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Ornstein–Zernike formalism and entropy in lattice gases*

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Abstract
Lattice gas based models are usually discussed in terms of spin averages instead of distribution functions. As they are very useful in the study of adsorption phenomena, a density functional (DF) formalism, which would unify the discussion of both the liquid and the adsorbed phases, seems a most useful alternative. Here we present a first step in that direction by deriving the two essential components needed for any DF theory. The first one is a fully developed Ornstein–Zernike (OZ) formalism which we arrive at in two steps. The first one is the definition (through functional differentiation of the grand canonical partition function) of the distribution and correlation functions hierarchies. In the second step we find that the rigid neighbourhood of a lattice gas forces us, if an authentic DF theory is our goal and even in the grand canonical ensemble, to define N-modified distribution and correlation functions much in the same way as we have recently done when discussing DF theory in the canonical ensemble. These N-modified hierarchies of correlation functions are, indeed, linked by a full set of n-body OZ equations. The second ingredient for any DF theory is an expression for the entropy (in terms of the already discussed correlation functions) which we obtain by following previous work by us in fluids. We also generalize the compressibility contribution to the entropy by using the already derived lattice gas formalism in a way immediately translatable to liquids. In summary, we show how a deep and intimate relationship between lattice gases and fluids can be obtained if both are discussed in a DF framework with functional differentiation techniques and, therefore, we think that the beginnings of a DF theory of lattice gases are established.

* To the memory of Yasha Rosenfeld, a great scientist and human being.
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1. Introduction

Finite temperature density functional (DF) theory is the offspring of the Hohenberg, Kohn, Sham and Mermin (HKSM) theorem [1] and, when applied to fluid systems, follows a deceptively simple template: a free energy functional is proposed, a variational calculation (usually with one-and two-body distribution functions as independent functions) is performed and the output is both a microscopic description, given by the distribution functions solving the variational equations, and some statistical mechanical quantities obtained as averages over these distribution functions. A closer examination shows two essential ingredients: an Ornstein–Zernike (OZ) formalism (a *sine qua non* condition for the validity of the HKSM theorem) and some proposal for the entropy functional. Let us also mention that the original HKSM theorem was derived in the grand canonical ensemble (GCE) and, very recently, we extended it to the canonical ensemble (CE) [2] by dropping off the asymptotic behaviour of the distribution functions and, thus, deriving new, N-modified hierarchies of distribution and correlation functions. Although this issue is ample proof of the quantity and diversity of DF applications, we can, nevertheless, mention some general reviews [3], as well as reviews on uniform and non-uniform systems [4], confined fluids [5], melting and freezing [6], etc. On the other hand, present theories of lattice gas systems fall short (see below) of meeting the requirements for a full DF theory. This paper attempts to fill this gap by deriving the two essential prerequisites for such a theory, i.e. an OZ formalism and a proposal for the entropy functional in a form suitable for DF calculations.

The term 'lattice gas' was coined by Yang and Lee in their classic work on a mathematical mechanism that triggers phase transitions [7] and it has been applied to numerous systems with particular emphasis on phase transitions and critical phenomena [8]. Let us mention in that respect that, for example, three-dimensional lattice gases and three-dimensional fluids belong to the same universality class. Roughly speaking, by lattice gas we will mean, in this paper, a mathematical lattice where each node can be in one of several possible (and mutually exclusive) discrete states. The physical problem that motivates us is the case of adsorption phenomena on a lattice like, for example, those in the electrode–electrolyte interface, where a quite natural language to use in its study is the one of lattice gases and its associated occupation number formalism [9]. However, this is not an easy task. One of the main problems is how to treat the different excluded volume effects when different molecules can be adsorbed on a lattice or, equivalently, how to write the entropy. This is the main reason for the failure of standard mean field theories in some of these systems. On the other hand, liquid state theory is formulated considering excluded volume effects as the more important ones. In fact, to include them is the absolutely indispensable condition in order to formulate any liquid state theory; an outstanding example is Rosenfeld's fundamental measure functional [4]. Some previous approaches to lattice gases using ideas borrowed from liquid state theory are those of [10–12]. Robledo and Farquhar [10] employed a random walk and lattice Green function formalism to study the decay of pair correlations in the framework of an OZ equation in the Percus–Yevick approximation. It is a very elegant work but its drawback is that it is restricted to nearest neighbours (nn) and it has not been possible (and it does not seem very feasible, either) to extend it to longer range interactions. This problem, in fact, has precluded its application to systems with adsorbates of different sizes where, sometimes, the nn occupation is forbidden. The reason is that an extension of lattice Green functions to more complex random walks seems extremely complicated (if feasible at all), even for next nn. Dickman *et al* [11] used a self-consistent Ornstein–Zernike approach (SCOZA) previously developed by Hoye and Stell [13] and, by demanding thermodynamic consistency, arrived at a partial differential equation that was quite successfully solved for several cases. They also considered

spin averages. Prestipino *et al* [12] developed a quasi-liquid formalism, quasi because, as in [10, 11], they work with spin averages instead of distribution functions. In summary, in all of these approaches, full distribution and correlation functions (as defined in [14]) are not considered and so they do not have a properly based OZ theory.

On the other hand, a full liquid state formalism applied to lattice gases is intrinsically attractive because, on the one hand, excluded volume effects can easily be taken into account *exactly* (the necessary distribution functions g are, by definition, $g \equiv 0$ in that range). Indeed, if we are considering, for example, adsorption of more than one species (see section 2), this approach seems simpler than the one which employs occupation number formalism. Also, the more modern and developed formalism in liquids is the OZ formalism which allows the introduction of both DF ideas as well as sophisticated free energy functionals, see e.g. [4]. As it has been very successful in dealing with the fluid phase in contact with the wall, the possibility of having a unified (i.e. same formalism) treatment seems rather interesting. Another convenient characteristic of this formalism is that it leads to equations that do not depend on derivatives of the interaction potential (which do not have a clear analogy in lattice gases). These features will be available to the study of lattice gases if a one to one correspondence can be established between liquids and lattice gases at a very basic level, i.e. the one of distribution functions hierarchies. We not only show in this paper that both problems are equivalent, i.e. isomorphic if treated with the adequate formalism (functional differentiation of thermodynamic potentials), but also show how a full OZ formalism can be obtained and, as a consequence, laid the foundation for a DF theory of lattice gases. The problem to solve is that an OZ theory does not immediately follow from the functional differentiation analysis because of the rigid topology of lattice gases and that leads us to the introduction of N-modified distribution and correlation functions. We then write down the decomposition of the entropy in terms of correlation functions of increasing complexity by mimicking previous work by us on liquid systems [15–17]. As in the course of the derivation we needed the generalization to mixtures in external fields of some recently derived terms [17], we did that by using the lattice gas language and then directly translated it to liquid state formalism showing, as a by-product, how useful this isomorphism can be. The layout of the paper is as follows: in section 2 we discuss the general functional formalism in the lattice gas case. In section 3 we show how a rigid neighbourhood invalidates a straightforward OZ approach and, after that, discuss how previous work [2] on the extension of DF theory to the CE can be used. The point we make there is that the fixed topology constraint of a lattice gas is, in spite of holding true to every order of the neighbourhood, a constraint of the same nature that the fixed N constraint found for fluids in the CE. Therefore, we prove that the HKSM theorem can be formulated by working with the N-modified distribution and correlation functions and, also, that these N-modified functions have the correct hierarchical structure needed in DF theory. In section 4 we discuss the entropy, obtain an exact decomposition of the entropy in correlation functions of increasing complexity and present several approximations to the entropy that can be useful in actual calculations. Section 5 summarizes our conclusions. Lastly, we want to emphasize that we believe the main result of this paper is how deeply intertwined lattice gases and fluids are when both of them are analysed with the functional differentiation formalism of OZ based theories and how this isomorphism opens the highway of DF to research in lattice gases.

2. General formalism

The physical system we consider is a crystalline lattice onto which different molecules can be adsorbed. In general, these molecules will have different sizes and adsorption energies. Of paramount importance are the different excluded volume effects, e.g. it can happen that when

molecule α sits on a given site it will prohibit occupation of its nn, while if that site is occupied by molecule β the occupation of those neighbours is allowed by any molecule different from α. Obviously, the richness of the available phases is almost endless, but it is also obvious that, in order to obtain them, an adequate treatment of the excluded volume effects is indispensable. Undoubtedly they are, by far, more fundamental than using accurate values for the adsorption energies. For an in-depth study of a real case see [9], where the adsorption of copper onto gold (111) in the presence of sulfuric acid is analysed with an extended hard hexagon model which includes a mean field treatment of the adsorbate nn and nnn interactions into Baxter's hard hexagon model [18], while the statistical weights that contribute to the entropy are analysed by the cluster variation method [19] in the Guggenheim–McGlashan approximation [20]. The model Hamiltonian of our general lattice gas problem is, in occupation number formalism,

$$\mathcal{H}(\{V^{(1)}\},\{V^{(2)}\}) = \sum_{\alpha=0}^{p}\sum_{\boldsymbol{i}} V_{\alpha}^{(1)}(\boldsymbol{i})c_{\alpha} + \sum_{\alpha,\lambda}\sum_{\boldsymbol{i},\boldsymbol{j}} V_{\alpha\lambda}^{(2)}(\boldsymbol{i},\boldsymbol{j})c_{\alpha}c_{\lambda} \tag{1}$$

where the Greek indexes label the different adsorbed molecules, $\alpha = 1, \ldots, p$ with 0 reserved for no adsorbed molecule, $\sum_{\boldsymbol{i}}$ is a sum over the sites $\boldsymbol{i}$ of the lattice Λ, $V_{\alpha}^{(1)}$, $V_{\alpha\lambda}^{(2)}$ represent the one- and two-body contributions to the energy and the occupation numbers c_{α} take the values $c_{\alpha} = \alpha$; $\alpha = 0, 1, \ldots, p$ for the p species that can be adsorbed. Notice that, although c_0 does not contribute to the energy, and the entropy can also be written without explicitly including the empty sites, we prefer not to dwell on these points at such an early state of the formalism. Also, the extension to more than two-body interactions is evident. It is clear that an accurate handling of the different excluded volume effects requires elaborated relations between the c operators, see, e.g., [9]. Here, we pursue another approach. We proceed to develop a functional differentiation formalism borrowing from the techniques and terminology used in fluids. As a first step, we introduce the distribution and correlation functions hierarchies and so we have that, *by definition*, each one of the correlation functions $h_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j}) \equiv -1$ for all the neighbours where the pair $\{\alpha,\lambda\}$ is excluded. This is, probably, an easier approach if a formalism can be built along these ideas. Writing $\Phi_{\alpha}(\boldsymbol{i}) = -\beta V_{\alpha}^{(1)}(\boldsymbol{i})c_{\alpha}$ to indicate the external field contribution on site $\boldsymbol{i}$ when that site is occupied by molecule α, keeping in mind that, in lattice gases, N plays the role of V in liquids (the partial densities ρ_{α} are $\rho_{\alpha} = N_{\alpha}/N$) and, with $H = -\beta\mathcal{H}$, the canonical and grand canonical partition functions are

$$Q(N,\boldsymbol{N},\beta) = \frac{1}{\boldsymbol{N}!}\sum_{\{\boldsymbol{N}\}} \mathrm{e}^{H} \qquad \Xi(N,\boldsymbol{z},\beta) = \sum_{\boldsymbol{N}} \boldsymbol{z}^{\boldsymbol{N}} Q(N,\boldsymbol{N},\beta) \tag{2}$$

