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Entropy of a One-Dimensional Mixed Lattice Gas

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This paper deals with the grand canonical entropy of a lattice gas mixture. The entropy is a function of the multisite densities corresponding to the interaction pattern of the system in question. It is first evaluated for a nearest-neighbor-interaction, one-dimensional simple lattice gas to show how the structure of bulk fluid is locally maintained. Generalization requires one set of interrelations among multisite densities presented in closed form for an arbitrary lattice, and one set between Boltzmann factors and multisite densities which is written down for simply connected lattices. Application is made to two-row lattices, which turn out to have local behavior from this viewpoint, as do all single-row or Bethe lattices with complete range-p interactions. Nonlocal examples are also given, and suggestions made for approximation sequences in general lattices.

KEY WORDS: Lattice gas; nonuniform fluid; entropy functional; nonlocal response; mixture; nonneighbor coupling; Bethe lattice.

1. INTRODUCTION

Analysis of exactly solvable models has always been one of the most effective ways of reaching an understanding of the conceptual structure of a quantitative field. But developing useful models is rarely a trivial undertaking, and may require an expansion of the domain in which questions are to be posed. Even in the restricted discipline associated with classical fluids in thermal equilibrium, we are beginning to run out of simple models, an asertion which depends upon the format in which we work. The current standard for nonuniform fluids is the density functional formalism, in which an arbitrary external potential $u(r)$ can be accommodated via the inverse relation

$$\mu - u(r) = \delta \bar{F}[n]/\delta n(r) \tag{1.1}$$

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where $u(r)$ is the density profile and $\bar{F}[n]$ the residual Helmholtz free energy in a grand ensemble at chemical potential μ. The functional $\bar{F}[n]$ has been found explicitly$^{(1,2)}$ for some simple models, and in each case can be interpreted in terms of a free energy density which depends only upon a few local averages of the spatial density $n(r)$. Extension of this structure to real fluids is a very active field (see, e.g., ref. 3), with verification in the main restricted to numerical comparisons.

An apparently more grandiose approach might encompass both arbitrary external and internal pair potentials, with the entropy functional as the relevant generator. The point is this. For a pair potential interaction $\phi(r, r')$, the grand potential Ω generates both one- and two-body densities $n(r)$ and $n_2(r, r')$ via

$$\begin{aligned} n(r) &= \delta\Omega[u, \phi]/\delta u(r) \\ n_2(r, r') &= 2\delta\Omega[u, \phi]/\delta\phi(r, r') \end{aligned} \tag{1.2}$$

The external potential can be eliminated in favor of $n(r)$ by a Legendre transformation:

$$\bar{F}[n, \phi] = \Omega[u, \phi] + \int [\mu - u(r)]\, n(r)\, dr \tag{1.3}$$

resulting in (1.1) as well as

$$n_2(r, r') = 2\delta\bar{F}[n, \phi]/\delta\phi(r, r') \tag{1.4}$$

But $\phi(r, r')$ can similarly be eliminated, in principle, in favor of $n_2(r, r')$:

$$TS[n, n_2] = \frac{1}{2}\iint n_2(r, r')\, \phi(r, r')\, dr\, dr' - \bar{F}[n, \phi] \tag{1.5}$$

so that

$$\begin{aligned} u(r) - \mu &= \delta T\, S[n, n_2]/\delta n(r) \\ \phi(r, r') &= 2\, \delta T\, S[n, n_2]/\delta n_2(r, r') \end{aligned} \tag{1.6}$$

The entropy designation follows from (1.3) and (1.5) in the form $TS = U - (G - PV)$. Although our ability to encompass both arbitrary internal and external potentials in this fashion would be highly suspect if the functional were to cover $[n, n_2]$ regions in which qualitative structural changes were to occur, it has recently been carried out without difficulty for one-dimensional classical fluids with nearest neighbor interaction.$^{(4)}$ And there is empirical evidence$^{(5)}$ that a major region of real fluids may be describable by a simple entropy functional.

