,\ldots,n_R}(-1)^{\sum_{k=1}^R n_k}\left(\sum_{k=1}^R n_k-1\right)!\times\prod_{k=1}^R\frac{1}{n_k!}\left(\frac{1}{k!}\sum_{\substack{i_1,\ldots,i_k=1\\(i_r\neq i_s)}}^N G_k(i^k)\right)^{n_k}\tag{3.30}$$

Hence, the excess entropy takes the following final form (valid only in the thermodynamic limit):

$$\begin{aligned}\frac{S^{(\mathrm{ex})}}{k_B}=&\,N(1-\rho)\ln(1-\rho)-\sum_{n=1}^N\frac{1}{n!}\sum_{\substack{i_1,\ldots,i_n=1\\(i_p\neq i_q)}}^N P_n(i^n)\ln G_n(i^n)\\&+\sum_{R>0}(-\rho)^R\sum_{n=1}^{N-1}\frac{1}{n!}\\&\times\sum_{\substack{i_1,\ldots,i_n=1\\(i_p\neq i_q)}}^N\left(\rho^n G_n(i^n)+\sum_{S=1}^{N-n}\frac{(-1)^S}{S!}\rho^{n+S}\sum_{\substack{i'_1,\ldots,i'_S=1\\(i'_p\neq i'_q,\,i'_p\neq i_r)}}^N G_{n+S}(i^n,i'^S)\right)\\&\times\sum_{n_1,\ldots,n_R}\left(\sum_{k=1}^R n_k-1\right)!\prod_{k=1}^R\frac{1}{n_k!}\left(\frac{-1}{k!}\sum_{\substack{i'_1,\ldots,i'_k=1\\(i'_p\neq i'_q,\,i'_p\neq i_r)}}^N\frac{G_{n+k}(i^n,i'^k)}{G_n(i^n)}\right)\\&+\left(1+\sum_{S=1}^N\frac{(-1)^S}{S!}\rho^S\sum_{\substack{i_1,\ldots,i_S=1\\(i_p\neq i_q)}}^N G_S(i^S)\right)\\&\times\sum_{R>0}(-\rho)^R\sum_{n_1,\ldots,n_R}\left(\sum_{k=1}^R n_k-1\right)!\prod_{k=1}^R\frac{1}{n_k!}\left(\frac{-1}{k!}\sum_{\substack{i_1,\ldots,i_k=1\\(i_p\neq i_q)}}^N G_k(i^k)\right)^{n_k}\end{aligned}\tag{3.31}$$

with $\sum_{i=1}^R in_i=R$, and where $P_n(i^n)$ in the first line is given by Eq. (2.20).

Equation (3.31) is our main result. This expression has several analogies with that reported by Hernando for a continuous system.[12] However, as we are going to show very soon, substantial differences between the two formulae appear when Eq. (3.31) is cast into the form of a multiparticle series expansion. For the sake of clarity, we stop at the third-order term in the series, which is enough for discussing our point.

It is now straightforward to group terms in Eq. (3.31) using the density as an "ordering parameter" (which is not tantamount to treating ρ as an expansion variable since the distribution functions $G_n(i^n)$ do also depend on the density). The first term can be written as:

$$(1-\rho)\ln(1-\rho) = -\rho + \frac{\rho^2}{2} + \frac{\rho^3}{6} + \mathcal{O}(\rho^4) \tag{3.32}$$

Introducing the reduced distribution functions

$$g_2(i_1, i_2) = \frac{G_2(i_1, i_2)}{G_1(i_1)\, G_1(i_2)}, \; g_3(i_1, i_2, i_3) = \frac{G_3(i_1, i_2, i_3)}{G_1(i_1)\, G_1(i_2)\, G_1(i_3)}, \ldots, \tag{3.33}$$

the second term becomes:

$$-\rho \sum_{i_1=1}^{N} G_1(i_1) \ln G_1(i_1) - \frac{\rho^2}{2} \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} G_2(i_1, i_2) \ln g_2(i_1, i_2)$$
$$-\frac{\rho^3}{6} \sum_{\substack{i_1, i_2, i_3=1 \\ (i_p \neq i_q)}}^{N} G_3(i_1, i_2, i_3) \ln \frac{g_3(i_1, i_2, i_3)}{g_2(i_1, i_2)\, g_2(i_1, i_3)\, g_2(i_2, i_3)} + \mathcal{O}(\rho^4) \tag{3.34}$$

Next, we move to the "configurational" contributions to the excess entropy. The first term is simply $\rho \sum_{i_1=1}^{N} G_1(i_1)$. The next term reads:

$$\frac{\rho^2}{2}\left(\sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} G_2(i_1, i_2) - \sum_{i_1, i_2=1}^{N} G_1(i_1)\, G_1(i_2) \right)$$
$$= \frac{\rho^2}{2} \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} G_1(i_1)\, G_1(i_2)(g_2(i_1, i_2) - 1) - \frac{\rho^2}{2} \sum_{i_1=1}^{N} G_1^2(i_1) \tag{3.35}$$

The latter "addendum" in Eq. (3.35) has no counterpart in the continuum. Here, we see at work for the first time the mechanism that is responsible for the appearance of novel terms in the entropy formula of a lattice system, some sort of "self-energy" terms induced by the regularization. This situation repeats at the next order which, after long but straightforward calculations, reads:

$$\frac{\rho^3}{6} \sum_{\substack{i_1, i_2, i_3 = 1 \\ (i_p \neq i_q)}}^{N} G_1(i_1)\, G_1(i_2)\, G_1(i_3)$$

$$\times [g_3(i_1, i_2, i_3) - 3g_2(i_1, i_2)\, g_2(i_1, i_3) + 3g_2(i_1, i_2) - 1]$$

$$-\frac{\rho^3}{6} \sum_{i_1 = 1}^{N} G_1^3(i_1) - \frac{\rho^3}{2} \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} G_1^2(i_1)\, G_1(i_2)(g_2(i_1, i_2) - 1)^2 \tag{3.36}$$

Again, the last two addenda can be read as self-energies.

Collecting together all partial results, the excess entropy can be finally written as:

$$\frac{S^{(\mathrm{ex})}}{k_B} = -\rho \sum_{i_1=1}^{N} G_1(i_1) \ln G_1(i_1) + \frac{\rho^2}{2} \sum_{i_1=1}^{N} (1 - G_1^2(i_1)) + \frac{\rho^3}{6} \sum_{i_1=1}^{N} (1 - G_1^3(i_1))$$

$$-\frac{\rho^2}{2} \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} G_1(i_1)\, G_1(i_2)[g_2(i_1, i_2) \ln g_2(i_1, i_2) - g_2(i_1, i_2) + 1]$$

$$-\frac{\rho^3}{2} \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} G_1^2(i_1)\, G_1(i_2)(g_2(i_1, i_2) - 1)^2$$

$$-\frac{\rho^3}{6} \sum_{\substack{i_1, i_2, i_3 = 1 \\ (i_p \neq i_q)}}^{N} G_1(i_1)\, G_1(i_2)\, G_1(i_3)$$

$$\times \left[g_3(i_1, i_2, i_3) \ln \frac{g_3(i_1, i_2, i_3)}{g_2(i_1, i_2)\, g_2(i_1, i_3)\, g_2(i_2, i_3)} - g_3(i_1, i_2, i_3) \right.$$

$$\left. + 3g_2(i_1, i_2)\, g_2(i_1, i_3) - 3g_2(i_1, i_2) + 1 \right] + \mathcal{O}(\rho^4) \tag{3.37}$$