where N is the system's size, $\boldsymbol{N} = (N_0, N_1, \ldots, N_p)$; $\sum_i N_i = N$ is the macro-description of the system's occupation, i.e. N_i is the number of molecules (spins) of type i and $\sum_{\{\boldsymbol{N}\}}$ sums over all the micro-configurations compatible with $\boldsymbol{N}$. In fact, the sum is over all the possible ways of assembling the coordinates set $\{\boldsymbol{N}\}$ of indistinguishable spins (as is the case for molecules in a mixture) in distinguishable lattice sites, $\boldsymbol{N}! = \prod_{\alpha=0}^{p} N_{\alpha}!$ cancels the overcounting and, lastly, $\boldsymbol{z}^{\boldsymbol{N}} = \prod_{\alpha=0}^{p} z_{\alpha}$ where $z_{\alpha} = \exp(\beta\mu_{\alpha})$ is the fugacity. If the available microscopic states to site $\boldsymbol{i}$ are σ_{α} and the actual state of that site is indicated by $\sigma(\boldsymbol{i})$, then the grand canonical probability distribution function of having site $\boldsymbol{i}$ occupied by a molecule α can be written in several equivalent forms:

$$n_{\alpha}^{(1)}(\boldsymbol{i}) = \langle\delta(\sigma(\boldsymbol{i}) - \sigma_{\alpha})\rangle = \frac{1}{\Xi}\sum_{\boldsymbol{N}} \frac{\boldsymbol{z}^{\boldsymbol{N}}}{(\boldsymbol{N} - \boldsymbol{1}_{\alpha})!}\sum_{\{\boldsymbol{N}\}|\boldsymbol{i},\alpha} \mathrm{e}^{H} = \frac{\mathrm{e}^{\Phi_{\alpha}(\boldsymbol{i})}}{\Xi}\frac{\delta\Xi}{\delta\mathrm{e}^{\Phi_{\alpha}(\boldsymbol{i})}} \tag{3}$$

where $\sum_{\{\boldsymbol{N}\}|\boldsymbol{i},\alpha}$ means that the site $\boldsymbol{i}$ is frozen in the state α and $(\boldsymbol{N} - \boldsymbol{1}_{\alpha})!$ (the overcount correction) takes this fact into account. In this paper we will follow the functional differentiation approach because of its transparency, easy physical interpretation in terms

of response functions and direct correspondence with liquid state theory. In this formulation the canonical distribution functions are formally the same with Q replacing Ξ. There is one important difference to liquid mixtures, though. As $c_0 \equiv 0$ (and it must be so because an empty site does not contribute to the energy), $\Phi_0(\boldsymbol{i}) \equiv 0$ and therefore $n_0(\boldsymbol{i})$ cannot be obtained from equation (3); it is obtained from the normalization given in equation (4). Due to this, the entropy can be written without explicitly including the empty sites. However, we prefer not to do that and refer to section 3, where a more comprehensive discussion of the relationship between the restrictions imposed by the fixed topology of lattice gases and an adequate DF treatment is given. The normalization equations for $n_\alpha^{(1)}(\boldsymbol{i})$ are, obviously,

$$\sum_{\alpha=0}^{p} n_\alpha^{(1)}(\boldsymbol{i}) \equiv 1 \qquad \forall \boldsymbol{i} \tag{4}$$

$$\langle n_\alpha^{(1)} \rangle = \sum_{\boldsymbol{i}} n_\alpha^{(1)}(\boldsymbol{i}) = \langle N_\alpha \rangle \tag{5}$$

are completely equivalent to the corresponding ones of fluids and give a foundation for calling them probability distribution functions. The CE version of equation (5) gives N_α. The link with the more usual averages notation of lattice gases is

$$\frac{\sum_\alpha n_\alpha^{(1)}(\boldsymbol{i}) c_\alpha}{\sum_\alpha n_\alpha^{(1)}(\boldsymbol{i})} = \langle c(\boldsymbol{i}) \rangle \tag{6}$$

$$\frac{\sum_\alpha \sum_{\boldsymbol{i}} n_\alpha^{(1)}(\boldsymbol{i}) c_\alpha}{\sum_\alpha \sum_{\boldsymbol{i}} n_\alpha^{(1)}(\boldsymbol{i})} = \frac{\sum_\alpha c_\alpha \langle N_\alpha \rangle}{N} = \langle c \rangle. \tag{7}$$

Equation (6) gives the mean occupation of site $\boldsymbol{i}$ and equation (7) the mean occupation number over the lattice.

The two-body distribution function is

$$n_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) = \frac{\mathrm{e}^{\Phi_\alpha(\boldsymbol{i})} \mathrm{e}^{\Phi_\lambda(\boldsymbol{j})}}{\Xi} \frac{\delta^2 \Xi}{\delta \mathrm{e}^{\Phi_\alpha(\boldsymbol{i})} \delta \mathrm{e}^{\Phi_\lambda(\boldsymbol{j})}} \tag{8}$$

and vanishes if $\boldsymbol{i} = \boldsymbol{j}$. Its associated correlation function is

$$t_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) = \mathrm{e}^{\Phi_\alpha(\boldsymbol{i})} \mathrm{e}^{\Phi_\lambda(\boldsymbol{j})} \frac{\delta^2 \ln \Xi}{\delta \mathrm{e}^{\Phi_\alpha(\boldsymbol{i})} \delta \mathrm{e}^{\Phi_\lambda(\boldsymbol{j})}} = n_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) - n_\alpha^{(1)}(\boldsymbol{i}) n_\lambda^{(1)}(\boldsymbol{j}) \tag{9}$$

and, in the more usual notation, it is $n_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) = n_\alpha^{(1)}(\boldsymbol{i}) n_\lambda^{(1)}(\boldsymbol{j})[1 + h_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j})]$. Their normalization equations are

$$\sum_{\alpha,\lambda} n_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) = 1 - \delta_{\boldsymbol{i}\boldsymbol{j}} \tag{10}$$

$$\sum_{\lambda} n_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) = n_\alpha^{(1)}(\boldsymbol{i})(1 - \delta_{\boldsymbol{i}\boldsymbol{j}}) \tag{11}$$

$$\langle n_{\alpha\lambda}^{(2)} \rangle = \sum_{\boldsymbol{i},\boldsymbol{j}} n_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) = \langle N_\alpha (N_\lambda - \delta_{\alpha\lambda}) \rangle \tag{12}$$

$$\sum_{\alpha,\lambda} \sum_{\boldsymbol{i},\boldsymbol{j}} n_{\alpha\lambda}^{(2)}(\boldsymbol{i}, \boldsymbol{j}) = \frac{N(N-1)}{2}. \tag{13}$$

Equations (10) and (11) show how the distribution functions $n_{00}^{(2)}(\boldsymbol{i}, \boldsymbol{j})$; $n_{\alpha 0}^{(2)}(\boldsymbol{i}, \boldsymbol{j})$ can be obtained and the CE version of equation (12) does not include the brackets. The averages giving the mean occupation of the pair of sites $\boldsymbol{i}, \boldsymbol{j}$ and the mean quadratic occupation number

over the lattice are

$$\frac{\sum_{\alpha,\lambda} n^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j})c_\alpha c_\lambda}{\sum_{\alpha,\lambda} n^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j})} = \langle c(\boldsymbol{i},\boldsymbol{j})\rangle_{\alpha\lambda} \qquad \boldsymbol{i} \neq \boldsymbol{j} \tag{14}$$

$$\frac{\sum_{\alpha,\lambda}\sum_{i,j} n^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j})c_\alpha c_\lambda}{\sum_{\alpha,\lambda}\sum_{i,j} n^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j})} = \frac{\sum_{\alpha,\lambda} c_\alpha c_\lambda \langle N_\alpha(N_\lambda - \delta_{\alpha\lambda})\rangle}{N(N-1)/2} = \langle c^2\rangle. \tag{15}$$

Besides the conventional distribution and correlation functions hierarchies for q bodies, composition set $\boldsymbol{\alpha}_q$ on the sites set $\{\boldsymbol{q}\}$ defined by (see, e.g., equations (3), (8) and (9))

$$n^{(q)}_{\boldsymbol{\alpha}_q}(\{\boldsymbol{q}\}) = \frac{\prod_{k=1}^{q} \mathrm{e}^{\Phi_{\alpha_k}(\boldsymbol{q}_k)}}{\Xi} \frac{\delta^q \Xi}{\prod_{k=1}^{q} \delta \mathrm{e}^{\Phi_{\alpha_k}(\boldsymbol{q}_k)}} \tag{16}$$

$$t^{(q)}_{\boldsymbol{\alpha}_q}(\{\boldsymbol{q}\}) = \prod_{k=1}^{q} \mathrm{e}^{\Phi_{\alpha_k}(\boldsymbol{q}_k)} \frac{\delta^q \ln \Xi}{\prod_{k=1}^{q} \delta \mathrm{e}^{\Phi_{\alpha_q}(\boldsymbol{q}_k)}} \tag{17}$$

we will also need the Lebowitz–Percus [14] full distribution and correlation functions:

$$\hat{n}^{(q)}_{\boldsymbol{\alpha}_q}(\{\boldsymbol{q}\}) = \frac{1}{\Xi} \frac{\delta^q \Xi}{\prod_{i=1}^{q} \delta \Phi_{\alpha_i}(\boldsymbol{q}_i)} \tag{18}$$

$$\hat{t}^{(q)}_{\boldsymbol{\alpha}_q}(\{\boldsymbol{q}\}) = \frac{\delta^q \ln \Xi}{\prod_{i=1}^{q} \delta \Phi_{\alpha_i}(\boldsymbol{q}_i)}. \tag{19}$$

The t, $\hat{t}$ functions are also called truncated correlation functions and the difference between both hierarchies is that in the full hierarchy the different coordinates can coincide, while in the other they cannot. In particular, while the one-body functions coincide, the two-body ones are related by

$$\hat{n}^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j}) = n^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j}) + n^{(1)}_{\alpha}(\boldsymbol{i})\delta_{\alpha\lambda}\delta_{ij} \tag{20}$$

with the relationship between $\hat{t}$ and t functions being the same as between $\hat{n}$ and n. The important point about the full distribution and correlation functions hierarchies is that, through them, a full set of n-body OZ equations can be defined. While this is true for fluids, in the lattice gas case its rigid topology forces us to analyse them more carefully, *even* in the GCE. It is also convenient to keep in mind that $\boldsymbol{\alpha}_q$, as employed, for example, in equations (16)–(19), is a symbol for the q-components species set appearing in the distribution functions and, obviously, can be any q-size combination of the p available species plus the empty sites.

3. Ornstein–Zernike formalism

First of all we shall analyse the role played by the already mentioned, but not yet discussed, rigid topology constraint. As the number of any-order neighbours is fixed on any lattice gas, this is a constraint that makes the set of distribution functions linearly dependent in their whole range (see equations (4), (10) and (11) for the one- and two-body functions). We will first show that this constraint is very similar to the one found in the CE for fluids, where the fixed N constraint makes impossible a straightforward OZ formalism. Let us recall a couple of results [2] obtained while pursuing the OZ formalism in the CE:

(i) the fixed N constraint makes the n-body correlation functions asymptotically incorrect (they do not have an irreducible n-body behaviour) and dropping off the asymptotic behaviour of the distribution functions affects them, in fact, throughout their whole range in order to restore the correct irreducible n-body behaviour and that is the definition of the N-modified distribution and correlation functions;

(ii) this dropping off causes the free flotation of the norm of the N-modified distribution functions of order higher than one. Although a lattice gas differs from fluids in that the topology constraint holds to every order of neighbourhood, not asymptotically, the above-mentioned results are of the sort we need for lattice gases because, for example, in the simplest case of two states (+, −) the normalization conditions equations (4), (10) and (11) give, for up to two-body functions,

$$\begin{aligned} n_- &= 1 - n_+ \\ n_{+-} &= n_+ - n_{++} \\ n_{--} &= 1 - 2n_+ + n_{++} \end{aligned} \tag{21}$$

showing that the two-body correlation functions ($t_{--} = -t_{+-} = t_{++}$ do not have an irreducible two-body behaviour (see equation (23))).