In the present paper, we start a more systematic approach to the construction of model entropy functionals by restricting attention to perhaps the simplest nontrivial category of fluids, that of a lattice gas mixture on the full one-dimensional integer lattice. Let us, for the purpose of orientation, consider first the thermodynamic limit of a uniform one-dimensional lattice gas with nearest neighbor interaction J and chemical potential μ. The simplest attack[6] is to compute the number of configurations $\{v_x = 0, 1\}$ of an L-site lattice which are consistent with N_+ occupied sites $(v = 1)$, N_0 unoccupied $(v = 0)$, N_{++} adjacent occupied pairs, and similarly N_{0+}, N_{+0}, N_{00}. There are clearly $N_+ - N_{++}$ clusters of occupied sites of length $\geqslant 1$, determined by $N_+ - N_{++}$ leading particles. These leading particles can be selected from the amalgamated sequence of N_+ occupied sites in

$$\binom{N_+}{N_+ - N_{++}}$$

ways. Similarly for the unoccupied sites, so that the total number of configurations is

$$e^S = \binom{N_+}{N_{++}}\binom{N_0}{N_{00}} \tag{1.7}$$

Letting $L \to \infty$, with $n_+ = N_+/L$, etc., and observing that $N_+ - N_{++} = N_{+0}$, we have

$$\begin{aligned} S/L = {} & n_+ \ln n_+ + n_0 \ln n_0 - n_{++} \ln n_{++} \\ & - n_{+0} \ln n_{+0} - n_{0+} \ln n_{0+} - n_{00} \ln n_{00} \end{aligned} \tag{1.8}$$

Alternatively, to make contact with (1.5) and (1.6), let $w = e^{\beta(\mu - u)}$ and $e = e^{-\beta J}$ be the external and internal Boltzmann factors at reciprocal temperature β, so that the partition function in transfer matrix form is

$$\begin{aligned} Z &= \operatorname{Tr}\left[\begin{pmatrix} 1 & 0 \\ 0 & w \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & e \end{pmatrix}\right]^L \\ &= \operatorname{Tr}\begin{pmatrix} 1 & 1 \\ w & ew \end{pmatrix}^L \\ &\sim \left(\frac{1}{2}\right)^L (1 + ew + s)^L, \qquad \text{where} \quad s = (1 - ew)^2 + 4w \end{aligned} \tag{1.9}$$

Hence

$$\frac{\Omega}{L} = -\frac{1}{\beta} \ln \frac{1}{2} (1 + ew + s) \tag{1.10}$$

yielding

$$
\begin{aligned}
n_{+} &= -\beta w \frac{\partial}{\partial w}\frac{\Omega}{L} = \frac{1}{s}\frac{2w - ew(1-ew) + ews}{1 + ew + s} \\
n_{++} &= -\beta e \frac{\partial}{\partial e}\frac{\Omega}{L} = \frac{1}{s}\frac{-ew(1-ew) + ews}{1 + ew + s}
\end{aligned}
\tag{1.11}
$$

On solving (1.11) for e and w, we find

$$
\begin{aligned}
\beta(u-\mu) &= \ln[n_{+}/(1-n_{+})] + 2\ln(1-2n_{+}+n_{++})/(n_{+}-n_{++}) \\
\beta J &= -\ln n_{+} + 2\ln(n_{+}-n_{++}) - \ln(1-2n_{+}+n_{++})
\end{aligned}
\tag{1.12}
$$

and quickly conclude from (1.6), in its uniform lattice form, that indeed (1.8) holds, to within an additive constant.

In the following sections, we first show that (1.8), interpreted as entropy density, extends directly to a nonuniform lattice gas. We then introduce the entropy functional for a general lattice gas mixture characterized by a local interaction pattern, and obtain a preliminary form for the profile equations. For the case of a one-dimensional lattice with fixed range of multisite interactions, and for a Bethe lattice as well, the profile equations are found explicitly in local form, as is the entropy functional. With this available as a tool, we show how reduction of the class of pairwise interactions applies to a primitive two-dimensional lattice, and continue by applying the same technique to bring in previously encountered nonlocal behavior. We conclude by suggesting how the present analysis may be extended to more complex but realistic fluids.

2. PROTOTYPE

The single-component, one-dimensional lattice gas with nearest neighbor interaction and external potential considered in (1.7)–(1.12) serves as a convenient entree to our discussion. Now, however, we allow for full nonuniformity of interaction strength, denoted by $J_{x,x+1}$, and external potential u_x, with corresponding Boltzmann factors $e_{x,x+1} = e^{-\beta J_{x,x+1}}$, $w_x = e^{\beta(\mu - u_x)}$, and $-\infty < x < \infty$ an integer. The partition function can therefore be written as

$$
Z = \sum_{\{v_x = 0,1\}} \prod_x e_{x,x+1}(v_x, v_{x+1}) \prod_x w_x(v_x)
\tag{2.1}
$$

where

$$
\begin{aligned}
e_{x,x+1}(v_x, v_{x+1}) &= e^{-\beta J_{x,x+1} v_x v_{x+1}} \\
w_x(v_x) &= e^{-\beta(u_x - \mu) v_x}
\end{aligned}
\tag{2.1}
$$