This formula (the "lattice entropy expansion") can be further simplified if the system is homogeneous (no one-body term in the potential), since in this case $G_1(i) = 1$. This follows from $\langle c_k \rangle^{(n)} = n/N$, i.e., $\langle c_k \rangle = \rho$ for any k (see the discussion following Eq. (2.5)). For a homogeneous system the excess entropy thus reads:

$$
\begin{aligned}
\frac{S^{(\mathrm{ex})}}{k_B} = & -\frac{\rho^2}{2} \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} (g_2(i_1, i_2) \ln g_2(i_1, i_2) - g_2(i_1, i_2) + 1) \\
& -\frac{\rho^3}{2} \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} (g_2(i_1, i_2) - 1)^2 \\
& -\frac{\rho^3}{6} \sum_{\substack{i_1, i_2, i_3 = 1 \\ (i_p \neq i_q)}}^{N} \left[g_3(i_1, i_2, i_3) \ln \frac{g_3(i_1, i_2, i_3)}{g_2(i_1, i_2)\, g_2(i_1, i_3)\, g_2(i_2, i_3)} - g_3(i_1, i_2, i_3) \right. \\
& \left. + 3 g_2(i_1, i_2)\, g_2(i_1, i_3) - 3 g_2(i_1, i_2) + 1 \right] + \mathcal{O}(\rho^4)
\end{aligned}
\tag{3.38}
$$

Note, in particular, the presence of a term $-\frac{1}{2}\rho^3 \sum_{i_1 \neq i_2} (g_2(i_1, i_2) - 1)^2$, which does not appear in the continuum entropy formula.[12]

Each sum in the power series (3.38) is $\mathcal{O}(N)$, and $S^{(\mathrm{ex})}$ is thus extensive. This is particularly transparent at the second-order level, since the double sum over $i_1 \neq i_2$ gives N times a $\mathcal{O}(1)$ number.

As noted above, the multiparticle expansion (3.38) is not a density-power series, since each coefficient is a function of ρ as well. Upon expanding the coefficients, we can obtain a true density-power series whose third-order term, for instance, results from the first-order contribution of the two-body term and from the zeroth-order contribution of the three-body term.

IV. THE FORMULA AT WORK: ONE-DIMENSIONAL ISING LATTICE GAS

Equation (3.38) gives the first few terms in the expansion of the excess entropy of a homogeneous lattice system in terms of distribution functions. We notice, in particular, that the nth order term is the place where n-body correlations first appear. It is generally believed that the truncated expansion loses validity at high density when many-body correlations cease to be negligible.

We now use the Ising lattice-gas model in one dimension to check our formula for the entropy. This system is simple enough to allow the explicit computation of the two- and three-body distribution functions.

The Ising lattice gas Hamiltonian reads

$$
\mathscr{H}[c] = -\varepsilon \sum_{\langle i, j \rangle} c_i c_j \tag{4.1}
$$

where the sum is over nearest-neighbor pairs of lattice sites only (there are ND such pairs in a D-dimensional cubic lattice with N sites). When $\varepsilon > 0$ (the "ferromagnetic" case), particles behave gregariously at low temperature. The grand-canonical partition function of the lattice system,

$$\Xi = \sum_{c_1, \dots, c_N} e^{\beta\mu \sum_i c_i} e^{\beta\varepsilon \sum_{\langle i,j \rangle} c_i c_j} \tag{4.2}$$

can be cast into a more convenient form if we introduce spin variables $s_i = 2c_i - 1$, arriving eventually at the partition function of an Ising model in D dimensions:

$$-\beta\mathscr{H}_{\mathrm{I}} = K \sum_{\langle i,\, j \rangle} s_i s_j + H \sum_i s_i \tag{4.3}$$

with

$$H = \frac{\beta\mu + D\beta\varepsilon}{2} \qquad \text{and} \qquad K = \frac{\beta\varepsilon}{4} \tag{4.4}$$

The partition function Ξ is precisely written as:

$$\Xi = \exp\left(\frac{\beta\mu}{2} N + \frac{\beta\varepsilon}{4} ND\right) Z_{\mathrm{I}} \tag{4.5}$$

As is well known, in two dimensions, the Ising first-order transition line $H = 0$, $K > \frac{1}{2}\ln(1 + \sqrt{2})$ turns into $\mu = -D\varepsilon$, $\beta\varepsilon > 2\ln(1 + \sqrt{2})$. We now specialize our discussion to the one-dimensional case where both the free energy and the radial correlations are known at any H. In particular, the former reads:

$$f_{\mathrm{I}} \equiv -\frac{1}{\beta} \lim_{N \to \infty} \frac{\ln Z_{\mathrm{I}}}{N} = -\frac{1}{\beta} \ln\left(e^K \cosh H + \sqrt{e^{2K} \sinh^2 H + e^{-2K}}\right) \tag{4.6}$$

Averages over $\mathscr{H}[c]$ are all written in terms of spin averages. In particular $\rho(\beta, \beta\mu) \equiv \mathscr{N}/N = (1 + m)/2$, where m is the magnetization per site given as a function of $K(\beta)$ and $H(\beta, -\beta\mu)$ by:

$$m = -\frac{\partial(\beta f_{\mathrm{I}})}{\partial H} = \frac{e^K \sinh H}{\sqrt{e^{2K} \sinh^2 H + e^{-2K}}} \tag{4.7}$$

The inverse formula,

$$\sinh\left(\frac{\beta\mu}{2}+\frac{\beta\varepsilon}{2}\right)=e^{-\beta\varepsilon/2}\,\frac{2\rho-1}{\sqrt{1-(2\rho-1)^2}} \tag{4.8}$$

implicitly defines $\beta\mu$ in terms of β and ρ. After eliminating $\beta\mu$ by this means, we obtain the entropy of the lattice gas from Eq. (3.1) through the substitutions $S[\beta, -\beta\mu]=k_B \ln \Xi$, $U=-\partial \ln \Xi/\partial\beta$, and $\mathcal{N}=N\rho$. After straightforward but rather lengthy algebraic calculations, we are finally led to the following expression for the entropy of the one-dimensional Ising lattice gas:

$$\begin{aligned}\frac{S}{Nk_B}=&(1-2\rho)\ln(\alpha^{-2}(2\rho-1)+\sqrt{1-(1-\alpha^{-4})(2\rho-1)^2})\\&-(1-\rho)\ln(1-(2\rho-1)^2)+\ln(\alpha^{-2}+\sqrt{1-(1-\alpha^{-4})(2\rho-1)^2})\\&+\frac{\beta\varepsilon}{2}\,\alpha^{-2}\,\frac{1-(2\rho-1)^2}{\alpha^{-2}+\sqrt{1-(1-\alpha^{-4})(2\rho-1)^2}}\end{aligned} \tag{4.9}$$

where $\alpha=\exp(\beta\varepsilon/4)$.

Now that we have got the exact expression of S in terms of temperature and density, we are in a position to check our formula. We can expand the right-hand side of Eq. (4.9) as a power series of ρ, truncating the expansion at the ρ^3 level, and then comparing it with that obtained from Eq. (3.38) upon inserting the exact expressions of the two- and three-body distribution functions.