We will proceed in several steps. First, we prove that, for lattice gases, a straightforward OZ formalism is not possible, *even* in the GCE. Then we will show how this can be solved by following the steps described in [2]. More specifically, we will define a hierarchy of N-modified distribution and correlation functions, prove that they are related through n-body OZ equations, define a N-modified free energy functional and show that it satisfies the HKSM theorem.

The whole point of DF theory is the ability to use densities as independent variables instead of external potentials. That means the ability to invert the linear response equation (see equations (18) and (19))

$$\delta n_\alpha^{(1)}(\boldsymbol{i}) = \sum_{\lambda,\boldsymbol{j}} \hat{t}_{\alpha\lambda}^{(2)}(\boldsymbol{i},\boldsymbol{j})\delta\Phi_\lambda(\boldsymbol{j}). \tag{22}$$

But, using equations (11) and (20) we obtain

$$\sum_\eta \hat{t}_{\eta\alpha}^{(2)}(\boldsymbol{k},\boldsymbol{i}) \equiv 0 \tag{23}$$

which is clearly incompatible with equation (22) being invertible. Notice that we have summed over species and that this result holds for every pair of lattice sites $\boldsymbol{k}$, $\boldsymbol{i}$; it is not an asymptotic result caused by fixed N restrictions. In other words, the rigid neighbourhood is responsible for us giving up any hope of obtaining a straightforward OZ theory, *even* in the GCE. As, on the other hand, things will be easier if we do not have to deal with averages in the normalization equations (such as (5) and (12)) and either way we proceed (CE or GCE) we will have to step through the same formalism, we will consider that our conventional distribution and correlation functions are the canonical ones.

Now we introduce the N-modified distribution and correlation functions and show that the same recipe lifts both the asymptotic and the topological constraints. As we will follow, almost *mutatis mutandis*, the discussion given in [2], we will be a bit more sketchy than there. The equivalent equations of [2] will be referred to by appending DF. The general idea is quite simple. If a given site $\boldsymbol{j}$ is held fixed in state λ we can write, asymptotically, the conditional probability of finding site $\boldsymbol{i}$ in state α as (equation (DF-20))

$$n_{\alpha\lambda;\infty}(\boldsymbol{i}|\boldsymbol{j}) = n_\alpha^{(1)}(\boldsymbol{i}) + \frac{\partial n_\alpha^{(1)}(\boldsymbol{i})}{\partial\rho_\lambda}\Delta\rho_\lambda(\boldsymbol{j}) = n_\alpha^{(1)}[1 + h_{\alpha\lambda}^{(2)}(\boldsymbol{i},\boldsymbol{j})] \tag{24}$$

where $\Delta\rho_\lambda(\boldsymbol{j})$ describes the effects caused in the neighbourhood of $\boldsymbol{i}$ due to having site $\boldsymbol{j}$ fixed in the state λ. Lebowitz and Percus, in their classic paper [14], have shown that, in the CE, the pair correlation function separates into the product of two one-variable functions, i.e. that it does not have a proper two-body behaviour. In fact, they proved that result for n-body

functions. Equation (24) is just another way of writing that result and, by invoking exchange symmetry arguments ($\{\boldsymbol{i}, \alpha\} \leftrightarrow \{\boldsymbol{j}, \lambda\}$), the pair correlation function can be written as

$$h^{(2)}_{\alpha\lambda} = \begin{cases} \tilde{h}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) + \Gamma_{\alpha\lambda} \dfrac{\partial \ln n^{(1)}_{\alpha}(\boldsymbol{i})}{\partial \rho_\alpha} \dfrac{\partial \ln n^{(1)}_{\lambda}(\boldsymbol{j})}{\partial \rho_\lambda} & \boldsymbol{i} - \boldsymbol{j} \notin \mathcal{E}_{\alpha\lambda} \\ \tilde{h}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) & \boldsymbol{i} - \boldsymbol{j} \in \mathcal{E}_{\alpha\lambda} \end{cases} \tag{25}$$

and, in this way, the N-modified pair correlation function $\tilde{h}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j})$ is defined as the pair correlation function stripped of its asymptotic behaviour; $\Gamma_{\alpha\lambda}$ is an as yet undetermined constant and $\mathcal{E}_{\alpha\lambda}$ is the set of excluded neighbours by the pair α, λ. The truncated N-modified correlation function associated with $\tilde{h}^{(2)}$ is (see equations (DF-25) and (DF-26))

$$\tilde{t}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) = n^{(1)}_{\alpha}(\boldsymbol{i}) n^{(1)}_{\lambda}(\boldsymbol{j}) \tilde{h}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) + n^{(1)}_{\alpha}(\boldsymbol{i}) \delta_{\alpha\lambda} \delta_{\boldsymbol{i}\boldsymbol{j}} \tag{26}$$

$$\tilde{t}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) = \begin{cases} \hat{t}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) - \Gamma_{\alpha\lambda} \dfrac{\partial n^{(1)}_{\alpha}(\boldsymbol{i})}{\partial \rho_\alpha} \dfrac{\partial n^{(1)}_{\lambda}(\boldsymbol{j})}{\partial \rho_\lambda} & \boldsymbol{i} - \boldsymbol{j} \notin \mathcal{E}_{\alpha\lambda} \\ \hat{t}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) & \boldsymbol{i} - \boldsymbol{j} \in \mathcal{E}_{\alpha\lambda}. \end{cases} \tag{27}$$

Notice that, in this way, all the irreducible two-body effects (including the hard core exclusion) are preserved. In other words, $\tilde{h}^{(2)}_{\alpha\lambda}$ is the correlation function with a proper irreducible two-body behaviour, not $h^{(2)}_{\alpha\lambda}$. Therefore, using that $\partial\rho_\alpha / \partial n^{(1)}_{\alpha}(\boldsymbol{i}) = 1/N$, we obtain the result (equivalent to equations (DF-27)–(DF-30))

$$\sum_{\boldsymbol{i},\boldsymbol{j}} \tilde{t}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) = -\Gamma_{\alpha\lambda} N^2 \tag{28}$$

$$\Gamma_{\alpha\lambda} = -\frac{1}{N^2} \sum_{\boldsymbol{i}} n^{(1)}_{\alpha}(\boldsymbol{i}) \left[\delta_{\alpha\lambda} + \sum_{\boldsymbol{j}} n^{(1)}_{\lambda}(\boldsymbol{j}) \tilde{h}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) \right] \tag{29}$$

and it is immediate to show that the normalization equation turns out to be

$$\sum_{\boldsymbol{i},\boldsymbol{j}} \tilde{n}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) = N_\alpha (N_\lambda - \delta_{\alpha\lambda}) - \Gamma_{\alpha\lambda} N^2. \tag{30}$$

The fluctuation related term ($\Gamma_{\alpha\lambda} N^2$) in equation (30) leads us to think that the asymptotic constraint has been lifted and this is confirmed by noticing that equation (30) holds true if the obvious equality

$$\sum_{\boldsymbol{i},\boldsymbol{j}} n^{(1)}_{\alpha}(\boldsymbol{i}) n^{(1)}_{\lambda}(\boldsymbol{j}) = N_\alpha N_\lambda \tag{31}$$

is fulfilled, regardless of the value of $\sum n_\alpha n_\lambda \tilde{h}_{\alpha\lambda}$. Therefore, equations (30) and (31) imply a free flotation of the normalization of $n_{\alpha\lambda}$ for a given pair α, λ and so we get rid of the asymptotic constraint.

Now let us turn to the topological constraint. If the sites $\boldsymbol{i}, \boldsymbol{j}$ do not belong to the exclusion set $\mathcal{E}_{\alpha\lambda}$, then

$$\sum_{\alpha\lambda} \tilde{n}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) = 1 - \sum_{\alpha\lambda} \Gamma_{\alpha\lambda} = 1 + \frac{1}{N} + \frac{1}{N^2} \sum_{\substack{\boldsymbol{k},\boldsymbol{m} \\ \alpha\lambda}} [\tilde{n}^{(2)}_{\alpha\lambda}(\boldsymbol{k}, \boldsymbol{m}) - n^{(1)}_{\alpha}(\boldsymbol{k}) n^{(1)}_{\lambda}(\boldsymbol{m})]. \tag{32}$$

This equation is not only independent of the pair $\boldsymbol{i}, \boldsymbol{j}$, it also depends on the system's fluctuations. As the sum over sites gives a free flotation, then the sum over species is also floating and, thus, the topology constraint is lifted. By comparing with equation (10) we also see that

$$\sum_{\lambda} \tilde{t}^{(2)}_{\alpha\lambda}(\boldsymbol{i}, \boldsymbol{j}) = -\sum_{\lambda} \Gamma_{\alpha\lambda} \tag{33}$$

and, in this way, the constraint given by equation (23) is lifted. Now we can prove that $\tilde{t}^{(2)^{-1}}$ exists. From equations (22) and (23) we obtain

$$\delta n_\alpha^{(1)}(\boldsymbol{i}) = \sum_{\alpha\lambda} \tilde{t}_{\alpha\lambda}^{(2)}(\boldsymbol{i},\boldsymbol{j})\delta\Phi_\lambda(\boldsymbol{j}) + \sum_{\alpha\lambda} \Gamma_{\alpha\lambda} \frac{\partial n_\lambda^{(1)}(\boldsymbol{j})}{\partial \rho_\lambda} \delta\Phi_\lambda(\boldsymbol{j}). \tag{34}$$

As the partial chemical potential μ_λ for λ molecules is $\mu_\lambda = N^{-1}(\partial F/\partial\rho_\lambda)_{N,T}$ and

$$-\beta\delta F = \sum_{\boldsymbol{j}} n_\lambda^{(1)}(\boldsymbol{j})\delta\Phi_\lambda(\boldsymbol{j}) \tag{35}$$

is the change in the free energy F due to changes in Φ_λ, we then have

$$\frac{\partial}{\partial\rho_\lambda} \sum_{\boldsymbol{j}} n_\lambda^{(1)}(\boldsymbol{j})\delta\Phi_\lambda(\boldsymbol{j}) = -\beta N \delta\mu_\lambda|_{\Phi_\lambda} \tag{36}$$

for the variation in μ_λ due to the Φ_λ variation. Using equation (28) and putting it all together, we end up with the equation equivalent to (33):

$$\delta n_\alpha^{(1)}(\boldsymbol{i}) = \sum_{\lambda,\boldsymbol{j}} \tilde{t}_{\alpha\lambda}^{(2)}(\boldsymbol{i},\boldsymbol{j})\delta\tilde{\Phi}_\lambda(\boldsymbol{j}) \tag{37}$$

$$\tilde{\Phi}_\lambda(\boldsymbol{j}) = \Phi_\lambda(\boldsymbol{j}) + \beta\mu_\lambda \tag{38}$$

and so the inverse of the two-body N-modified full correlation function exists and is given by

$$\tilde{t}_{\eta\alpha}^{(2)^{-1}}(\boldsymbol{k},\boldsymbol{i}) = \frac{\delta\tilde{\Phi}_\eta(\boldsymbol{k})}{\delta n_\alpha^{(1)}(\boldsymbol{i})} = \frac{\delta_{\alpha\eta}\delta_{\boldsymbol{ik}}}{n_\alpha^{(1)}(\boldsymbol{i})} - \tilde{c}_{\eta\alpha}^{(2)}(\boldsymbol{k},\boldsymbol{i}) \tag{39}$$

which defines the two-body N-modified direct correlation function $\tilde{c}_{\eta\alpha}^{(2)}(\boldsymbol{k},\boldsymbol{i})$. Now it is immediate to prove that, if $\tilde{t}^{(2)}$ and $\hat{t}^{(2)^{-1}}$ are inverses from each other, the relationship between $\tilde{h}^{(2)}$ and $\tilde{c}^{(2)}$ is the OZ equation:

$$\tilde{h}_{\eta\lambda}^{(2)}(\boldsymbol{k},\boldsymbol{j}) - \tilde{c}_{\eta\lambda}^{(2)}(\boldsymbol{k},\boldsymbol{j}) = \sum_{\alpha,\boldsymbol{i}} \tilde{n}_\alpha^{(1)}(\boldsymbol{i})\tilde{c}_{\eta\alpha}^{(2)}(\boldsymbol{k},\boldsymbol{i})\tilde{h}_{\alpha\lambda}^{(2)}(\boldsymbol{i},\boldsymbol{j}). \tag{40}$$