Z converges if $u_x \to \infty$ sufficiently rapidly as $|x| \to \infty$. It is important to note that with the above definition

$$e_{x,x+1}(0, \alpha) = e_{x,x+1}(\alpha, 0) = 1, \qquad w_x(0) = 1 \tag{2.2}$$

We will be interested in singlet and successive pair densities, as well as successive higher densities. It will be useful to generalize to the associated particle–hole occupation densities, readily calculated as

$$\begin{aligned}
n_{x+1}(\alpha) &= \Pr(v_{x+1} = \alpha)\\
&= Z_{x+1}(\alpha)\, \hat{Z}_{x+1}(\alpha)\, w_{x+1}(\alpha)/Z
\end{aligned}$$

$$\begin{aligned}
&n_{x+1\cdots x+q}(\alpha_1 \cdots \alpha_q)\\
&\quad = \Pr(v_{x+1} = \alpha_1, \ldots, v_{x+q} = \alpha_q)\\
&\quad = Z_{x+1}(\alpha_1)\, \hat{Z}_{x+q}(\alpha_q)\, w_{x+1}(\alpha_1) \cdots w_{x+q}(\alpha_q)\, e_{x+1,x+2}(\alpha_1, \alpha_2)\\
&\qquad \times \cdots e_{x+q-1,x+q}(\alpha_{q+1}, \alpha_q)/Z
\end{aligned} \tag{2.3}$$

Here

$$\begin{aligned}
Z_x(\alpha) &= \sum_{\{v_y = 0,1;\, y < x-1\}} \prod_{y < x-1} e_{y,y+1}(v_y, v_{y+1}) \prod_{y < x} w_y(v_y)\, e_{x-1,x}(v_{x-1}, \alpha)\\
\hat{Z}_x(\alpha) &= \sum_{\{v_y = 0,1;\, y > x\}} \prod_{y > x} e_{y,y+1}(v_y, v_{y+1}) \prod_{y > x} w_y(v_y)\, e_{x,x+1}(\alpha, v_{x+1})
\end{aligned} \tag{2.4}$$

and Pr denotes probability. The corresponding particle occupation densities are therefore $n_x = n_x(1)$, $n_{x,x+1} = n_{x,x+1}(1, 1), \ldots$.

The short range of the interaction together with the linear ordering of sites is responsible for the factorized form$^{(7)}$ of (2.3). This factorization is more usefully expressed in terms of a "superposition relation" among the distributions, to wit

$$\begin{aligned}
&n_{x+1,x+2,\ldots,x+q}(\alpha_1, \alpha_2, \ldots, \alpha_q)\\
&\quad = n_{x+1,x+2}(\alpha_1, \alpha_2) \cdots n_{x+q-1,x+q}(\alpha_{q-1}, \alpha_q)/n_{x+2}(\alpha_2) \cdots n_{x+q-1}(\alpha_{q-1})
\end{aligned} \tag{2.5}$$

which follows at once from (2.3). But of course there are also interrelations between distributions and Boltzmann factors. In particular, we see that

$$\begin{aligned}
&n_{x+1,\ldots,x+q}(\alpha_1 \cdots \alpha_q)\\
&\quad \times [w_{x+2}(\alpha_2) \cdots w_{x+q-1}(\alpha_{q-1})\, e_{x+1,x+2}(\alpha_1, \alpha_2) \cdots\\
&\quad \times e_{x+q-1,x+q}(\alpha_{q-1}, \alpha_q)]^{-1}
\end{aligned} \tag{2.6}$$

is independent of $\alpha_2, \dots, \alpha_{q-1}$. Thus,

$$\begin{aligned} &n_{x+1,\dots,x+q}(\alpha_1 \cdots \alpha_q) \\ &\quad = n_{x+1,\dots,x+q}(\alpha_1 0 \cdots 0 \alpha_q) \\ &\qquad \times w_{x+2}(\alpha_2) \cdots w_{x+q-1}(\alpha_{q-1})\, e_{x+1,x+2}(\alpha_1, \alpha_2) \cdots \\ &\qquad \times e_{x+q-1,x+q}(\alpha_{q-1}, \alpha_q) \end{aligned} \tag{2.7}$$

which we further specialize to

$$\begin{aligned} &n_{x+1,\dots,x+q}(0, \alpha_2 \cdots \alpha_{q-1}, 0) \\ &\quad = n_{x+1,\dots,x+q}(0 \cdots 0) \\ &\qquad \times w_{x+2}(\alpha_2) \cdots w_{x+q-1}(\alpha_{q-1})\, e_{x+1,x+2}(\alpha_1, \alpha_2) \cdots \\ &\qquad \times e_{x+q-1,x+q}(\alpha_{q-1}, \alpha_q) \end{aligned} \tag{2.8}$$