Using the approximation:

$$\begin{aligned}&\sqrt{1-(1-\alpha^{-4})(2\rho-1)^2}\\&\quad=\alpha^{-2}+2\alpha^{-2}(\alpha^4-1)\,\rho-2\alpha^2(\alpha^4-1)\,\rho^2\\&\qquad+4\alpha^2(\alpha^4-1)^2\,\rho^3-2\alpha^2(5\alpha^{12}-14\alpha^8+13\alpha^4-4)\,\rho^4+\mathcal{O}(\rho^5)\end{aligned} \tag{4.10}$$

we obtain the following exact result:

$$\begin{aligned}\frac{S}{Nk_B}=&-\rho\ln\rho-(1-\rho)\ln(1-\rho)-[\beta\varepsilon e^{\beta\varepsilon}-(e^{\beta\varepsilon}-1)]\,\rho^2\\&-[(e^{\beta\varepsilon}-1)^2-2\beta\varepsilon e^{\beta\varepsilon}(e^{\beta\varepsilon}-1)]\,\rho^3+\mathcal{O}(\rho^4)\end{aligned} \tag{4.11}$$

A few comments on this equation. First of all, we easily recognize general properties of the entropy expansion of a homogeneous system such as the zeroth-order ideal-gas term and a missing linear term. Secondly, the ρ^2 term is always negative (it vanishes for $\beta\varepsilon = 0$ only).

We now calculate the distribution functions that are needed in order to evaluate all terms in the truncated expansion (3.38). These functions are more easily computed within the transfer-matrix framework. Given the Hamiltonian (4.3), one first defines the transfer matrix:

$$\mathscr{T} = \begin{pmatrix} e^{K+H} & e^{-K} \\ e^{-K} & e^{K-H} \end{pmatrix} \tag{4.12}$$

whose eigenvalues and eigenvectors are (see, for instance, ref. 37): $\lambda_{1,2} = e^K \cosh H \pm \sqrt{e^{2K} \sinh^2 H + e^{-2K}}$, with $v_1 = \binom{\alpha_1}{\alpha_2}$, $v_2 = \binom{\alpha_2}{-\alpha_1}$, respectively, and

$$\alpha_{1,2}^2 = \frac{1}{2}\left(1 \pm \frac{e^K \sinh H}{\sqrt{e^{2K} \sinh^2 H + e^{-2K}}}\right) \tag{4.13}$$

Using the matrix $\mathscr{A}_{s_1, s_1'} = s_1 \delta_{s_1, s_1'}$, we obtain $\langle s_1 \rangle = (1/Z_N) \operatorname{tr}(\mathscr{A} T^N)$ and $\langle s_1 s_{1+R} \rangle = (1/Z_N) \operatorname{tr}(\mathscr{A} T^R \mathscr{A} T^{N-R})$, for $R > 0$, where tr(ace) means summing over all spin states, and $Z_N = \operatorname{tr}(\mathscr{T}^N)$. All traces are easily computed if the matrix $\mathscr{S}$, the orthogonal matrix which diagonalizes $\mathscr{T}$, is introduced. In the thermodynamic limit, multiple insertion of $\mathscr{S}\mathscr{S}^{-1}$ in the above formulae gives:

$$\begin{aligned} \langle s_1 \rangle &= \alpha_1^2 - \alpha_2^2 = \cos\phi, \\ \langle s_1 s_{1+R} \rangle &= \langle s_1 \rangle^2 + 4\alpha_1^2 \alpha_2^2 \left(\frac{\lambda_2}{\lambda_1}\right)^R = \cos^2\phi + \sin^2\phi \exp\left(-\frac{R}{\xi}\right) \end{aligned} \tag{4.14}$$

where $\cot\phi = e^{2K} \sinh H$ (with $0 < \phi < \pi$) and $\xi^{-1} = \ln(\lambda_1/\lambda_2)$. The same technique is employed to calculate triplet correlations. We obtain, for $R_1, R_2 > 0$:

$$\begin{aligned} &\langle s_1 s_{1+R_1} s_{1+R_1+R_2} \rangle \\ &\quad = \cos^3\phi + \cos\phi \sin^2\phi \left[\left(\frac{\lambda_2}{\lambda_1}\right)^{R_1} + \left(\frac{\lambda_2}{\lambda_1}\right)^{R_2} - \left(\frac{\lambda_2}{\lambda_1}\right)^{R_1+R_2}\right] \end{aligned} \tag{4.15}$$

After recalling that $s_i = 2c_i - 1$, meaning $\cos\phi = 2\rho - 1$, we finally get (for $i < j$ and $i < j < k$, respectively):

$$g_{ij} = 1 + \frac{1-\rho}{\rho}\left(\frac{\lambda_2}{\lambda_1}\right)^{j-i};$$
$$g_{ijk} = 1 + \frac{1-\rho}{\rho}\left[\left(\frac{\lambda_2}{\lambda_1}\right)^{j-i} + \left(\frac{\lambda_2}{\lambda_1}\right)^{k-j}\right] + \left(\frac{1-\rho}{\rho}\right)^2 \left(\frac{\lambda_2}{\lambda_1}\right)^{k-i} = g_{ij}\, g_{jk} \tag{4.16}$$

It is evident that these functions are translationally invariant. Moreover, the triplet distribution function obeys a factorization rule that is ultimately related to the simple connectivity of the 1D lattice, along with the absence of three and higher-site interactions in the Ising Hamiltonian. In turn, the entropy reduces to a functional of g_{ij} only which, however, does not seem amenable to be written in closed form.

In order to extract the leading terms in the entropy expansion we use the fact that:

$$\frac{\lambda_2}{\lambda_1} = \rho[\alpha^4 - 1 - (2\alpha^8 - 3\alpha^4 + 1)\,\rho + (\alpha^4 - 1)(5\alpha^8 - 6\alpha^4 + 1)\,\rho^2] + \mathcal{O}(\rho^4) \tag{4.17}$$

which yields the following second-order approximation for the two-body distribution functions:

$$g_{01} = \alpha^4 - 2\alpha^4(\alpha^4 - 1)\,\rho + \alpha^4(5\alpha^8 - 9\alpha^4 + 4)\,\rho^2 + \mathcal{O}(\rho^3);$$
$$g_{02} = 1 + (\alpha^4 - 1)^2\,\rho - (\alpha^4 - 1)(4\alpha^8 - 5\alpha^4 + 1)\,\rho^2 + \mathcal{O}(\rho^3);$$
$$g_{03} = 1 + (\alpha^4 - 1)^3\,\rho^2 + \mathcal{O}(\rho^3);$$
$$g_{04} = g_{05} = \cdots = 1 + \mathcal{O}(\rho^3) \tag{4.18}$$

Trivial substitution of Eq. (4.18) into the expression of the two-body entropy per site yields:

$$\frac{\rho^2}{2N} \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} (-g_2(i_1, i_2) \ln g_2(i_1, i_2) + g_2(i_1, i_2) - 1)$$
$$= -\rho^2 \sum_{j>0} (g_{0j} \ln g_{0j} - g_{0j} + 1)$$
$$= -\beta\varepsilon e^{\beta\varepsilon} + (e^{\beta\varepsilon} - 1) + 2\beta\varepsilon e^{\beta\varepsilon}(e^{\beta\varepsilon} - 1)\,\rho + \mathcal{O}(\rho^2) \tag{4.19}$$

We now list only the three-body distribution functions that are significant at low density:

$$\begin{aligned}
&g_{012}=\alpha^8-4\alpha^8(\alpha^4-1)\,\rho+\mathcal{O}(\rho^2);\\
&g_{013}=g_{023}=\alpha^4+\alpha^4(\alpha^8-4\alpha^4+3)\,\rho+\mathcal{O}(\rho^2);\\
&g_{024}=1+2(\alpha^4-1)^2\,\rho+\mathcal{O}(\rho^2);\\
&g_{014}=g_{034}=g_{015}=g_{045}=\cdots=\alpha^4-2\alpha^4(\alpha^4-1)\,\rho+\mathcal{O}(\rho^2)
\end{aligned} \tag{4.20}$$