The procedure for generating higher-order OZ equations is described in many places, see, e.g., [2] and references therein. Briefly, the idea is to write the Taylor expansions of both $n_\alpha^{(1)}(\boldsymbol{i})$ and $\Phi_\lambda(\boldsymbol{j})$, insert one into the other and, by equating powers in the expansion, n-body OZ equations are obtained that link the total and direct correlation functions in a hierarchical way. These higher-order OZ equations are essential in order to have a physically consistent DF theory, i.e. the distribution and correlation functions must have the correct *hierarchical* structure; otherwise, they would be statistically meaningless and useless for writing the entropy. Former OZ proposals [11, 13] relied on the SCOZA formalism, where the equality between two different routes to the pressure is enforced and a partial differential equation for the Fourier coefficients of the direct correlation function is solved. In summary, they directly started with the OZ equation in Fourier space, the relationship between the fixed topology constraint and the existence of an OZ theory was not discussed and, also, the insertion of those results in a hierarchical formalism was not considered. They are very interesting works with good numerical results but they were not aimed at formulating a general DF theory of lattice gases.

As the translating procedure between [2] and the lattice gas case should be abundantly clear, we can refrain from wading through the maze of intermediate results of [2] and just quote the very important ones together with a brief explanation. The idea is to get a HKSM-like theorem that allows us to write a free energy functional in terms of densities and which is minimized by the equilibrium profiles. Equation (23) shows that a straightforward approach is unfeasible because $\hat{t}^{(2)^{-1}}$ does not exist. As the N-modified distribution and correlation

functions lift that restriction, we will write, while keeping the same formal structure as in GCE DF theory, an N-modified free energy $\tilde{\mathcal{F}}$ and N-modified grand thermodynamic potential $\tilde{\Omega}$ in terms of these N-modified hierarchies. We will then show that $\tilde{\Omega}$ is minimized by the equilibrium densities, identify the first members of the N-modified direct correlation hierarchy with functional derivatives of the excess N-modified free energy with respect to the density profiles and, by showing that they have the right hierarchical structure, close the proof of the HKSM-like theorem for lattice gases. In this way, a general foundation for a DF theory of lattice gases is obtained. Specifically, we have:

(i) An N-modified free energy $\tilde{\mathcal{F}}$ and N-modified grand thermodynamic potential $\tilde{\Omega}$ defined by

$$\beta\tilde{\mathcal{F}}[\{\tilde{n}^{(1)}\}] = \langle \beta U_N + \ln P_N \rangle \tag{41}$$

$$\beta\tilde{\Omega}[\{\tilde{n}^{(1)}\}] = \beta\mathcal{F}[\{\tilde{n}^{(1)}\}] - \sum_{\alpha,\boldsymbol{i}} \tilde{n}_\alpha^{(1)}(\boldsymbol{i})\tilde{\Phi}_\alpha(\boldsymbol{i}) \tag{42}$$

where P_N is the canonical probability density, U_N is the *interaction* energy contribution, the average is a canonical one and the N-modified distribution functions are used. Let us emphasize that the entropic term $\ln P_N$ depends on all the n-body configurations and, therefore, is responsible for the need of a full *hierarchy* of distribution functions. The variational principle that determines the density profile is a consequence of the Gibbs–Bogoliubov (GB) inequality [24] which states that, given two functionals $\tilde{\Omega}$, Ω'

$$\tilde{\Omega} = \left\langle \beta\left(H - \sum_\alpha \mu_\alpha\right) - \ln P_N \right\rangle = \sum_{\{\boldsymbol{N}\}} P_N(\{\boldsymbol{N}\})\left\{\beta\left(H - \sum_\alpha \mu_\alpha\right) - \ln P_N(\{\boldsymbol{N}\})\right\} \tag{43}$$

Ω' the same functional of $P'_N(\{\boldsymbol{N}\})$ as $\tilde{\Omega}$ is of $P_N(\{\boldsymbol{N}\})$, both $P'_N(\{\boldsymbol{N}\})$, $P_N(\{\boldsymbol{N}\})$ satisfying

$$\sum_{\{\boldsymbol{N}\}} P'_N(\{\boldsymbol{N}\}) = \sum_{\{\boldsymbol{N}\}} P_N(\{\boldsymbol{N}\}) \tag{44}$$

then, if P_N is the equilibrium distribution, GB states that

$$\beta\Omega' \geqslant \beta\tilde{\Omega}. \tag{45}$$

Therefore, the variational principle that determines the density profile is

$$\frac{\delta\beta\tilde{\Omega}[\{\tilde{n}^{(1)}\}]}{\delta\tilde{n}_\alpha^{(1)}(\boldsymbol{i})} = 0. \tag{46}$$

(ii) The variational equations are obtained by the following procedure: we define 'ideal' and 'excess' contributions to the N-modified free energy. The ideal contribution solely depends on one-particle distribution functions, it does not include either interaction potentials or higher-order functions. It is needed for the correct start of the N-modified direct correlation functions hierarchy. The excess term is everything else:

$$\beta\tilde{\mathcal{F}}^{(id)} = \sum_{\boldsymbol{i}} n_\alpha^{(1)}(\boldsymbol{i})[\ln n_\alpha^{(1)}(\boldsymbol{i}) - 1]. \tag{47}$$

Equation (46) can then be written as

$$\frac{\delta\tilde{\mathcal{F}}}{\delta n_\alpha^{(1)}(\boldsymbol{i})} = \tilde{\phi}_\alpha(\boldsymbol{i}) \tag{48}$$

and, defining the one-body N-modified direct correlation function as

$$\tilde{c}_\alpha^{(1)}(\boldsymbol{i}) = \beta\frac{\delta\tilde{\mathcal{F}}}{\delta\tilde{n}_\alpha^{(1)}(\boldsymbol{i})} = \ln(\tilde{n}_\alpha^{(1)}(\boldsymbol{i})) - \tilde{\Phi}_\alpha(\boldsymbol{i}) \tag{49}$$

equation (39) can also be written as

$$\tilde{c}^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j}) = \frac{\delta\tilde{c}^{(1)}_{\alpha}(\boldsymbol{i})}{\delta\tilde{n}^{(1)}_{\lambda}(\boldsymbol{j})}. \tag{50}$$

These equations start the N-modified direct correlation functions hierarchy and, hence, we have completed the task of generating the N-modified hierarchies.

(iii) These N-modified hierarchies are given by ($n^{(1)}_{\alpha} \equiv \tilde{n}^{(1)}_{\alpha}$)

$$\tilde{n}^{(s)}_{\alpha_1\ldots\alpha_s}(\boldsymbol{i}_1\ldots\boldsymbol{i}_s) = \frac{1}{Q}\frac{\delta^s Q}{\prod_{k=1}^{s}\delta\tilde{\Phi}_{\alpha_k}(\boldsymbol{i}_k)} \tag{51}$$

$$\tilde{t}^{(s)}_{\alpha_1\ldots\alpha_s}(\boldsymbol{i}_1\ldots\boldsymbol{i}_s) = \frac{\delta^s \ln Q}{\prod_{k=1}^{s}\delta\tilde{\Phi}_{\alpha_k}(\boldsymbol{i}_k)} = \frac{\delta\tilde{t}^{(s-1)}_{\alpha_1\ldots\alpha_{s-1}}(\boldsymbol{i}_1\ldots\boldsymbol{i}_{s-1})}{\delta\tilde{\Phi}_{\alpha_s}(\boldsymbol{i}_s)} \tag{52}$$

$$\tilde{c}^{(s)}_{\alpha_1\ldots\alpha_s}(\boldsymbol{i}_1\ldots\boldsymbol{i}_s) = \beta\frac{\delta^s\tilde{\mathcal{F}}}{\prod_{k=1}^{s}\delta\tilde{n}^{(1)}_{\alpha_k}(\boldsymbol{i}_k)} = \frac{\delta\tilde{c}^{(s-1)}_{\alpha_1\ldots\alpha_{s-1}}(\boldsymbol{i}_1\ldots\boldsymbol{i}_{s-1})}{\delta\tilde{n}^{(1)}_{\alpha_s}(\boldsymbol{i}_s)}. \tag{53}$$

Therefore, the moral of this section is that the lattice gas problem can be translated to liquid theory language with an unequivocal correspondence between both systems at a very formal and basic level. In this way, the OZ *based* theory of liquids can be immediately translated to lattice gases. Also, let us mention that the chain rule allows us to write (using equation (39)), for any quantity Ψ,

$$\frac{\delta\Psi}{\delta\tilde{n}_{\alpha}(\boldsymbol{i})} = \sum_{\lambda,\boldsymbol{j}}\frac{\delta\Psi}{\delta\tilde{\Phi}_{\lambda}(\boldsymbol{j})}\frac{\delta\tilde{\Phi}_{\lambda}(\boldsymbol{j})}{\delta\tilde{n}_{\alpha}(\boldsymbol{i})} = \frac{1}{\tilde{n}_{\alpha}(\boldsymbol{i})}\frac{\delta\Psi}{\delta\tilde{\Phi}_{\alpha}(\boldsymbol{i})} - \sum_{\lambda,\boldsymbol{j}}\tilde{c}^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j})\frac{\delta\Psi}{\delta\tilde{\Phi}_{\lambda}(\boldsymbol{j})} \tag{54}$$

an equation that might be handy in formulating variational principles.