The profile equations, i.e., the expressions for $e_{x+1,x+2}(\alpha_1, \alpha_2)$ and $w_x(\alpha)$ in terms of the singlet and successive pair densities, readily follow from (2.5) and (2.8). First, using (2.8), we have

$$\begin{aligned} w_x(\alpha) &= \frac{n_{x-1,x,x+1}(0, \alpha, 0)}{\eta_{x-1,x,x+1}(0, 0, 0)} \\ e_{x+1,x+2}&(\alpha_1, \alpha_2) \\ &= \frac{n_{x,x+1,x+2,x+3}(0, \alpha_1, \alpha_2, 0)}{n_{x,x+1,x+2,x+3}(0, 0, 0, 0)} \\ &\quad \times \frac{n_{x,x+1,x+2}(0, 0, 0)}{n_{x,x+1,x+2}(0, \alpha_1, 0)} \frac{n_{x+1,x+2,x+3}(0, 0, 0)}{n_{x+1,x+2,x+3}(0, \alpha_2, 0)} \end{aligned} \tag{2.9}$$

and then, applying (2.5),

$$\begin{aligned} w_x(\alpha) &= \frac{n_{x-1,x}(0, \alpha)\, n_{x,x+1}(\alpha, 0)}{n_x(\alpha)} \frac{n_x(0)}{n_{x-1,x}(0, 0)\, n_{x,x+1}(0, 0)} \\ e_{x+1,x+2}(\alpha_1, \alpha_2) &= \frac{n_{x+1,x+2}(\alpha_1, \alpha_2)\, n_{x+1,x+2}(0, 0)}{n_{x+1,x+2}(\alpha_1, 0)\, n_{x+1,x+2}(0, \alpha_2)} \end{aligned} \tag{2.10}$$

If we set $\alpha_1 = \alpha_2 = \alpha = 1$ in (2.10) and recall that, since $\delta_{v,0} + \delta_{v,1} = 1$, then $n_x(0) = 1 - n_x$, $n_{x,x+1}(0, 1) = n_{x+1} - n_{x,x+1}$, $n_{x,x+1}(1, 0) = n_x - n_{x,x+1}$, and $n_{x,x+1}(0, 0) = 1 - n_x - n_{x+1} + n_{x,x+1}$, we conclude from (2.10) that

$$\begin{aligned}\beta(u_x-\mu)&=\ln n_x-\ln(1-n_x)\\&\quad+\ln(1-n_{x-1}-n_x+n_{x-1,x})+\ln(1-n_x-n_{x+1}+n_{x,x+1})\\&\quad-\ln(n_x-n_{x-1,x})-\ln(n_{x+1}-n_{x,x+1})\\\beta J_{x+1,x+2}&=\ln(n_{x+2}-n_{x+1,x+2})+\ln(n_{x+1}-n_{x+1,x+2})\\&\quad-\ln n_{x+1,x+2}-\ln(1-n_{x+1}-n_{x+2}+n_{x+1,x+2})\end{aligned}\tag{2.11}$$

which is the obvious naive generalization of (1.12). Furthermore, using the ordered lattice version of (1.6) (the factor of 2 does not appear, since the ordered expression $n_{x,x+1}$ is used), we see that the relations (2.11) are generated, to within an additive constant, by

$$\begin{aligned}&S[n_x, n_{x,x+1}]\\&\quad=\sum_x [n_x\ln n_x+(1-n_x)\ln(1-n_x)-n_{x,x+1}\ln n_{x,x+1}\\&\qquad-(n_x-n_{x,x+1})\ln(n_x-n_{x,x+1})-(n_{x+1}-n_{x,x+1})\ln(n_{x+1}-n_{x,x+1})\\&\qquad-(1-n_{x+1}-n_x+n_{x,x+1})\ln(1-n_{x+1}-n_x+n_{x,x+1})]\end{aligned}\tag{2.12}$$

which is the obvious naive generalization of (1.8).