We also notice that $g_{ijk}=g_{ikj}=g_{kji}=\cdots$, since $c_i c_j c_k=c_i c_k c_j=c_k c_j c_i=\cdots$. Collecting together all this information, we can evaluate the three-body entropy per site. The first term reads:

$$\begin{aligned}
&-\frac{\rho^3}{6N}\sum_{\substack{i_1,i_2,i_3=1\\(i_p\neq i_q)}}^{N} g_3(i_1,i_2,i_3)\ln\frac{g_3(i_1,i_2,i_3)}{g_2(i_1,i_2)\,g_2(i_1,i_3)\,g_2(i_2,i_3)}\\
&\quad=-\frac{\rho^3}{6}\left[6g_{012}\ln\frac{g_{012}}{g_{01}g_{02}g_{12}}+6(N-4)\,g_{013}\ln\frac{g_{013}}{g_{01}g_{03}g_{13}}+\mathcal{O}(\rho)\right]\\
&\quad=\mathcal{O}(\rho^4)
\end{aligned} \tag{4.21}$$

This term does not give a contribution at third order. The next term is:

$$\begin{aligned}
&\frac{\rho^3}{6N}\sum_{\substack{i_1,i_2,i_3=1\\(i_p\neq i_q)}}^{N}(g_3(i_1,i_2,i_3)-1)\\
&\quad=\frac{\rho^3}{6}\left[6(g_{012}-1)+6(N-4)(g_{013}-1)+\mathcal{O}(\rho)\right]\\
&\quad=\rho^3[\alpha^8-4\alpha^4+3+N(\alpha^4-1)]+\mathcal{O}(\rho^4)
\end{aligned} \tag{4.22}$$

which is not intensive. This is due to the fact that it is only the whole three-body entropy that must eventually be extensive (single pieces do not necessarily show this property). The forthcoming term reads:

$$\begin{aligned}
&\frac{\rho^3}{2N}\sum_{\substack{i_1,i_2,i_3=1\\(i_p\neq i_q)}}^{N} g_2(i_1,i_2)(1-g_2(i_1,i_3))\\
&\quad=\frac{\rho^3}{2}\left[2\alpha^4(1-\alpha^4)+(2(N-2)-2)(1-\alpha^4)\right]\\
&\quad=\rho^3[-\alpha^8+4\alpha^4-3-N(\alpha^4-1)]+\mathcal{O}(\rho^4)
\end{aligned} \tag{4.23}$$

which cancels exactly the preceding one. Finally:

$$-\frac{\rho^3}{2N} \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} (g_2(i_1, i_2) - 1)^2 = 2\rho^3 \sum_{j>0} (g_{0j} - \tfrac{1}{2} g_{0j}^2 - \tfrac{1}{2})$$

$$= \rho^3(-\alpha^8 + 2\alpha^4 - 1) + \mathcal{O}(\rho^4) \qquad (4.24)$$

Collecting together all the partial results, we finally obtain the following expansion for the excess entropy per site:

$$\frac{S^{(\mathrm{ex})}}{Nk_B} = -[\beta\varepsilon e^{\beta\varepsilon} - (e^{\beta\varepsilon} - 1)]\,\rho^2 + [2\beta\varepsilon e^{\beta\varepsilon}(e^{\beta\varepsilon} - 1) - (e^{\beta\varepsilon} - 1)^2]\,\rho^3 + \mathcal{O}(\rho^4) \qquad (4.25)$$

which reproduces Eq. (4.11). It is curious to observe that the third-order term in this expansion precisely comes from the $\mathcal{O}(\rho)$ term of $-\frac{1}{2}(g_2 \ln g_2 - g_2 + 1)$ and from the zeroth-order term of $-\frac{1}{2}(g_2 - 1)^2$. This last term has no counterpart in the continuum entropy formula.

V. BACK TO THE CONTINUUM: ANOTHER DERIVATION OF THE ENTROPY FORMULA

This paragraph deviates in part from the main body of the text, being devoted to a novel derivation of the entropy formula for a continuous system in the canonical ensemble. We now suppose that the system under study has continuous degrees of freedom, volume V and particle number N, while being in contact with a heat bath. We use the notation $\mathbf{r}^N = \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\}$ for the system configuration. Let $U_N(\mathbf{r}^N)$ be the potential. The canonical partition function takes the form $Z_N = Z_N^{(\mathrm{id})} Q_N$, where $Z_N^{(\mathrm{id})}$ is the ideal-gas partition function and Q_N is the configurational integral. The Massieu function for the canonical equilibrium reads:

$$\frac{S[\beta]}{k_B} = \ln Z = \frac{S^{(\mathrm{id})}}{k_B} - \frac{DN}{2} + \frac{S^{(\mathrm{ex})}}{k_B} - \beta \langle U_N \rangle \qquad (5.1)$$

where

$$\frac{S^{(\mathrm{ex})}}{k_B} = -\int \frac{d\mathbf{r}^N}{V^N} \frac{e^{-\beta U_N(\mathbf{r}^N)}}{Q_N} \ln \frac{e^{-\beta U_N(\mathbf{r}^N)}}{Q_N} \qquad (5.2)$$

We now define (for $k = 1,..., N-1$):

$$P^{(k)}(\mathbf{r}^k) = \int \frac{d\mathbf{r}_{k+1} \cdots d\mathbf{r}_N}{V^{N-k}} \frac{e^{-\beta U_N(\mathbf{r}^N)}}{Q_N} \tag{5.3}$$

and

$$P^{(N)}(\mathbf{r}^N) = \frac{e^{-\beta U_N(\mathbf{r}^N)}}{Q_N} \tag{5.4}$$

Note that $P^{(k)} = 1$ for an ideal gas. Moreover, $P^{(1)} = 1$ for a homogeneous system. The normalization of Eqs. (5.3) and (5.4) is to be intended in the following sense:

$$\int \frac{d\mathbf{r}_1 \cdots d\mathbf{r}_k}{V^k} P^{(k)}(\mathbf{r}^k) = 1 \tag{5.5}$$

We also notice that:

$$\int \frac{d\mathbf{r}_{k+1}}{V} P^{(k+1)}(\mathbf{r}^{k+1}) = P^{(k)}(\mathbf{r}^k) \tag{5.6}$$

In the foregoing, we shall use the shorthand notation $P_{i_1 \cdots i_k} = P^{(k)}(\mathbf{r}_{i_1},..., \mathbf{r}_{i_k})$. Finally, distribution functions are defined (for $n = 2,..., N$) as:

$$g_{12\cdots n} = \left(1 - \frac{1}{N}\right)\left(1 - \frac{2}{N}\right) \cdots \left(1 - \frac{n-1}{N}\right) \frac{P_{12\cdots n}}{P_1 P_2 \cdots P_n} \tag{5.7}$$

with the property

$$\int \frac{d\mathbf{r}_{k+1}}{V} P_{k+1} g_{1\cdots k+1} = \frac{N-k}{N} g_{1\cdots k} \tag{5.8}$$