4. The entropy

4.1. The exact expression

In this section we will work with the N-modified distribution and correlation functions introduced in section 2 but, for the sake of readability, we will omit the tilde over them. Also, we will rely on the equivalence between CE and GCE (when the system is not very near to critical points) in order to work in the GCE and, in this way, avoid the quite difficult problem of boundary conditions in the CE, as shown in the approach to entropy pioneered by Nettleton and Green [21]. As we will translate the entropy derivation given in [15, 16] and later extended in [17] we will try to write a compressed and self-consistent account of their derivations; their equations will be referred to by preceding them with I, II or III, respectively. In the lattice gas case there is no kinetic energy integration and equation (I-16) for the entropy becomes

$$\frac{S}{k} = \beta\langle(U - \Omega - \boldsymbol{\mu}\cdot\boldsymbol{N})\rangle. \tag{55}$$

The angular brackets indicate a grand canonical average, $\boldsymbol{\mu}\cdot\boldsymbol{N} = \sum_{\alpha}\mu_{\alpha}N_{\alpha}$ and Ω is the grand thermodynamic potential. Our goal is to write the entropy as an expansion in correlation functions and, in order to do that, we use as a starting point the moment–cumulant expansion [15]. Given a random variable X we write

$$X(\boldsymbol{\xi}) = \sum_{R\geqslant 1}\sum_{\alpha_R}\frac{\boldsymbol{\xi}^{\boldsymbol{R}}}{\boldsymbol{R}!}\mu_{\alpha_R} \tag{56}$$

$$\ln[1 + X(\boldsymbol{\xi})] = \sum_{R\geqslant 1}\sum_{\alpha_R}\frac{\boldsymbol{\xi}^{\boldsymbol{R}}}{\boldsymbol{R}!}\kappa_{\alpha_R} \tag{57}$$

for its moment ($\mu_{\boldsymbol{\alpha}_R}$) and cumulant ($\kappa_{\boldsymbol{\alpha}_R}$) expansion, which are linked by

$$\mu_{\boldsymbol{\alpha}_R} = \sum_{k=1}^{R} \{k\{\boldsymbol{r}_i\}_{\boldsymbol{R}}\} \prod_{i=1}^{k} \kappa_{\boldsymbol{r}_i} \tag{58}$$

$$\kappa_{\boldsymbol{\alpha}_R} = \sum_{k=1}^{R} \{k\{\boldsymbol{r}_i\}_{\boldsymbol{R}}\} (-1)^{k-1} (k-1)! \prod_{i=1}^{k} \mu_{\boldsymbol{r}_i}. \tag{59}$$

For distribution functions the expansion is

$$n^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\}) = \sum_{k=1}^{M} \{k\{\boldsymbol{m}_i\}_{\boldsymbol{M}}\} \prod_{i=1}^{k} C^{(\boldsymbol{m}_i)}_{\boldsymbol{\alpha}_{\boldsymbol{m}_i}}(\{\boldsymbol{m}_i\}) \tag{60}$$

$$C^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\}) = h^{(M)}_{\boldsymbol{\alpha}_M} \prod_{i=1}^{M} n^{(1)}_{\boldsymbol{\alpha}_i}(\boldsymbol{i}) = \sum_{k=1}^{M} \{k\{\boldsymbol{m}_i\}_{\boldsymbol{M}}\} (-1)^{k-1} (k-1)! \prod_{i=1}^{k} n^{(\boldsymbol{m}_i)}_{\boldsymbol{\alpha}_{\boldsymbol{m}_i}}(\{\boldsymbol{m}_i\}). \tag{61}$$

Here we have worked with the partitions of the set $\{\boldsymbol{M}\}$ in k disjoint subsets $\{\boldsymbol{m}_i\}_{\boldsymbol{M}}$, $1 \leqslant i \leqslant k$, which is symbolized by $\{k\{\boldsymbol{m}_i\}_{\boldsymbol{M}}\}$, where $\{\boldsymbol{m}_i\}_{\boldsymbol{M}}$ indicates the ith subset $\{\boldsymbol{m}_i\}$ of $\{\boldsymbol{M}\}$ and, therefore, $\sum_{k=1}^{M}\{k\{\boldsymbol{m}_i\}_{\boldsymbol{M}}\}$ represents the sum over all the partitions in k subsets and, for each k, is $1 \leqslant i \leqslant k$. This partition involves both the composition and coordinate sets and the empty sites are counted in both sets. Notice that equation (61) is the one that forces $h^{(M)}$ to behave in a proper irreducible M-body way (see, e.g., [25]). On the other hand, equations (60) and (61) have the same formal structure as the expansion of the nth derivative of the exponential of a function and of the logarithm of a function, respectively [15], i.e.

$$\frac{\partial^{\boldsymbol{M}} \mathrm{e}^{f(\boldsymbol{x})}}{\partial \boldsymbol{x}^{\boldsymbol{M}}} = \mathrm{e}^{f(\boldsymbol{x})} \sum_{k=1}^{M} \{k\{\boldsymbol{m}_i\}_{\boldsymbol{M}}\} \prod_{i=1}^{k} \frac{\partial^{\boldsymbol{m}_i} f(\boldsymbol{x})}{\partial \boldsymbol{x}^{\boldsymbol{m}_i}} \tag{62}$$

$$\frac{\partial^{\boldsymbol{M}} \ln f(\boldsymbol{x})}{\partial \boldsymbol{x}^{\boldsymbol{M}}} = \sum_{k=1}^{M} \{k\{\boldsymbol{m}_i\}_{\boldsymbol{M}}\} (-1)^{k-1} (k-1)! \prod_{i=1}^{k} \frac{1}{f(\boldsymbol{x})} \frac{\partial^{\boldsymbol{m}_i} f(\boldsymbol{x})}{\partial \boldsymbol{x}^{\boldsymbol{m}_i}} \tag{63}$$

and so we are led to look for a suitable way of writing $\exp[-\beta(U_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\}) - \Omega - \boldsymbol{M} \cdot \mu)]$ in order to use the expansions given in equations (60)–(63). Therefore, we define the operator $\Gamma^{(\boldsymbol{R})}$ and the dimensionless function $F^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\})$ (equations (I-17) and (I-18)) by

$$\Gamma^{(\boldsymbol{R})} = \boldsymbol{z}^{\boldsymbol{R}} \frac{\partial^{\boldsymbol{R}}}{\partial \boldsymbol{z}^{\boldsymbol{R}}} \tag{64}$$

$$F^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\}) = \exp(-\beta\Omega) \frac{n^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\})}{\boldsymbol{z}^{\boldsymbol{M}}}. \tag{65}$$

In general, the M-body distribution function can be written in terms of the probability of finding M molecules in the configuration $\{\boldsymbol{M}\}$:

$$n^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\}) = \sum_{N \geqslant 0} \sum_{\{\boldsymbol{\alpha}_N\}} \sum_{\{\boldsymbol{N}\}} \frac{1}{\boldsymbol{N}!} P_{\boldsymbol{\alpha}_{N+M}}(\{\boldsymbol{N} + \boldsymbol{M}\}). \tag{66}$$

Here, and in the following equations, we will need to distinguish between the different subindexes implied in $\sum_{\boldsymbol{N}}$ (as in equations (2) and (3)). The separation is between $\sum_{N \geqslant 0}$ (sum over the order of the sets), $\sum_{\{\boldsymbol{\alpha}_N\}}$ (the compositions) and $\sum_{\{\boldsymbol{N}\}}$ (the coordinates). As we also have

$$P_{\boldsymbol{\alpha}_N}(\{\boldsymbol{N}\}) = \boldsymbol{z}^{\boldsymbol{N}} \mathrm{e}^{-\beta[U_N(\{\boldsymbol{N}\}) - \Omega]} = \sum_{R \geqslant 0} \sum_{\{\boldsymbol{\alpha}_R\}} \sum_{\{\boldsymbol{R}\}} \frac{(-1)^{\boldsymbol{R}}}{\boldsymbol{R}} n^{(N+R)}_{\boldsymbol{\alpha}_{N+R}}(\{\boldsymbol{N} + \boldsymbol{R}\}) \tag{67}$$

we can write

$$F^{(M)}_{\alpha_M}(\{M\}) = \sum_{N\geqslant 0}\sum_{\{\alpha_N\}}\sum_{\{N\}}\frac{z^N}{N!}\mathrm{e}^{-\beta U_{\alpha_{N+M}}(\{N+M\})}. \tag{68}$$

Now it is immediate to obtain

$$\frac{1}{F^{(M)}_{\alpha_M}(\{M\})}\sum_{R\geqslant 0}\sum_{\{\alpha_R\}}\frac{(-1)^R}{R!}\Gamma^{(R)}F^{(M)}_{\alpha_M}(\{M\}) = \frac{\exp -\beta(U_{\alpha_M}(\{M\}) - \Omega - M\cdot\mu)}{n^{(M)}_{\alpha_M}(\{M\})} = A^{(M)}_{\alpha_M}(\{M\}) \tag{69}$$

and, therefore, we have that

$$\frac{S}{k} = -\langle \ln n^{(M)}_{\alpha_M}(\{M\})\rangle - \langle \ln A^{(M)}_{\alpha_M}(\{M\})\rangle. \tag{70}$$

If in equation (69) we use equation (62) with the substitution of $f(x)$ by $\ln F^{(M)}_{\alpha_M}(\{M\})$, the result is

$$A^{(M)}_{\alpha_M}(\{M\}) = \sum_{R\geqslant 0}\sum_{\{\alpha_R\}}\frac{(-1)^R}{R!}\sum_{i=1}^{R}\{k\{r_i\}_R\}\prod_{i=1}^{k}\Gamma^{(r_i)}[\ln F^{(M)}_{\alpha_M}(\{M\})]. \tag{71}$$

Defining the random variable X of equation (57) by

$$\ln[1 + X(\xi)] = \sum_{R\geqslant 1}\sum_{\{\alpha_R\}}\frac{(-1)^R\xi^R}{R!}\Gamma^{(R)}[\ln F^{(M)}_{\alpha_M}(\{M\})] \tag{72}$$

and using equations (58) and (59), we obtain that $A^{(M)}_{\alpha_M} = 1 + X(\mathbf{1})$ and, therefore,

$$\ln A^{(M)}_{\alpha_M}(\{M\}) = \sum_{R\geqslant 1}\sum_{\{\alpha_R\}}\frac{(-1)^R}{R!}\Gamma^{(R)}[\ln F^{(M)}_{\alpha_M}(\{M\})]. \tag{73}$$

It can also be noticed that, when calculating the average in the RHS of equation (73), the importance of writing Ξ as in equation (2) becomes evident. The operator $\Gamma^{(R)}$ (equation (64)) introduces a factor $N!/(N-R)!$ and, should the $N!$ term in equation (2) be missing, we would not have been able to obtain the equation equivalent to (I-29).

The average of $\Gamma^{(N)}[\ln F^{(M)}_{\alpha_M}]$ can be found through the use of equation (63) which implies the decomposition

$$\Gamma^{(R)}[\ln F^{(N)}_{\alpha_N}(\{N\})] = \sum_{k=1}^{R}\{k\{r_i\}_R\}(-1)^{k-1}(k-1)!\prod_{i=1}^{k}\frac{z^{r_i}}{F^{(N)}_{\alpha_N}}\frac{\partial^{r_i}F^{(N)}_{\alpha_N}}{\partial z^{r_i}}. \tag{74}$$

In this way, we have (sum over coordinate sets only)

$$\frac{z^{r_i}}{F^{(N)}_{\alpha_N}(\{N\})}\frac{\partial^{r_i}}{\partial z^{r_i}}F^{(N)}_{\alpha_N}(\{N\}) = \sum_{\{r_i\}}\frac{n_{\alpha_{N+r_i}}{}^{(N+r_i)}(\{N+r_i\})}{n^{(N)}_{\alpha_N}(\{N\})} \tag{75}$$

and the second term of equation (73) becomes

$$\langle\Gamma^{(R)}[\ln F^{(N)}_{\alpha_N}(\{N\})]\rangle = \sum_{N,M\geqslant 0}\sum_{\substack{\{\alpha_N\}\\ \{\alpha_M\}}}\frac{(-1)^M}{N!M!}\sum_{\{N+M+R\}}n^{(N+M)}_{\alpha_{N+M}}(\{N+M\})\sum_{k=1}^{R}\{k\{r_i\}_R\} \times (-1)^{k-1}(k-1)!\prod_{i=1}^{k}\frac{n^{(N+r_i)}_{\alpha_{N+r_i}}(\{N+r_i\})}{n^{(N)}_{\alpha_N}(\{N\})}. \tag{76}$$