Finally, let us for completeness perform a partial reversion to recover the free energy functional known from previous work.[(8)] This of course is given by

$$\beta\bar{F}[n_x, J_{x,x+1}]=\sum n_{x,x+1}\beta J_{x,x+1}-S[n_x, n_{x,x+1}]\tag{2.13}$$

if we can solve for $n_{x,x+1}$ in terms of the $\{n_x\}$ and $\{J_{x,x+1}\}$. In the present case, there is no trouble in doing so, directly from the second equation of (2.11). We find

$$n_{x,x+1}=[(1-e_{x,x+1})(n_x+n_{x+1})-1+q_{x,x+1}]/2(1-e_{x,x+1})\tag{2.14}$$

where

$$q^2_{x,x+1}=[(1-e_{x,x+1})(n_x+n_{x+1})-1]^2+4e_{x,x+1}(1-e_{x,x+1})\,n_xn_{x+1}$$

as well as

$$\begin{aligned}n_x-n_{x,x+1}&=[(1-e_{x,x+1})(n_x-n_{x+1})+1-q_{x,x+1}]/2(1-e_{x,x+1})\\n_{x+1}-n_{x,x+1}&=[(1-e_{x,x+1})(n_{x+1}-n_x)+1-q_{x,x+1}]/2(1-e_{x,x+1})\\1-n_x-n_{x,x+1}&+n_{x,x+1}\\&=[(1-e_{x,x+1})(2-n_x-n_{x+1})-1+q_{x,x+1}]/2(1-e_{x,x+1})\end{aligned}\tag{2.15}$$

leading to the rather complicated

$$
\begin{aligned}
&\beta \bar{F}[n_x, J_{x,x+1}] \\
&\quad = \sum [\ln 2(1-e_{x,x+1}) - n_x \ln n_x - (1-n_x)\ln(1-n_x)] \\
&\qquad + \sum \frac{1}{2(1-e_{x,x+1})} \{ [(1-e_{x,x+1})(n_x+n_{x+1}) - 1 + q_{x,x+1}] \\
&\qquad \times \ln[(1-e_{x,x+1})(n_x+n_{x+1}) - 1 + q_{x,x+1}] \\
&\qquad + [(1-e_{x,x+1})(n_x-n_{x+1}) + 1 - q_{x,x+1}] \\
&\qquad \times \ln[(1-e_{x,x+1})(n_x-n_{x+1}) + 1 - q_{x,x+1}] \\
&\qquad + [(1-e_{x,x+1})(n_{x+1}-n_x) + 1 - q_{x,x+1}] \\
&\qquad \times \ln[(1-e_{x,x+1})(n_{x+1}-n_x) + 1 - q_{x,x+1}] \\
&\qquad + [(1-e_{x,x+1})(2-n_x-n_{x+1}) - 1 + q_{x,x+1}] \\
&\qquad \times \ln[(1-e_{x,x+1})(2-n_x-n_{x+1}) - 1 + q_{x,x+1}] \\
&\qquad - [(1-e_{x,x+1})(n_x+n_{x+1}) - 1 + q_{x,x+1}] \ln e_{x,x+1} \} \qquad (2.16)
\end{aligned}
$$

3. GENERAL ENTROPY FUNCTIONAL

Let us defer specialization to one-dimensional or other simply connected lattices until it becomes absolutely necessary to do so. We have in mind then a periodic lattice with a full set of periods $\{x\}$, in which any site y can be empty, $v_y = 0$, or occupied by one of D components, $v_y = 1,..., D$. An interaction pattern will be characterized by a set of subsets of sites $A = \{A_i\}$, where each A_i contains the origin and no two A_i differ only by a lattice period. This means that the total interaction energy of the system, referred to the accumulated chemical potential, is given by

$$\Phi\{v\} = \sum_i \sum_x \phi_{[x+A_i]}[v_y;\, y \in x + A_i] \tag{3.1}$$

For example, in the case (2.1) of external potential and nearest neighbor internal potential on a one-dimensional integer lattice, but generalized to D components, then $A_1 = [0]$, $A_2 = [0, 1]$, and $\phi_x(v) = u_x(v) - \mu_v$, $\phi_{x,x+1}(v, v') = J_{x,x+1}(v, v')$. In order to separate the contributions of the various A_i, we will again adopt the convention that ϕ vanishes if any of its sites is empty:

$$\phi_{(x+A_i)}[v_y,\, y \in x + A_i] = 0 \tag{3.2}$$

if

$$\prod_{y \in x+A_i} v_y = 0$$

The grand potential

$$\Omega[\Phi] = -\frac{1}{\beta} \ln \sum_{\{v_y\}} e^{-\beta\Phi\{v\}} \tag{3.3}$$

now serves as generating functional for the multisite densities corresponding to any interaction cluster:

$$\begin{aligned} &n_{[x+A_i]}[\alpha_y;\, y \in x+A_i] \\ &\quad = \sum_{\{v_y\}} \left(\prod_{z \in x+A_i} \delta_{v_z,\alpha_z} \right) e^{\beta(\Omega(\Phi) - \Phi\{v\})} \\ &\quad = \partial\Omega[\Phi]/\partial\phi_{[x+A_i]}[\alpha_y;\, y \in x+A_i] \end{aligned} \tag{3.4}$$

Joint densities belonging to groupings not present in the interaction pattern must be obtained via successive differentiation, as indeed can any of the multisite densities of (3.4).