Simplifying the notation for the sake of clarity, we state that the entropy expansion is simply given by the identity:

$$-\frac{S^{(\text{ex})}}{k_B} = \int P_{1\cdots N} \ln P_{1\cdots N}$$

$$= N \int P_1 \ln P_1 + \int P_{1\cdots N} \ln \frac{P_{1\cdots N}}{P_1 \cdots P_N}$$

$$
\begin{aligned}
&= N \int P_1 \ln P_1 + \binom{N}{2} \int P_{12} \ln \frac{P_{12}}{P_1 P_2} \\
&\quad + \binom{N}{3} \left\{ \int P_{123} \ln \frac{P_{123}}{P_1 P_2 P_3} - \binom{3}{2} \int P_{12} \ln \frac{P_{12}}{P_1 P_2} \right\} \\
&\quad + \binom{N}{4} \left\{ \int P_{1234} \ln \frac{P_{1234}}{P_1 P_2 P_3 P_4} - \binom{4}{3} \int P_{123} \ln \frac{P_{123}}{P_1 P_2 P_3} \right. \\
&\quad \left. + \binom{4}{2} \int P_{12} \ln \frac{P_{12}}{P_1 P_2} \right\} \\
&\quad + \cdots + \left\{ \int P_{1 \dots N} \ln \frac{P_{1 \dots N}}{P_1 \cdots P_N} - \binom{N}{N-1} \int P_{1 \dots N-1} \ln \frac{P_{1 \dots N-1}}{P_1 \cdots P_{N-1}} \right. \\
&\quad \left. + \cdots + (-1)^N \binom{N}{2} \int P_{12} \ln \frac{P_{12}}{P_1 P_2} \right\}
\end{aligned} \tag{5.9}
$$

which stems from the following combinatorial formula (valid for $0 \leqslant k < N$):

$$
\begin{aligned}
\sum_{n=k}^{N} (-1)^n \binom{N}{n} \binom{n}{k} &= (-1)^k \sum_{n=0}^{N-k} (-1)^n \binom{N}{n+k} \binom{n+k}{k} \\
&= (-1)^k \binom{N}{k} \sum_{n=0}^{N-k} (-1)^n \binom{N-k}{n} = 0
\end{aligned} \tag{5.10}
$$

The procedure adopted above to obtain the entropy expansion bypasses the more standard use of the potentials of average force.[14]

Now, it can be proven sistematically, i.e., order by order, that the various terms in Eq. (5.9) have the usual form when expressed in terms of distribution functions. In fact, we shall stop at the third-order term in the expansion.

Taking advantage of Eq. (5.7), the second term in Eq. (5.9) can be written as:

$$
\begin{aligned}
&\binom{N}{2} \int \frac{d\mathbf{r}_1 \, d\mathbf{r}_2}{V^2} P_{12} \ln \frac{P_{12}}{P_1 P_2} \\
&\quad = \binom{N}{2} \ln \frac{N}{N-1} + \frac{1}{2} \rho^2 \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, P_1 P_2 g_{12} \ln g_{12} \\
&\quad = \frac{1}{2} \rho^2 \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, P_1 P_2 (g_{12} \ln g_{12} - g_{12} + 1) + N \left(\frac{N-1}{2} \ln \frac{N}{N-1} - \frac{1}{2} \right)
\end{aligned} \tag{5.11}
$$

The rearrangement in Eq. (5.11) ensures a faster convergence of the integrand. Note, moreover, that the additional number in Eq. (5.11) is $\mathcal{O}(1)$ in the thermodynamic limit.

The next piece of Eq. (5.9) reads:

$$\binom{N}{3}\left\{\int \frac{d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3}{V^3}\, P_{123} \ln \frac{P_{123}}{P_1 P_2 P_3} - 3\int \frac{d\mathbf{r}_1\, d\mathbf{r}_2}{V^2}\, P_{12} \ln \frac{P_{12}}{P_1 P_2}\right\}$$

$$= \binom{N}{3} \ln \frac{(N-1)^2}{N(N-2)} + \frac{1}{6}\rho^3 \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, P_1 P_2 P_3 g_{123} \ln \frac{g_{123}}{g_{12} g_{13} g_{23}}$$

$$= \frac{1}{6}\rho^3 \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3$$

$$\times P_1 P_2 P_3 \left(g_{123} \ln \frac{g_{123}}{g_{12} g_{13} g_{23}} - g_{123} + 3 g_{12} g_{13} - 3 g_{12} + 1 \right)$$

$$+ N\left[\frac{(N-1)(N-2)}{6} \ln \frac{(N-1)^2}{N(N-2)} - \frac{1}{6}\right] \tag{5.12}$$

Again, rearranging the terms in Eq. (5.12) in such a way as to reproduce the grand-canonical three-body entropy[12] leaves outside the integral a number which is $\mathcal{O}(1)$ in the $N \to \infty$ limit. More generally, we surmise that at each order in the expansion, completing the integral as stated above produces a residual $\mathcal{O}(1)$ quantity.

The spurious terms appearing at each order in the expansion can be easily re-summed by means of Eq. (5.10), obtaining:

$$\binom{N}{2} \ln \frac{N}{N-1} + \binom{N}{3}\left\{\ln \frac{N^2}{(N-1)(N-2)} - 3 \ln \frac{N}{N-1}\right\}$$

$$+ \binom{N}{4}\left\{\ln \frac{N^3}{(N-1)(N-2)(N-3)} - 4 \ln \frac{N^2}{(N-1)(N-2)} + 6 \ln \frac{N}{N-1}\right\}$$

$$+ \cdots + \left\{\ln \frac{N^{N-1}}{(N-1)(N-2)\cdots 2\cdot 1} - N \ln \frac{N^{N-2}}{(N-1)(N-2)\cdots 3\cdot 2}\right.$$

$$\left. + \cdots + (-1)^N \binom{N}{2} \ln \frac{N}{N-1}\right\}$$

$$= \ln \frac{N^{N-1}}{(N-1)!} = \ln \frac{N^N}{N!} \tag{5.13}$$

It then follows:

$$
\begin{aligned}
\frac{S^{(\text{ex})}}{k_B} = & -\ln \frac{N^N}{N!} + N\left(\frac{1}{2}+\frac{1}{6}+\cdots\right) - \rho \int d\mathbf{r}_1 P_1 \ln P_1 \\
& -\frac{1}{2}\rho^2 \int d\mathbf{r}_1\, d\mathbf{r}_2\, P_1 P_2 (g_{12}\ln g_{12} - g_{12} + 1) \\
& -\frac{1}{6}\rho^3 \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, P_1 P_2 P_3 \\
& \times \left(g_{123} \ln \frac{g_{123}}{g_{12}g_{13}g_{23}} - g_{123} + 3g_{12}g_{13} - 3g_{12} + 1 \right) + \cdots
\end{aligned}
\tag{5.14}
$$

We emphasize that Eq. (5.14) contains only a finite number of terms, the last term being the N-body entropy.

The first two terms on the right-hand side of Eq. (5.14) can be written in a more transparent way after using the N-particle ideal-gas entropy:

$$
\frac{DN}{2} + \ln\left[\frac{1}{N!}\left(\frac{V}{\Lambda^D}\right)^N\right] = N\left[\frac{D}{2} - \ln(\rho\Lambda^D)\right] - \ln\frac{N!}{N^N}
\tag{5.15}
$$

We show below that $\frac{1}{2}+\frac{1}{6}+\cdots$ is just the Mengoli series (stopped at $1/N(N-1)$). Hence, Eq. (5.14) becomes:

$$
\begin{aligned}
\frac{S}{k_B} = & \frac{S^{(\text{id})}}{k_B} - 1 - \rho \int d\mathbf{r}_1\, P_1 \ln P_1 - \frac{1}{2}\rho^2 \int d\mathbf{r}_1\, d\mathbf{r}_2\, P_1 P_2 (g_{12}\ln g_{12} - g_{12} + 1) \\
& -\frac{1}{6}\rho^3 \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, P_1 P_2 P_3 \\
& \times \left(g_{123} \ln \frac{g_{123}}{g_{12}g_{13}g_{23}} - g_{123} + 3g_{12}g_{13} - 3g_{12} + 1 \right) + \cdots
\end{aligned}
\tag{5.16}
$$

where

$$
\frac{S^{(\text{id})}}{k_B} = N\left[\frac{D+2}{2} - \ln(\rho\Lambda^D)\right]
\tag{5.17}
$$

is the ideal-gas entropy *in the thermodynamic limit*. Equation (5.16) is the entropy formula in the canonical ensemble. At variance with the analogous expansion in the grand-canonical ensemble, it is valid for arbitrary N.