Notice that in equation (76) the sum involves both the composition and coordinate sets ($\boldsymbol{\alpha}_{N+M+R}$ and $\{\boldsymbol{N}+\boldsymbol{M}+\boldsymbol{R}\}$, respectively) of $(N+M+R)$-bodies where the summand contains the $(N+M)$-body distribution function times a sum over all the conditional probabilities of having $(N+r_i)$ in a given configuration when N of them are held fixed. Let us now tackle the first term of equation (70). As we can generally write that

$$n^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\}) = \exp[W^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\})] = \exp\left[\sum_{\boldsymbol{m}\subseteq\boldsymbol{M}} \omega^{(m)}_{\boldsymbol{\alpha}_m}(\{\boldsymbol{m}\})\right] \tag{77}$$

the potential of average force $W^{(M)}_M$ thus defined can be decomposed into its irreducible m-body components and generalized superposition approximations (SAs) of order k are obtained if $\omega^{(m)} \equiv 0, m > k$ [22]. Here, we also partition both composition and coordinates sets. In this way we find that the irreducible components are given by

$$\omega^{(m)}_{\boldsymbol{\alpha}_m}(\{\boldsymbol{m}\}) = \ln\left[\frac{n^{(m)}_{\boldsymbol{\alpha}_m}\prod_{\{\boldsymbol{m}-\boldsymbol{2}\}\subseteq\{\boldsymbol{m}\}} n^{(m-2)}_{\boldsymbol{\alpha}_{m-2}}\cdots}{\prod_{\{\boldsymbol{m}-\boldsymbol{1}\}\subseteq\{\boldsymbol{m}\}} n^{(m-1)}_{\boldsymbol{\alpha}_{m-1}}\prod_{\{\boldsymbol{m}-\boldsymbol{3}\}\subseteq\{\boldsymbol{m}\}} n^{(m-1)}_{\boldsymbol{\alpha}_{m-3}}\cdots}\right]. \tag{78}$$

Then, it is obtained that

$$\langle \ln n^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\})\rangle = \sum_{\{\boldsymbol{m}\}\subseteq\{\boldsymbol{M}\}} \langle\omega^{(m)}_{\boldsymbol{\alpha}_m}\rangle = \sum_{m=1}^{M}\sum_{\{\boldsymbol{\alpha}_m\}}\frac{1}{\boldsymbol{m}!}\sum_{\{\boldsymbol{m}\}} n^{(m)}_{\boldsymbol{\alpha}_m}(\{\boldsymbol{m}\})\omega^{(m)}_{\boldsymbol{\alpha}_m}. \tag{79}$$

This term already goes beyond the Guggenheim–McGlashan [20] entropy equation. Lastly, the final *exact* result for the entropy is

$$\begin{aligned}\frac{S}{k} = N &- \sum_{M\geqslant 1}\sum_{\{\boldsymbol{\alpha}_M\}}\frac{1}{\boldsymbol{M}!}\sum_{\{\boldsymbol{M}\}} n^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\})\omega^{(M)}_{\boldsymbol{\alpha}_M}(\{\boldsymbol{M}\}) \\ &- \sum_{R\geqslant 1}\sum_{N,M\geqslant 0}{}'\sum_{\{\boldsymbol{\alpha}_{N+M+R}\}}\frac{(-1)^{M+R}}{\boldsymbol{N}!\boldsymbol{M}!\boldsymbol{R}!}\sum_{\{\boldsymbol{N}+\boldsymbol{M}+\boldsymbol{R}\}} n^{(N+M)}_{\boldsymbol{\alpha}_{N+M}}(\{\boldsymbol{N}+\boldsymbol{M}\}) \\ &\times \sum_{k=1}^{R}\{k\{\boldsymbol{r}_i\}_{\boldsymbol{R}}\}(-1)^{k-1}(k-1)!\prod_{i=1}^{k}\frac{n^{(N+r_i)}_{\boldsymbol{\alpha}_{N+r_i}}(\{\boldsymbol{N}+\boldsymbol{r}_i\})}{n^{(N)}_{\boldsymbol{\alpha}_N}(\{\boldsymbol{N}\})}\end{aligned} \tag{80}$$

and shows the entropy decomposed in a term with the traditional contribution of terms of the form $n_\alpha \ln n_\alpha$ plus a sum of increasingly complex contributions. The prime in the summation means that the term $R = 1$, $N = M = 0$ has been separated (it gives N) and must be omitted from the sum.

4.2. The ring approximation

Explicitly, the first terms of the entropy equation (80) are

$$\begin{aligned}\frac{S}{k} = N &- \sum_{\alpha}\sum_{i} n^{(1)}_{\alpha}(\boldsymbol{i})\ln n^{(1)}_{\alpha}(\boldsymbol{i}) - \sum_{\alpha,\lambda}\frac{1}{\boldsymbol{2}!}\sum_{\boldsymbol{i},\boldsymbol{j}} n^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j})\ln\frac{n^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j})}{n^{(1)}_{\alpha}(\boldsymbol{i})n^{(1)}_{\lambda}(\boldsymbol{j})} \\ &- \cdots + \sum_{\alpha,\lambda}\frac{1}{\boldsymbol{2}!}\sum_{\boldsymbol{i},\boldsymbol{j}} n^{(1)}_{\alpha}(\boldsymbol{i})n^{(1)}_{\lambda}(\boldsymbol{j})h^{(2)}_{\alpha\lambda}(\boldsymbol{i},\boldsymbol{j}) + \cdots\end{aligned} \tag{81}$$

and more of them are given in [15] (equations (37) and the following). It is important to keep in mind that, for example, $\boldsymbol{2}!$ is either 1 ($\alpha \neq \lambda$) or 2 ($\alpha = \lambda$).

In equation (80) the beginnings of a separation of the entropy into different formal contributions can be found. We have:

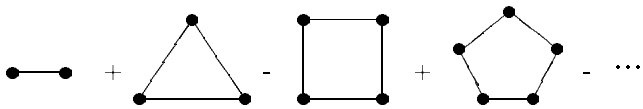
(i) the 'ideal' contribution N (see also equation (47));
(ii) the ever present logarithmic contribution $\sum n^{(m)}\omega^{(m)}$; and
(iii) everything else, which is the complex summation following the logarithmic term.

We shall presently discuss this last contribution and will show how to calculate to infinite order four subsets of terms. The first subset leads to the so-called ring approximation (RA) and is dealt with in this subsection: the other three subsets stem from susceptibility related terms and are discussed in the next subsection.

The distribution functions can be factored out by using the SA (see equation (78)). Here we discuss the results obtained with the second-order SA while how to deal with the third-order SA is discussed, for fluids, in [26]. Explicitly, with the second-order SA we write an M-body distribution function as

$$n^{(M)}_{\alpha_M}(\{M\}) = \left[\prod_{i=1}^{M} n^{(1)}_{\alpha_i}(\boldsymbol{i})\right] \prod_{\{i_1,i_2\}\subseteq\{M\}} [1 + h^{(2)}_{\alpha_{i_1},\alpha_{i_2}}(\boldsymbol{i_1}, \boldsymbol{i_2})]. \tag{82}$$

In [16] it is shown that the leading terms arising from applying the SA to the last summation in equation (80) have, with the exception of the first one, the topology of rings. Specifically, the leading terms, in diagrammatic form, are

$\frac{S^{(\Sigma)}}{k} =$ 

The standard conventions adopted are [24]: (1) a black $n^{(1)}$-circle (unlabelled) is associated with the function $n^{(1)}_{\alpha_i}(\boldsymbol{i})$ and a summation over species α_i and coordinates $\boldsymbol{i}$ is implied; (2) a full line joining two black $n^{(1)}$-circles represents an $h^{(2)}_{\alpha_1\alpha_2}(\mathbf{1}, \mathbf{2})$ bond; (3) the value of a diagram is I/σ, where I is the value of the sum calculated with some arbitrary labelling of the black circles and σ is the symmetry number of the diagram (the number of permutations of black circles that do not change the topology of the diagram). For the specific case of n-order ring terms, $\sigma = 2n$ [16]. In particular, the association of the first terms of our diagrammatic expansion is

 $= \sum_{\alpha_1,\alpha_2} \frac{1}{\mathbf{2}!} \sum_{i_1,i_2} n^{(1)}_{\alpha_{i_1}}(\boldsymbol{i_1}) n^{(1)}_{\alpha_{i_2}}(\boldsymbol{i_2}) h^{(2)}_{\alpha_1\alpha_2}(\boldsymbol{i_1}, \boldsymbol{i_2}).$

This one does not have the ring topology and is the last term of equation (81). The first ring term is

$= \frac{1}{6} \sum_{\alpha_1,\alpha_2,\alpha_3} \sum_{i_1,i_2,i_3} \left(\prod_{k=1}^{3} n^{(1)}_{\alpha_k}(\boldsymbol{i})\right) h^{(2)}_{\alpha_1\alpha_2}(\boldsymbol{i_1}, \boldsymbol{i_2}) h^{(2)}_{\alpha_1\alpha_3}(\boldsymbol{i_1}, \boldsymbol{i_3}) h^{(2)}_{\alpha_2\alpha_3}(\boldsymbol{i_2}, \boldsymbol{i_3}).$

The simplest neglected term (always within the second-order SA) is

.

The sum of ring terms gives the RA which can be diagrammatically summed to infinite order [16]. As the resummation was based on the topology of diagrams, the result can be

immediately transcribed to lattice gases and here we present, in our notation, the result given in [16] (equations (II-11)–(II-13)), with a couple of misprints corrected:

$$\frac{S}{k} = N - \sum_{M\geqslant 1}\sum_{\{\alpha_M\}}\frac{1}{M!}\sum_{\{M\}} n^{(M)}_{\alpha_M}(\{M\})\omega^{(M)}_{\alpha_M}(\{M\}) + \sum_{\{\alpha_2\}}\frac{1}{2}\sum_{\{2\}} n^{(1)}_{\alpha_1}(\mathbf{1})n^{(1)}_{\alpha_2}(\mathbf{2})h^{(2)}_{\alpha_2}(\mathbf{1},\mathbf{2})$$
$$+ \frac{1}{2}\sum_{q\geqslant 3}\frac{(-1)^{q-1}}{q}\sum_{\{\alpha_q\}}\sum_{\{q\}}\left(\prod_{k=1}^{q} n^{(1)}_{\alpha_k}(\boldsymbol{k})\right)$$
$$\times h^{(2)}_{\alpha_1\alpha_2}(\mathbf{1},\mathbf{2})h^{(2)}_{\alpha_2\alpha_3}(\mathbf{2},\mathbf{3})\cdots h^{(2)}_{\alpha_{q-1}\alpha_q}(\boldsymbol{q}-\mathbf{1},\mathbf{1})h^{(2)}_{\alpha_q\alpha_1}(\boldsymbol{q},\mathbf{1}) + \cdots. \tag{83}$$

This expression, in the case of an homogeneous system, can be analytically summed (equation (II-40)). It can also be mentioned that in equations (II-40) and (II-41) a minus sign is missing.