The dependence of Ω and the $\{n_{[x+A_i]}\}$ on the $\{\phi_{[x+A_i]}\}$ becomes very sensitive in the vicinity of singular thermodynamic regions. This suggests an inverse formulation,(9) in which the $\{n_{[x+A_i]}\}$ are taken as the independent variables, a suggestion which is reinforced by the exact solvability of a number of model systems in inverse form. For the inverse formulation to exist, $\phi_{[x+A_i]}$ must be solvable uniquely in terms of the $n_{[x+A_i]}$, but this is automatic if the system may be approximated as one with a finite number of degrees of freedom: then Ω is concave in $\{\phi\}$, since $\partial^2\Omega/\partial\phi\,\partial\phi = -\beta\langle(n-\bar{n})(n-\bar{n})\rangle$ is negative definite; hence $\sum n\phi - \Omega$ is convex, with a unique minimum at $n = \partial\Omega/\partial\phi$. To switch to the full set of $\{n_{[x+A_i]}\}$ as independent variables, we perform the complete Legendre transform

$$TS[n_{[x+A_i]}] = -\Omega[\Phi] + \sum_{i,x} \sum_{\alpha} \phi_{[x+A_i]}[\alpha]\, n_{[x+A_i]}[\alpha] \tag{3.5}$$

where α denotes the full set of relevant site occupations. The identification TS follows most pictorially from that of the right-hand side as $PV + U - G$ in a uniform state, but more precisely from the fact that now

$$\phi_{[x+A_i]}(\alpha) = \partial TS/\partial n_{[x+A_i]}[\alpha] \tag{3.6}$$

Our objective is to find the explicit expression $TS[n_{[x+A_i]}]$ for a given interaction pattern A. The simplest path to take is that of first expressing the $\{\phi_{[x+A_i]}\}$ in terms of the $\{n_{[y+A_j]}\}$ and then using (3.6) to determine TS to within a trivial additive constant, obtainable by choosing any special solved example. It is convenient to divide the task into two parts, as in Section 2, the first available for quite general lattices, the second requiring intense specialization. Suppose then, to start, that we focus on a subset of sites C whose mutual interaction is to be found in terms of available density information. For this purpose, we now surround C by enough empty sites that C does not interact with any other sites of the lattice. Clearly, this requires expanding C to a $\hat{C}$ covering all sites reached from C by some element in A:

$$\hat{C} = \{y \mid y - z \in C \text{ for some } z \in A_i\} \tag{3.7}$$

If this is done, then $\{v(y)\}$ for $y \in C$ will be coupled only via the total interaction ϕ_c^T in C. In other words, we have, in obvious notation,

$$n_{C,\hat{C}-C}[\alpha, 0] = n_{C,\hat{C}-C}[0, 0] \exp(-\beta\phi_C^T[\alpha]) \tag{3.8}$$

to be "solved" as

$$\beta\phi_C^T[\alpha] = \ln n_{C,\hat{C}-C}[0, 0] - \ln n_{C,\hat{C}-C}[\alpha, 0] \tag{3.9}$$

Equation (3.9) is almost our desired expression. It can now be used inductively to find $\phi_{[x+A_i]}[\alpha]$: choose $C = [x + A_i]$, and observe that

$$\phi_{[x+A_i]}^T[\alpha] = \sum_{(y,j \mid y+A_j \subset x+A_i)} \phi_{[y+A_j]}[\alpha] \tag{3.10}$$

But of course (3.4) and (3.10) require knowledge of densities other than the $n_{[x+A_i]}$. To reduce our expression to this information requires strong assumptions on the form of the lattice.

4. CONSEQUENCES OF LATTICE DECOMPOSABILITY

If interactions are restricted to a finite range p, then fixing the occupations of a set of sites C of diameter p will make it difficult for sites outside of C to influence each other. Diameter, for our purposes, can be defined as the maximum number of vertices on a nonintersecting path on C. This is the basis of the shielding approximation for substrate-bounded fluids.$^{(10)}$ For a lattice which is simply connected, only one path connects a given pair of sites. Fixing the occupation of such a set along this path literally decomposes the lattice into two or more independent parts, and in particular decouples the pair of sites in question. Under these circumstances, all densities can be obtained in terms of those on C and its relatives, allowing us to complete the evaluation of (3.9), (3.10).