We finally show that each of the numbers appearing on the left-hand side of Eq. (5.13) behaves like $N/k(k-1)$ ($k = 2, 3,\ldots, N$), for large N. To this end, consider the generic term:

$$\ln \frac{N^{k-1}}{(N-1)\cdots(N-k+1)} - \binom{k}{k-1} \ln \frac{N^{k-2}}{(N-1)\cdots(N-k+2)} + \cdots + (-1)^k \binom{k}{2} \ln \frac{N}{N-1} = \sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} \ln\left(1 - \frac{k-n}{N}\right) \tag{5.18}$$

Since we are going to take the $N \to \infty$ limit of this expression, we expand the right-hand side of Eq. (5.18) in powers of N^{-1} to get:

$$-\frac{1}{N} \sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} (k-n) - \frac{1}{2N^2} \sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} (k-n)^2 + \cdots \tag{5.19}$$

In order to calculate the leading term in Eq. (5.19), we preliminary show (for $k = 2, 3,\ldots$) that:

$$\sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} (k-n)^d = \begin{cases} -(-1)^k, & \text{for } d = 0 \\ 0, & \text{for } d = 1, 2,\ldots, k-2 \\ -(k-1)!, & \text{for } d = k-1 \end{cases} \tag{5.20}$$

For $d = 0$ and for $k = 2, 3$, the proof of Eq. (5.20) is straightforward. When $k > 3$ and $d = 1, 2,\ldots, k-1$, we carry on by induction over k. We find:

$$\begin{aligned} &\sum_{n=1}^{k} (-1)^n \binom{k}{n-1} (k+1-n)^d \\ &= k \sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} (k+1-n)^{d-1} + (-1)^k k \\ &= k \sum_{m=0}^{d-1} \binom{d-1}{m} \sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} (k-n)^m + (-1)^k k \\ &= k \sum_{m=1}^{d-1} \binom{d-1}{m} \sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} (k-n)^m \end{aligned} \tag{5.21}$$

When $d \leqslant k-1$, the above number is zero, due to Eq. (5.20). Instead, when $d=k$ the result is:

$$k \sum_{n=1}^{k-1} (-1)^n \binom{k-1}{n-1} (k-n)^{k-1} = -k! \tag{5.22}$$

which completes the proof of Eq. (5.20). Using this equation, it is now easy to see that the first term surviving in Eq. (5.19) is $d=k-1$, which eventually leads to

$$\binom{N}{k}\left[\ln \frac{N^{k-1}}{(N-1)\cdots(N-k+1)} + \cdots + (-1)^k \binom{k}{2} \ln \frac{N}{N-1}\right] \sim \frac{N}{k(k-1)} \tag{5.23}$$

as anticipated above.

We add a final comment to Eq. (5.9). This equation gives the excess entropy as a sum of N terms whose values become progressively smaller and smaller provided the density is not too high. Hence, the approximation obtained upon truncating the sum at a given order improves with the number of terms that are being kept. This procedure can be made more systematic by introducing a functional $S^* = -\langle \ln P^*_{1\cdots N} \rangle$, which for $P^*_{1\cdots N} = P_{1\cdots N}$ gives back the total excess entropy. In particular, the truncation of Eq. (5.9) after the first, second, and third term respectively, can be accomplished by assuming:

$$\begin{aligned} P^*_{1\cdots N} &= \prod_i P_i, \\ P^*_{1\cdots N} &= \left(\prod_i P_i^{-1}\right)^{N-2} \prod_{i<j} P_{ij}, \\ P^*_{1\cdots N} &= \left(\prod_i P_i\right)^{(N-2)(N-3)/2} \left(\prod_{i<j} P_{ij}^{-1}\right)^{N-3} \prod_{i<j<k} P_{ijk} \end{aligned} \tag{5.24}$$

VI. LATTICE ENTROPY EXPANSION IN THE CANONICAL ENSEMBLE

We now come back to the lattice-gas system. We start from the partition function of a n-particle system on a lattice with N sites, $Z_n = Z_n^{(\mathrm{id})} Q_n$. The configurational integral reads:

$$Q_n = \frac{(N-n)!}{N!} \sum_{\substack{i_1,\ldots,i_n=1 \\ (i_p \neq i_q)}}^{N} e^{-\beta U_n(i^n)} \tag{6.1}$$

We then define distribution functions (for $k=1,\ldots,n-1$):

$$P^{(k)}(i^k)=\frac{(N-n)!}{(N-k)!}\sum_{\substack{i_{k+1},\ldots,i_n=1\\(i_p\neq i_q)}}^{N}\frac{e^{-\beta U_n(i^n)}}{Q_n}\tag{6.2}$$

each being 1 for the ideal gas. We also define:

$$P^{(n)}(i^n)=\frac{e^{-\beta U_n(i^n)}}{Q_n}\tag{6.3}$$

In the following, we shall use the shorthand notation $P_{i_1\cdots i_k}=P^{(k)}(i_1,\ldots,i_k)$. Useful identities which hold for any k are:

$$\sum_{\substack{i_1,\ldots,i_k=1\\(i_p\neq i_q)}}^{N}P_{i_1\cdots i_k}=\frac{N!}{(N-k)!}\tag{6.4}$$

and

$$\sum_{i_{k+1}\neq i_1,\ldots,i_k}^{N}P_{i_1\cdots i_{k+1}}=(N-k)\,P_{i_1\cdots i_k}\tag{6.5}$$

Both of the two have an obvious counterpart in the continuum. Using Eq. (2.13), the reduced distribution functions become:

$$g_{i_1\cdots i_m}\equiv\frac{\langle c_{i_1}\cdots c_{i_m}\rangle^{(n)}}{\langle c_{i_1}\rangle^{(n)}\cdots\langle c_{i_m}\rangle^{(n)}}=g_m^*\,\frac{P_{i_1\cdots i_m}}{P_{i_1}\cdots P_{i_m}}\tag{6.6}$$

for $m=2,\ldots,n$, where

$$g_m^*\equiv\rho^{-m}\,\frac{n(n-1)\cdots(n-m+1)}{N(N-1)\cdots(N-m+1)}=g^{(\mathrm{id})}_{i_1\cdots i_m}\tag{6.7}$$

and $\rho=n/N$. The sum-rules

$$\rho^m\sum_{\substack{i_1,\ldots,i_m=1\\(i_p\neq i_q)}}^{N}P_{i_1}\cdots P_{i_m}g_{i_1\cdots i_m}=\frac{n!}{(n-m)!}\tag{6.8}$$

and

$$\rho\sum_{i_{m+1}\neq i_1,\ldots,i_m}^{N}P_{i_{m+1}}g_{i_1\cdots i_{m+1}}=(n-m)\,g_{i_1\cdots i_m}\tag{6.9}$$

hold for any m. Finally, the excess entropy is given by:

$$\frac{S^{(\mathrm{ex})}}{k_B} = -\frac{(N-n)!}{N!} \sum_{\substack{i_1,\ldots,i_n=1 \\ (i_p \neq i_q)}}^{N} \frac{e^{-\beta U_n(i^n)}}{Q_n} \ln \frac{e^{-\beta U_n(i^n)}}{Q_n} \tag{6.10}$$