4.3. Susceptibilities-related contributions and the renormalized ring approximation

In [17] we discussed the contribution to entropy that arises from density fluctuations. The last term of equation (81) (the one not included in the RA) is, in fact, the first term of a series that we shall now discuss. The series, as taken from equation (80) with the distribution functions written in terms of generalized SA, taking out the ring terms of the RA and neglecting an infinite number of terms that do not fit in the pattern, is

$$\frac{S^{(c)}}{k} = \sum_{p\geqslant 2}\sum_{\{\alpha_p\}}\frac{1}{p!}\sum_{\{p\}}[n^{(p)}_{\{\alpha_p\}}(\{\boldsymbol{p}\}) - \Gamma^{(p)}_{\{\alpha_p\}}(\{\boldsymbol{p}\})] \tag{84}$$

$$\Gamma^{(p)}_{\{\alpha_p\}}(\{\boldsymbol{p}\}) = \frac{\prod_{\{\boldsymbol{p}-\mathbf{1}\}\subseteq\{\boldsymbol{p}\}} n^{(p-1)}_{\{\alpha_{p-1}\}}\prod_{\{\boldsymbol{p}-\mathbf{3}\}\subseteq\{\boldsymbol{p}\}} n^{(p-3)}_{\{\alpha_{p-3}\}}\cdots}{\prod_{\{\boldsymbol{p}-\mathbf{2}\}\subseteq\{\boldsymbol{p}\}} n^{(p-2)}_{\{\alpha_{p-2}\}}\prod_{\{\boldsymbol{p}-\mathbf{4}\}\subseteq\{\boldsymbol{p}\}} n^{(p-4)}_{\{\alpha_{p-4}\}}\cdots}. \tag{85}$$

The second term of the series ($p = 3$) can be transformed to

$$\frac{S^{(c)}_3}{k} = \sum_{\{\alpha_3\}}\frac{1}{\mathbf{3}!}\sum_{\{\mathbf{3}\}}\left(\prod_{i=1}^{3} n^{(1)}_{\{\alpha_i\}}(\{\boldsymbol{i}\})\right)[h^{(3)}_{\alpha_3}(\{\mathbf{3}\}) - \sum_{i=1}^{3}\prod_{k\neq i} h^{(2)}_{\alpha_i\alpha_k}(\{\boldsymbol{i},\boldsymbol{k}\})$$
$$- h^{(2)}_{\alpha_1\alpha_2}(\{\mathbf{1},\mathbf{2}\})h^{(2)}_{\alpha_1\alpha_3}(\{\mathbf{1},\mathbf{3}\})h^{(2)}_{\alpha_2\alpha_3}(\{\mathbf{2},\mathbf{3}\})] \tag{86}$$

and clearly identifies the three subsets of terms we are going to sum. Let us mention that, in [17], the derivation of the compressibility related terms was for a one-component, homogeneous system; here we will generalize it. This is necessary because in lattice gases we inevitably have a mixture of at least two components and, if adsorption phenomena are mapped onto a lattice gas, there are usually external fields (e.g. adsorption of one species is preferred at the expense of some other species and is usually triggered by external fields). Therefore, we consider a general mixture under the influence of species-dependent external fields. There are three different subsets of terms that will be summed to infinite order. Lastly, let us mention that in [17] we also proved that, in the thermodynamic limit, the compressibility related contribution is a functional of only the one-body distribution function and, therefore, does not contribute to equations derived through variational principles; it only contributes to the system's size constraint. That means that it does not contribute to variational formulations although it does to numerical evaluations of the entropy.

(a) The first subset of terms to be summed is

$$\frac{S_a}{k} = \sum_{s=2}^{\infty}\sum_{\{\alpha_s\}}\frac{1}{s!}\sum_{\{s\}}\left(\prod_{i=1}^{s} n^{(1)}_{\alpha_i}(\boldsymbol{i})\right)h^{(s)}_{\alpha_s}(\{\boldsymbol{s}\}) = \sum_{s=2}^{\infty}\frac{\langle C^{(s)}\rangle}{s!} \tag{87}$$

and also serves as the definition of $\langle C^{(s)}\rangle$, its first term is the fourth one of equation (81) and its analogue is equation (III-18).

On the other hand, the moment–cumulation relation (equation (61)) allows us to relate $\langle C^{(s)}\rangle$ to $\langle n^{(p)}\rangle$. The normalization of the distribution functions (see, e.g., equations (5) and (12)) is

$$\langle n^{(m)}_{\boldsymbol{\alpha}_m}(\{\boldsymbol{m}\})\rangle = \langle N_{\alpha_1}(N_{\alpha_2} - \delta_{\alpha_2\alpha_1})\ldots(N_{\alpha_m} - \delta_{\alpha_m\alpha_1} - \cdots - \delta_{\alpha_m\alpha_{m-1}})\rangle \tag{88}$$

and can be cast in the form similar to equation (III-20):

$$\langle n^{(m)}_{\boldsymbol{\alpha}_m}(\{\boldsymbol{m}\})\rangle = \sum_{\alpha_t\in\{\boldsymbol{\alpha}_m\}|\neq} \sum_{k_1=1}^{n_{\alpha_1}}\cdots\sum_{k_t=1}^{n_{\alpha_t}}\left\langle\prod_{i=1}^{t} N_{\alpha_i}^{k_i}\right\rangle\prod_{i=1}^{t} s(n_{\alpha_i}, k_i) \tag{89}$$

where the notation means that there are t *different* species in the composition set $\boldsymbol{\alpha}_m$, each one of them appearing n_{α_i}, $i = 1, \ldots, t$ times, that the products are over the t *different* components in the m-components set $\boldsymbol{\alpha}_m$, N_{α_i} is the number of molecules of type α_i, the angular brackets is a grand canonical average and $s(r, k)$ are Stirling numbers of the first kind [23].

Now we define the n-body susceptibilities by

$$\gamma^{(n)}_{\boldsymbol{\alpha}} = \begin{cases} \dfrac{\langle (N_\alpha - \langle N_\alpha\rangle)^n\rangle}{N} & \boldsymbol{\alpha} = (\alpha, \overset{n}{\ldots}, \alpha) \\ \dfrac{\langle \prod_{\alpha_i\in\{\boldsymbol{\alpha}_m\}|\neq}(N_\alpha - \langle N_{\alpha_i}\rangle)^{r_i}\rangle}{N} & \boldsymbol{\alpha} = (\alpha_1, \overset{r_1}{\ldots}, \alpha_1, \ldots, \alpha_t, \overset{r_t}{\ldots}, \alpha_t). \end{cases} \tag{90}$$

It is obvious that the number of n-body susceptibilities depends on the number of available species p and, by definition, $\gamma^{(1)} \equiv 1$. Now, using equations (89) and (90), it is possible to write equation (87) in terms of the n-body susceptibilities given in (90), all in the same vein as equations (III-22)–(III-24). The general expression is quite cumbersome and, as we are going to sum exclusively the contribution of the diagonal susceptibilities (one species, k-body) to all orders and the non-diagonal k-body two-species susceptibilities (also to all k-body orders), we will just write the needed equations. The diagonal r-body susceptibility contribution summed to infinite order is

$$\Gamma^{(r)}_{\boldsymbol{\alpha}} = N\gamma^{(r)}_{\boldsymbol{\alpha}}\sum_{k=r}^{\infty}\frac{s(k, r)}{k!}. \tag{91}$$

Using the result [23]

$$\sum_{k=r}^{\infty}\frac{s(k, r)}{k!}x^k = \frac{[\ln(1 + x)]^r}{r!} \tag{92}$$

we obtain the total contribution of the diagonal r-body susceptibility to the entropy as

$$\Gamma^{(r)}_{\boldsymbol{\alpha}} = N\gamma^{(r)}_{\boldsymbol{\alpha}}\begin{cases} (\ln 2 - 1) & r = 1 \\ \dfrac{(\ln 2)^r}{r!} & r > 1 \end{cases} \tag{93}$$

which is the (partial) generalization of equation (III-26). Now we consider the contribution of the simplest non-diagonal susceptibility, i.e. the two-body two-species one, let us say $\gamma^{(2)}_{\alpha\lambda}$. For the rth-order term given by the expansion of equation (87) we have $r - 1$ terms with α and λ appearing n_α and $r - n_\alpha$ times, respectively; $n_\alpha = 1, \ldots, r - 1$ and all these terms with statistical weight equal to 1. Then the rth contribution of each $\alpha\lambda$ pair to the entropy is

$$N\gamma^{(2)}_{\alpha\lambda}\sum_{n_\alpha=1}^{r-1}\frac{s(n_\alpha, 1)}{n_\alpha!}\frac{s(r - n_\alpha, 1)}{(r - n_\alpha)!}. \tag{94}$$

Using the recurrence [23]

$$\left(\frac{m}{s}\right)s(r,m) = \sum_{k=m-s}^{r-s} r!\frac{s(r-k,s)}{(r-k)!}\frac{s(k,m-s)}{k!} \tag{95}$$

the contribution given in equation (94) reduces, with $s = m - s = 1$, $k = r_\alpha$, to

$$2N\gamma^{(2)}_{\alpha\lambda}\frac{s(r,2)}{r!}.$$

Lastly, we use the sum given in equation (92) to obtain that the contribution to the entropy arising from $\gamma^{(2)}_{\alpha\lambda}$ after summing over all the n-body contributions is

$$\Gamma^{(2)}_{\alpha\lambda} = N\gamma^{(2)}_{\alpha\lambda}(\ln 2)^2. \tag{96}$$

The process can be repeated for the evaluation of the contribution of the k-body two-species susceptibilities $\gamma^{(k)}_{\alpha\overset{r}{\ldots}\alpha\lambda\overset{k-r}{\ldots}\lambda}$ and the general result, for the case of α appearing r times and $\lambda\, k - r$ times is

$$\Gamma^{(k)}_{\alpha\overset{r}{\ldots}\alpha\lambda\overset{k-r}{\ldots}\lambda} = N\gamma^{(k)}_{\alpha\overset{r}{\ldots}\alpha\lambda\overset{k-r}{\ldots}\lambda}\frac{(\ln 2)^k}{r!(k-r)!}. \tag{97}$$

Equations (93), (96) and (97) give the whole two-species contribution to equation (87). It is clear that this summation was possible because of (95) and that the evaluation of higher-order contributions depends on finding more and more complicated recurrences in the Stirling numbers. As three-body susceptibilities are notoriously hard to calculate and rarely used, we stop the resummation of the series given in equation (87). The density fluctuations contribution to the entropy evaluated up to now is

$$\frac{S_a}{k} = N\sum_\alpha\left[\ln 2 - 1 + \sum_{n=2}^{\infty}\frac{(\ln 2)^n}{n!}\gamma^{(n)}_\alpha\right] + N\sum_{n=2}^{\infty}\sum_{r=1}^{n-1}\frac{(\ln 2)^n}{r!(n-r)!}\sum_{i=0}^{p-1}\sum_{j=i+1}^{p}\gamma^{(n)}_{\alpha_i\overset{r}{\ldots}\alpha_i\alpha_j\overset{n-r}{\ldots}\alpha_j}. \tag{98}$$

The relationship between the susceptibilities and the correlation functions is easily obtained from equations (88)–(90). In particular, for the most important of all, we have

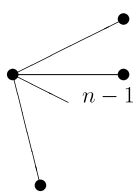
$$\gamma^{(2)}_{\alpha\lambda} = \frac{1}{N}\sum_{\mathbf{1}} n^{(1)}_\alpha(\mathbf{1})\left[\delta_{\alpha\lambda} + \sum_{\mathbf{2}} n^{(1)}_\lambda(\mathbf{2})h^{(2)}_{\alpha\lambda}(\mathbf{1},\mathbf{2})\right] = \frac{1}{N}\sum_{\mathbf{1}} n^{(1)}_\alpha(\mathbf{1})\tilde{\gamma}^{(2)}_{\alpha\lambda}(\mathbf{1}) \tag{99}$$

which defines a local compressibility $\tilde{\gamma}^{(2)}_{\alpha\lambda}(\mathbf{1})$.