To be explicit, suppose first that we have a one-dimensional integer lattice with all $A_i \subset A$ of diameter $\leqslant p+1$. If $q \geqslant p+2$, the conditional density

$$\begin{aligned} &n_{x+1\cdots x+q}(\alpha_1 \alpha_q \mid \alpha_2 \cdots \alpha_{q-1}) \\ &\quad = n_{x+1\cdots x+q}(\alpha_1 \alpha_2 \cdots \alpha_2)/n_{x+2\cdots x+q-1}(\alpha_2 \cdots \alpha_{q-1}) \end{aligned} \tag{4.1}$$

then decomposes appropriately. To see this in detail, observe that now (2.3) generalizes to

$$\begin{aligned} &n_{x+1\cdots x+q}(\alpha_1 \cdots \alpha_q) \\ &\quad = Z_{x+1\cdots x+p}(\alpha_1 \cdots \alpha_p)\, \hat{Z}_{x+q+1-p\cdots x+q}(\alpha_{q-1-p} \cdots \alpha_q) \\ &\quad\quad \times \{\exp[-\beta\phi^T_{x+1\cdots x+q}(\alpha_1 \cdots \alpha_q)]\}/Z \end{aligned} \tag{4.2}$$

where

$$\begin{aligned} Z_{x+1\cdots x+p}(v_{x+1} \cdots v_{x+p}) &= \sum_{\{v_y = 0,1;\, y \leqslant x\}} \prod_{y \leqslant x} \prod_{s=0}^{p-1} e_{y,\, y+1 \cdots y+s}(v_y, \dots, v_{y+s}) \\ \hat{Z}_{x+q+1-p\cdots x+q}&(v_{x+q-1-p} \cdots v_{x+q}) \\ &= \sum_{\{v_y = 0;\, y > x+q\}} \prod_{y > x+q} \prod_{s=0}^{p-1} e_{y-s,\dots,y}(v_{y-s} \cdots v_y) \end{aligned} \tag{4.3}$$

It follows at once that

$$\begin{aligned} &n_{x+1\cdots x+q}(\alpha_1 \alpha_q \mid \alpha_2 \cdots \alpha_{q-1}) \\ &\quad = \frac{Z_{x+1\cdots x+p}(\alpha_1 \cdots \alpha_p)}{Z_{x+1\cdots x+p}(\alpha_2 \cdots \alpha_p)} \frac{\hat{Z}_{x+q+1-p\cdots x+q}(\alpha_{q+1-p} \cdots \alpha_q)}{\hat{Z}_{x+q+1-p\cdots x+q-1}(\alpha_{q+1-p} \cdots \alpha_{q-1})} \\ &\quad\quad \times \exp[-\beta\phi^T_{x+1\cdots x+p}(\alpha_1 \cdots \alpha_p) \exp[-\beta\phi^T_{x+q+1-p\cdots x+q}(\alpha_{q+1-p} \cdots \alpha_q)] \\ &\quad = n_{x+1\cdots x+q-1}(\alpha_1 \mid \alpha_2 \cdots \alpha_{q-1})\, n_{x+2\cdots x+q}(\alpha_q \mid \alpha_2 \cdots \alpha_{q-1}) \end{aligned} \tag{4.4}$$

which in the form

$$\begin{aligned} &n_{x+1\cdots x+q}(\alpha_1 \cdots \alpha_q) \\ &\quad = \frac{n_{x+1\cdots x+q-1}(\alpha_1 \cdots \alpha_{q-1})\, n_{x+1\cdots x+q}(\alpha_2 \cdots \alpha_q)}{n_{x+2\cdots x+q-1}(\alpha_2 \cdots \alpha_{q-1})} \end{aligned} \tag{4.5}$$

allows us to conclude by induction that

$$n_{x+1\cdots x+q}(\alpha_1\cdots\alpha_q)=\prod_{s=0}^{q-p-1} n_{x+1+s\cdots x+1+p+s}(\alpha_{1+s}\cdots\alpha_{1+p+s})\times\left[\prod_{s=0}^{q-p-1} n_{x+2+s\cdots x+1+p+s}(\alpha_{2+s}\cdots\alpha_{1+p+s})\right]^{-1} \tag{4.6}$$