In a way analogous to Eq. (5.10), we can write an identity also for the lattice entropy, whose leading terms at low density are:

$$\frac{S_1^{(\mathrm{ex})}}{k_B} = -\binom{n}{1} \frac{(N-1)!}{N!} \sum_{i_1=1}^{N} P_{i_1} \ln P_{i_1} = -\rho \sum_{i_1=1}^{N} P_{i_1} \ln P_{i_1} \tag{6.11}$$

$$\frac{S_2^{(\mathrm{ex})}}{k_B} = -\binom{n}{2} \left[\frac{(N-2)!}{N!} \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} P_{i_1 i_2} \ln P_{i_1 i_2} - 2 \frac{(N-1)!}{N!} \sum_{i_1=1}^{N} P_{i_1} \ln P_{i_1} \right]$$

$$= -\frac{1}{2} \rho^2 \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} P_{i_1} P_{i_2} g_{i_1 i_2} \ln g_{i_1 i_2} + \binom{n}{2} \ln \left(\frac{n-1}{n} \frac{N}{N-1} \right) \tag{6.12}$$

$$\frac{S_3^{(\mathrm{ex})}}{k_B} = -\binom{n}{3} \left[\frac{(N-3)!}{N!} \sum_{\substack{i_1, i_2, i_3=1 \\ (i_p \neq i_q)}}^{N} P_{i_1 i_2 i_3} \ln P_{i_1 i_2 i_3} - 3 \frac{(N-2)!}{N!} \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} P_{i_1 i_2} \ln P_{i_1 i_2} \right.$$

$$\left. + 3 \frac{(N-1)!}{N!} \sum_{i_1=1}^{N} P_{i_1} \ln P_{i_1} \right]$$

$$= -\frac{1}{6} \rho^3 \sum_{\substack{i_1, i_2, i_3=1 \\ (i_p \neq i_q)}}^{N} P_{i_1} P_{i_2} P_{i_3} g_{i_1 i_2 i_3} \ln \frac{g_{i_1 i_2 i_3}}{g_{i_1 i_2} g_{i_1 i_3} g_{i_2 i_3}}$$

$$+ \binom{n}{3} \ln \left[\frac{n(n-2)}{(n-1)^2} \frac{(N-1)^2}{N(N-2)} \right] \tag{6.13}$$

In order to make a comparison with the grand-canonical series, we need to consider the general term appearing in the entropy expansion, i.e.:

$$-\binom{n}{m} \frac{(N-m)!}{N!} \sum_{\substack{i_1,\ldots,i_m=1 \\ (i_p \neq i_q)}}^{N} P_{i_1 \cdots i_m} \ln \frac{P_{i_1 \cdots i_m}}{P_{i_1} \cdots P_{i_m}}$$

$$= -\frac{1}{m!} \rho^m \sum_{\substack{i_1,\ldots,i_m=1 \\ (i_p \neq i_q)}}^{N} P_{i_1} \cdots P_{i_m} g_{i_1 \cdots i_m} \ln g_{i_1 \cdots i_m} + \binom{n}{m} \ln g_m^* \tag{6.14}$$

Using the same trick as before (see Eq. (5.11)) to sum up the numbers $\binom{n}{m} \ln g_m^* = -\binom{n}{m} \ln[n^{m-1}/(n-1) \cdots (n-m+1)] + \binom{n}{m} \ln[N^{m-1}/(N-1) \cdots (N-m+1)]$, we obtain:

$$-\ln \frac{n^n}{n!} + \ln \frac{N^{n-1}}{(N-1)(N-2)\cdots(N-n+1)} = -\ln \frac{n^n}{n!} + \ln \left[\frac{N^n (N-n)!}{N!} \right] \tag{6.15}$$

which, added to the n-particle ideal-gas entropy

$$\ln \binom{N}{n} = -N[\rho \ln \rho + (1-\rho) \ln(1-\rho)] + \ln \frac{n^n}{n!} + \ln \frac{N!}{N^N} + \ln \frac{(N-n)^{N-n}}{(N-n)!} \tag{6.16}$$

yields the total entropy as:

$$\frac{S}{k_B} = \frac{S^{(\mathrm{id})}}{k_B} + N(1-\rho)\ln(1-\rho) - \rho \sum_{i_1=1}^{N} P_{i_1} \ln P_{i_1} - \frac{1}{2} \rho^2 \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} P_{i_1} P_{i_2} g_{i_1 i_2} \ln g_{i_1 i_2} - \frac{1}{6} \rho^3 \sum_{\substack{i_1, i_2, i_3 = 1 \\ (i_p \neq i_q)}}^{N} P_{i_1} P_{i_2} P_{i_3} g_{i_1 i_2 i_3} \ln \frac{g_{i_1 i_2 i_3}}{g_{i_1 i_2} g_{i_1 i_3} g_{i_2 i_3}} + \cdots \tag{6.17}$$

where

$$\frac{S^{(\mathrm{id})}}{k_B} = -N[\rho \ln \rho + (1-\rho)\ln(1-\rho)] \tag{6.18}$$

is the ideal-gas entropy in the thermodynamic limit (note, however, that ρ is the density of the interacting system).

Equation (6.17) is the lattice-gas analogue of the cumulant expansion reported by several authors.[2, 14] However, it is of little interest here, since our main purpose is to trace a comparison with the grand-canonical entropy series, Eq. (3.38). For the entropy expansion to be formally the same in any ensemble, the number $N(1-\rho)\ln(1-\rho)$ in Eq. (6.17) must represent the sum of all configurational terms in the excess entropy. In fact, this can be proven by rearranging terms in Eq. (6.17) with the use of Eqs. (6.8) and (6.9). We consider only the two- and the three-body terms:

$$
\begin{aligned}
-\frac{1}{2}\rho^2 \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} P_{i_1} P_{i_2} g_{i_1 i_2} \ln g_{i_1 i_2}
&= \frac{n}{2} - \frac{n}{2}\rho + \frac{1}{2}\rho^2 \sum_{i_1=1}^{N} (1 - P_{i_1}^2) \\
&\quad - \frac{1}{2}\rho^2 \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} P_{i_1} P_{i_2} (g_{i_1 i_2} \ln g_{i_1 i_2} - g_{i_1 i_2} + 1)
\end{aligned} \tag{6.19}
$$

$$
\begin{aligned}
-\frac{1}{6}\rho^3 \sum_{\substack{i_1, i_2, i_3=1 \\ (i_p \neq i_q)}}^{N} P_{i_1} P_{i_2} P_{i_3} g_{i_1 i_2 i_3} \ln \frac{g_{i_1 i_2 i_3}}{g_{i_1 i_2} g_{i_1 i_3} g_{i_2 i_3}}
&= \frac{n}{6} - \frac{n}{6}\rho^2 + \frac{1}{6}\rho^3 \sum_{i_1=1}^{N} (1 - P_{i_1}^3) - \frac{1}{2}\rho^3 \sum_{\substack{i_1, i_2=1 \\ (i_1 \neq i_2)}}^{N} P_{i_1} P_{i_2}^2 (g_{i_1 i_2} - 1)^2 \\
&\quad - \frac{1}{6}\rho^3 \sum_{\substack{i_1, i_2, i_3=1 \\ (i_p \neq i_q)}}^{N} P_{i_1} P_{i_2} P_{i_3} \\
&\quad \times \left(g_{i_1 i_2 i_3} \ln \frac{g_{i_1 i_2 i_3}}{g_{i_1 i_2} g_{i_1 i_3} g_{i_2 i_3}} - g_{i_1 i_2 i_3} + 3 g_{i_1 i_2} g_{i_1 i_3} - 3 g_{i_1 i_2} + 1 \right)
\end{aligned} \tag{6.20}
$$

Apart from additional terms that are eventually to be summed up, Eqs. (6.19) and (6.20) contain the same sums of distribution functions which appear in the grand-canonical entropy expansion, including the novel term at the third-order level. As to the additional terms, we surmise, by analogy with the continuum case, that all of them amount to:

$$
\begin{aligned}
n \sum_{k=2}^{n} \frac{1 - \rho^{k-1}}{k(k-1)} &= n - 1 - n \sum_{k=2}^{n} \left(\frac{\rho^{k-1}}{k-1} - \frac{\rho^{k-1}}{k} \right) \\
&\sim -N(1-\rho)\ln(1-\rho)
\end{aligned} \tag{6.21}
$$