(b) The second term in equation (86) is the first one in a series of so-called (in diagrammatic terminology) 'star' products given in equation (27):

$$\begin{aligned}\frac{S_b}{k} &= -\sum_{n\geqslant 3}\Psi_n \\ \Psi_n &= \sum_{\boldsymbol{\alpha}_n}\frac{1}{\boldsymbol{n}!}\sum_{\{\boldsymbol{n}\}}\sum_{i=1}^{(n)} n^{(1)}_{\alpha_i}(\boldsymbol{i})\prod_{k\neq i}[n^{(1)}_{\alpha_k}(\boldsymbol{k})h^{(2)}_{\alpha_i\alpha_k}(\{\boldsymbol{i},\boldsymbol{k}\})]\end{aligned} \tag{100}$$

which shows that all the terms have a common vertex. Diagrammatically, they can be written as

$\Psi_n =$ 

where the diagrammatic conventions are those already mentioned. Notice that the diagram describing Ψ_n has n black circles and $n-1$ bonds. All these diagrams can be analytically summed. Let us first define a $(p+1)\times(p+1)$ matrix $G_{\alpha_i\alpha_j}$ by

$$G_{\alpha_i\alpha_j}(\boldsymbol{i}) = \sum_{\boldsymbol{j}} n^{(1)}_{\alpha_j}(\boldsymbol{j}) h^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{i},\boldsymbol{j}) = \tilde{\gamma}^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{i}) - \delta_{\alpha_i\alpha_j}.$$

Diagrammatically, the matrix elements are

$G_{\alpha_i\alpha_j}(\boldsymbol{i}) =$

with the proviso that in the decorated black circle the sum over species is not performed (only the one over the lattice) and the white circle is a white-1 circle labelled α_i, $\boldsymbol{i}$, i.e. there is no factor or sum attached to it. Now we apply the star product lemma of diagrammatic expansions [24] which says that, if $\{G\}$ is a set of star-irreducible diagrams and $\{H\}$ is the set of all the diagrams in $\{G\}$ plus all its possible star products, then

$$\mathcal{H} = \sum_{H_i\subseteq\{H\}} H_i = \exp\left(\sum_{G_i\subseteq\{G\}} G_i\right) - 1.$$

Let us apply this lemma to each row of the matrix $G_{\alpha_i\alpha_j}$. We take the ith row as the set $\{G\}$ to which the lemma is applied. Then

$$\mathcal{H}_{\alpha_i}(\boldsymbol{i}) = \exp\left(\sum_{\alpha_j} G_{\alpha_i\alpha_j}(\boldsymbol{i})\right) - 1.$$

If from each $\mathcal{H}_{\alpha_i}(\boldsymbol{i})$ we subtract the sum of the diagrams in $\{G\}$ (in equation (100) the sum starts with $n=3$ vertices), multiply by $n^{(1)}_{\alpha_i}(\boldsymbol{i})$, sum over the lattice and then sum over the species α_i we get the 'star' product fluctuation density contribution to the entropy of equation (100) as

$$\begin{aligned}\frac{S_b}{k} &= -\sum_{i=0}^{p}\sum_{\boldsymbol{i}} n^{(1)}_{\alpha_i}(\boldsymbol{i})\left\{\exp\left(\sum_{\alpha_j} G_{\alpha_i\alpha_j}(\boldsymbol{i})\right) - 1 - \sum_{\alpha_j} G_{\alpha_i\alpha_j}(\boldsymbol{i})\right\} \\ &= -\sum_{i=0}^{p}\sum_{\boldsymbol{i}} n^{(1)}_{\alpha_i}(\boldsymbol{i})\left\{\exp\left(\sum_{\alpha_j} \tilde{\gamma}^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{i}) - 1\right) - \sum_{\alpha_j} \tilde{\gamma}^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{i})\right\}. \qquad (101)\end{aligned}$$

Notice that, as we have one vertex common to all h-bonds and we are also summing over that vertex, the sum over all the pairs i, j ($\sum_{i,j}$) does not imply any overcounting. Also, equation (101) is the generalization to inhomogeneous mixtures of equation (III-28) and, thanks to the biunivocity between lattice gases and liquids established in section 2, can be immediately translated to liquid language as

$$\frac{S_b^{liq}}{k} = -\sum_{i=0}^{p}\int \mathrm{d}\boldsymbol{x}\, n^{(1)}_{\alpha_i}(\boldsymbol{x})\left\{\exp\left(\sum_{\alpha_j} \tilde{\gamma}^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{x}) - 1\right) - \sum_{\alpha_j} \tilde{\gamma}^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{x})\right\}. \qquad (102)$$

(c) The last series of terms in equation (86) is the first one of a sum of rings, all of them with the same sign. It is equation (III-29) and therefore we have

$$\frac{S_c}{k} = -\frac{1}{2}\sum_{s\geqslant 3}\frac{1}{s}\sum_{\{\boldsymbol{\alpha}_s\}}\sum_{\{\boldsymbol{s}\}}\left(\prod_{i=1}^{s} n^{(1)}_{\alpha_i}(\boldsymbol{i})\right) h^{(2)}_{\alpha_1\alpha_2}(\mathbf{1},\mathbf{2}) h^{(2)}_{\alpha_2\alpha_3}(\mathbf{2},\mathbf{3})\ldots h^{(2)}_{\alpha_s\alpha_1}(\boldsymbol{s},\mathbf{1}). \qquad (103)$$

When added to the ring approximation term giving a ring sum over all the even-order rings, it is the renormalized ring approximation (RRA) shown in equation (III-31). The result, in our notation, is

$$\frac{S^{(RRA)}}{k} = -\frac{1}{2}\sum_{s\geqslant 2}\frac{1}{s}\sum_{\{\boldsymbol{\alpha}_{2s}\}}\sum_{\{\mathbf{2}\boldsymbol{s}\}}\left(\prod_{i=1}^{2s} n^{(1)}_{\alpha_i}(\boldsymbol{i})\right) h^{(2)}_{\alpha_1\alpha_2}(\mathbf{1},\mathbf{2}) h^{(2)}_{\alpha_2\alpha_3}(\mathbf{2},\mathbf{3})\ldots h^{(2)}_{\alpha_{2s}\alpha_1}(\mathbf{2}\boldsymbol{s},\mathbf{1}). \qquad (104)$$

This term can be analytically summed on homogeneous systems (if such a system exists in lattice gases) obtaining the result (equation (III-32))

$$\frac{S^{(RRA)}}{k} = \frac{1}{2}\sum_{\{\tilde{\Lambda}_k\}}\{\ln[|1-(\tilde{H}(\boldsymbol{k}))^2|] + \mathrm{Tr}[(\tilde{H}(\boldsymbol{k}))^2]\} \tag{105}$$

where the matrix elements of $\tilde{H}$ are $\tilde{H}_{\alpha\lambda}(\boldsymbol{k}) = (\rho_\alpha\rho_\lambda)^{1/2}\tilde{h}_{\alpha\lambda}(\boldsymbol{k})$, $\tilde{h}_{\alpha\lambda}(\boldsymbol{k})$ is the Fourier transform of the pair correlation function, the argument of the logarithm is the determinant of the matrix $1-(\tilde{H}(\boldsymbol{k}))^2$, the other term is the trace of the corresponding matrix and $\{\tilde{\Lambda}_k\}$ is the reciprocal space lattice. The more interesting case (for adsorption problems) of inhomogeneous systems needs a careful analysis; it is, probably, a stumbling block to a direct application of the entropy equation presented in this paper. However, we believe that much can be done, because if the renormalized ring term is approximated by some homogeneous system, this approximation should not be used in any variational principle, only in approximating the numerical value of the entropy (see the discussion in [17]) and the inaccuracies involved do not seem much worse than those due to truncation in the expansion. In other words, any average performed via the distribution functions is not affected by inaccuracies in the ring approximation. Finally, for the sake of completeness, let us collect together the different terms and write the entropy equation (equations (83), (98), (101) and (104))

$$\begin{aligned}\frac{S}{k} = N &- \sum_{M\geqslant 1}\sum_{\{\boldsymbol{\alpha}_M\}}\frac{1}{M!}\sum_{\{M\}} n^{(M)}_{\boldsymbol{\alpha}_M}(\{M\})\omega^{(M)}_{\boldsymbol{\alpha}_M}(\{M\}) + N\sum_{\alpha}\left[\ln 2 - 1 + \sum_{n=2}^{\infty}\frac{(\ln 2)^n}{n!}\gamma^{(n)}_{\alpha}\right] \\ &+ N\sum_{n=2}^{\infty}\sum_{r=1}^{n-1}\frac{(\ln 2)^n}{r!(n-r)!}\sum_{i=0}^{p-1}\sum_{j=i+1}^{p}\gamma^{(n)}_{\alpha_i\overset{r}{\ldots}\alpha_i\alpha_j\overset{n-r}{\ldots}\alpha_j} \\ &- \sum_{i=0}^{p}\sum_{\boldsymbol{i}} n^{(1)}_{\alpha_i}(\boldsymbol{i})\left\{\exp\left(\sum_{\alpha_j}\tilde{\gamma}^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{i}) - 1\right) - \sum_{\alpha_j}\tilde{\gamma}^{(2)}_{\alpha_i\alpha_j}(\boldsymbol{i})\right\} \\ &- \frac{1}{2}\sum_{s\geqslant 2}\frac{1}{s}\sum_{\{\boldsymbol{\alpha}_{2s}\}}\sum_{\{\boldsymbol{2s}\}}\left(\prod_{i=1}^{2s} n^{(1)}_{\alpha_i}(\boldsymbol{i})\right)h^{(2)}_{\alpha_1\alpha_2}(\boldsymbol{1},\boldsymbol{2})h^{(2)}_{\alpha_2\alpha_3}(\boldsymbol{2},\boldsymbol{3})\ldots h^{(2)}_{\alpha_{2s}\alpha_1}(\boldsymbol{2s},\boldsymbol{1}).\end{aligned} \tag{106}$$

5. Conclusions

In adsorption related phenomena the would-be adsorbed molecules can be (very usefully) analysed through DF techniques while the adsorbed molecules in the crystalline lattice are usually reduced to and discussed in terms of a system of spins in a lattice with some or several spin averages as the quantities to be determined. As we believe that a unified treatment can lead to new avenues of research and also that probability distribution functions are more fundamental quantities than spin averages, we undertook a treatment of lattice gases in a full DF formalism. In that respect it is inevitable to have, first of all, a full OZ formalism, i.e. a set of equations that link the direct and total correlation functions hierarchies if the HKSM theorem holds true. Through the use of a functional differentiation approach we first obtained the lattice gas distribution and correlation functions hierarchies (analogous to those well known in the theory of inhomogeneous fluids) and found that it was still insufficient to formulate an OZ theory. The cause can be traced back to the fixed topology of lattice gases which implies a constraint of similar nature to the one found for fluids in the CE. Therefore, we proceeded along the lines previously developed in [2] and found that the same procedure that gets rid of the asymptotic behaviour in fluids also gets rid of the topological constraint in lattice gases. In this way, we were able to generate N-modified correlation functions, develop a full OZ formalism and prove

that the HKSM theorem is also valid in the lattice gas case. The other fundamental ingredient is an expression for the entropy as a functional of the already discussed correlation functions. This was obtained by retracing the steps we previously followed [15–17] for the entropy of fluids and we have written not only a general, exact (and, as such, intractable) expression for the entropy (equation (80)) but also an approximated and potentially useful expression for it (equation (106)). In that respect, we generalized the compressibility contribution to entropy derived in [17] and showed that this generalization is also applicable to fluids. This result is an example of what for us is the main conclusion of this paper: that, when analysed with the full DF formalism, both fluids and lattice gases show a truly deep relationship and that this isomorphism should open the DF point of view to lattice gases as well as lead to new perspectives. Lastly, a word of caution about the use of these equations. They are the result of summing infinite subsets of terms and their convergence properties are unknown. In fact, it may well happen, as is the case for hard sphere fluids, where the PY approximation performs better than the HNC, that some systems perform better with a less complete summation scheme.

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