The term on the right-hand side of Eq. (6.21) is the leading one in the $n \to \infty$ (thermodynamic) limit. Granted the above assumption, the entropy expansion can be re-written (discarding $\mathcal{O}(1)$ terms) as:

$$\begin{aligned}\frac{S}{k_B} = {} & \frac{S^{(\mathrm{id})}}{k_B} - \rho \sum_{i_1=1}^{N} P_{i_1} \ln P_{i_1} + \frac{1}{2}\rho^2 \sum_{i_1=1}^{N} (1 - P_{i_1}^2) + \frac{1}{6}\rho^3 \sum_{i_1=1}^{N} (1 - P_{i_1}^3) \\ & - \frac{1}{2}\rho^2 \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} P_{i_1} P_{i_2} (g_{i_1 i_2} \ln g_{i_1 i_2} - g_{i_1 i_2} + 1) \\ & - \frac{1}{2}\rho^3 \sum_{\substack{i_1, i_2 = 1 \\ (i_1 \neq i_2)}}^{N} P_{i_1} P_{i_2}^2 (g_{i_1 i_2} - 1)^2 \\ & - \frac{1}{6}\rho^3 \sum_{\substack{i_1, i_2, i_3 = 1 \\ (i_p \neq i_q)}}^{N} P_{i_1} P_{i_2} P_{i_3} \\ & \times \left(g_{i_1 i_2 i_3} \ln \frac{g_{i_1 i_2 i_3}}{g_{i_1 i_2} g_{i_1 i_3} g_{i_2 i_3}} - g_{i_1 i_2 i_3} + 3 g_{i_1 i_2} g_{i_1 i_3} - 3 g_{i_1 i_2} + 1 \right) + \cdots \end{aligned} \tag{6.22}$$

which is formally the same as the grand-canonical entropy expansion (3.37) for an inhomogeneous lattice-gas system.

VII. CONCLUSIONS

In this paper we have derived a formula expressing the statistical entropy of a lattice-gas system in terms of multi-particle correlations, both in the grand-canonical and in the canonical ensemble. We have also shown that, in the thermodynamic limit, the expansion turns out to be the same in the two ensembles.

The lattice entropy expansion shows some differences with respect to the same series in the continuum. In particular, the pair entropy of the inhomogeneous lattice system contains an additional term, whereas the three-body entropy includes an extra term also in the absence of external fields. Indeed, in the one-dimensional Ising model, this last term contributes to the total entropy evaluated at third order in the density, whereas the term involving the three-body distribution function does not.

We plan to investigate, in a forthcoming paper, the relation between the fine structure of the statistical entropy and the phase transitions undergone by some specific lattice-gas models in two dimensions.[38]

REFERENCES

1. H. S. Green, *The Molecular Theory of Fluids* (North Holland, Amsterdam, 1952).
2. J. M. Richardson, *J. Chem. Phys.* **23**, 2304 (1955).
3. R. E. Nettleton and M. S. Green, *J. Chem. Phys.* **29**, 1365 (1958).

4. T. Morita and K. Hiroike, *Prog. Theor. Phys.* **25**, 237 (1961).
5. C. De Dominicis, *J. Math. Phys.* **5**, 983 (1962).
6. J. Yvon, *Correlations and Entropy in Classical Statistical Mechanics* (Pergamon, Oxford, 1969).
7. H. J. Raveché, *J. Chem. Phys.* **55**, 2242 (1971).
8. R. J. Baxter, in *Physical-Chemistry: An Advanced Treatise*, H. Eyring, D. Henderson, and W. Jost, eds. (Academic Press, New York, 1971).
9. J. K. Percus, *Acc. Chem. Res.* **27**, 224 (1994).
10. D. C. Wallace, *Phys. Lett. A* **122**, 418 (1987); *J. Chem. Phys.* **87**, 2282 (1987); *Phys. Rev. A* **38**, 469 (1988); *Phys. Rev. A* **39**, 4843 (1989).
11. A. Baranyai and D. J. Evans, *Phys. Rev. A* **40**, 3817 (1989).
12. J. A. Hernando, *Mol. Phys.* **69**, 319 (1990).
13. R. Kikuchi, *Phys. Rev.* **81**, 988 (1951).
14. A. G. Schlijper and G. K. Harris, *J. Chem. Phys.* **95**, 7603 (1991); A. G. Schlijper, *Prog. Theor. Phys. Suppl.* **115**, 69 (1994).
15. B. B. Laird and A. D. J. Haymet, *Phys. Rev. A* **45**, 5680 (1992); *J. Chem. Phys.* **97**, 2153 (1992).
16. T. Lazaridis and M. E. Paulaitis, *J. Chem. Phys.* **96**, 3847 (1992).
17. D. C. Wallace, *Int. J. Quantum Chem.* **52**, 425 (1994).
18. T. Lazaridis and M. Karplus, *J. Chem. Phys.* **105**, 4294 (1996).
19. M. Dzugutov, *Nature* **381**, 137 (1996).
20. A. Baranyai and D. J. Evans, *Phys. Rev. A* **42**, 849 (1990).
21. A. Baranyai and D. J. Evans, *Z. Naturforsch.* **46a**, 27 (1991).
22. G. Hummer and D. M. Soumpasis, *J. Chem. Phys.* **98**, 581 (1993).
23. O. Gereben, L. Putsztai, and A. Baranyai, *J. Phys. C* **6**, 10939 (1994).
24. P. V. Giaquinta and G. Giunta, *Physica A* **187**, 145 (1992).
25. P. V. Giaquinta, G. Giunta, and S. Prestipino Giarritta, *Phys. Rev. A* **45**, 6966 (1992).
26. C. Caccamo, P. V. Giaquinta, and G. Giunta, *J. Phys.: Condens. Matter* **5**, B75 (1993).
27. A. Cheng, M. L. Klein, and C. Caccamo, *Phys. Rev. Lett.* **71**, 1200 (1993).
28. E. Lomba, J. L. Lopez-Martin, H. M. Cataldo, and C. F. Tejero, *Phys. Rev. E* **49**, 5164 (1994).
29. E. Lomba and N. E. Almarza, *J. Chem. Phys.* **100**, 8367 (1994).
30. F. Saija, P. V. Giaquinta, G. Giunta, and S. Prestipino Giarritta, *J. Phys.: Condens. Matter* **6**, 9853 (1994).
31. P. V. Giaquinta, *Atti Accademia Peloritana dei Pericolanti* (Messina), **LXXI**, 353 (1995).
32. F. Saija and P. V. Giaquinta, *J. Phys.: Condens. Matter* **8**, 8137 (1996).
33. C. Caccamo and G. Pellicane, *Physica A* **235**, 149 (1997).
34. P. V. Giaquinta, G. Giunta, and G. Malescio, *Physica A* **250**, 91 (1998).
35. D. Costa, F. Saija, and P. V. Giaquinta, *Chem. Phys. Lett.* **283**, 86 (1998); Erratum: *ibidem* **299**, 252 (1999).
36. F. Saija, G. Pastore, and P. V. Giaquinta, *J. Phys. Chem. B* **102**, 10368 (1998).
37. J. M. Yeomans, *Statistical Mechanics of Phase Transitions* (Clarendon Press, Oxford, 1992).
38. M. G. Donato, S. Prestipino, and P. V. Giaquinta, "Entropy and multi-particle correlations in two-dimensional lattice gases," *European Physical Journal B* (1999), submitted.