Suppose now that A includes *all* interaction subsets $A_i\subset A^{p+1}=[0,\dots,p]$ which contain 0. Equation (4.6) is first written more concisely as

$$n_\Lambda[\alpha]=\prod_{\substack{|\Lambda'|=p+1\\ \alpha'\subset\alpha}}^{\Lambda'\subset\Lambda} n_{\Lambda'}[\alpha']\Bigg/\prod_{\substack{|\Lambda'|=p\\ \alpha'\subset\alpha}}^{\Lambda'\subset\Lambda} n_{\Lambda'}[\alpha'] \tag{4.7}$$

where Λ' is connected and $|\Lambda|\geqslant p+2$, connected. Here, as always, $[\alpha]$ indicates the relevant occupations for the density in question. In order to determine the entropy for the interaction scheme A, we will choose as independent variables all multisite densities $n_\Lambda[\alpha]$ of diameter $d(\Lambda)\leqslant p+1$, i.e., those of the form $n_{x+A_i}[\alpha]$. Furthermore, since $\delta_{v,0}=1-\sum_{\alpha>0}\delta_{v,\alpha}$, only those with no unoccupied site, $\prod_x\alpha_x>0$, are independent. In the present case, (3.9) reads

$$\begin{aligned}\beta\phi^T_{x+A_i}[\alpha]&=\ln n_{x-p+A^{2p+d(A_1)}}[0]\\&\quad-\ln n_{x+\Lambda_i,x+[A^{2p+d(A_i)}-(p+A_i)]}[\alpha,0]\end{aligned} \tag{4.8}$$

and so, applying (4.7), we quickly find, for any Λ with $d(\Lambda)\leqslant p+1$,

$$\beta\phi^T_\Lambda[\alpha]=\sum_{\substack{|\Lambda'|=p,\,p+1\\ \alpha'\subset\alpha}}^{\Lambda\cdot\Lambda'\neq\varnothing}(-1)^{p+1+|\Lambda'|}(\ln n_{\Lambda'}[0]-\ln n_{\Lambda\cdot\Lambda',\Lambda'-\Lambda\cdot\Lambda'}[\alpha',0]) \tag{4.9}$$

To recognize the entropy from its derivatives, we must start by observing that, again from $\delta_{v,0}=1-\sum_{\alpha>0}\delta_{v,\alpha}$, if $\alpha>0$, $\alpha'>0$, then

$$\begin{aligned}&\partial n_{\Lambda',\Lambda-\Lambda'}[\alpha',0]/\partial n_{\Lambda''}[\alpha'']\\&\quad=\begin{cases}(-1)^{|\Lambda''-\Lambda'|} & \text{if}\quad \Lambda'\subset\Lambda''\subset\Lambda,\ \alpha'\subset\alpha''\\ 0 & \text{otherwise.}\end{cases}\end{aligned} \tag{4.10}$$

The notation $\alpha>0$ means that the components $\alpha_x>0$ for all x. It is simplest now to write down the entropy as the obvious extrapolation of (2.12),

$$S=\sum_\alpha\sum_{|\Lambda|=p,\,p+1}(-1)^{p+|\Lambda|}n_\Lambda[\alpha]\ln n_\Lambda[\alpha] \tag{4.11}$$

Λ running over contiguous (connected) subsets, and then verify that the full set of interactions is thereby produced. For checking (4.11), we first separate out the empty sites:

$$S = \sum_{\alpha > 0} \sum_{\substack{\Lambda' \subset \Lambda \\ |\Lambda| = p, p+1}} (-1)^{p+|\Lambda|} n_{\Lambda', \Lambda - \Lambda'}[\alpha', 0] \ln n_{\Lambda', \Lambda - \Lambda'}[\alpha', 0] \tag{4.12}$$

and then apply (4.10), using quotes for a tentative identification,

$$\text{“}\beta\phi_{\Lambda''}[\alpha'']\text{”} = \sum_{\substack{\alpha' \subset \alpha'' \\ \Lambda' \subset \Lambda'' \subset \Lambda \\ |\Lambda| = p, p+1}} (-1)^{p+|\Lambda|+|\Lambda''-\Lambda'|} (\ln n_{\Lambda', \Lambda - \Lambda'}[\alpha', 0] + 1) \tag{4.13}$$

It follows from (3.10) [the +1 in (4.13) cancels out] that

$$\text{“}\beta\phi^{T}_{\Lambda'''}[\alpha''']\text{”} = \sum_{\substack{\alpha' \subset \alpha'' \subset \alpha''' \\ \Lambda' \subset \Lambda'' \subset \Lambda \\ \phi \neq \Lambda'' \subset \Lambda'''}}^{|\Lambda| = p, p+1} (-1)^{p+|\Lambda|+|\Lambda''-\Lambda'|} \ln n_{\Lambda', \Lambda - \Lambda'}[\alpha', 0] \tag{4.14}$$

But it is clear that

$$\sum_{\substack{\Lambda' \subset \Lambda'' \subset \Lambda \\ \Lambda'' \subset \Lambda'''}}^{\Lambda'' \neq \varnothing} (-1)^{|\Lambda''-\Lambda'|} = \sum_{\Lambda' \subset \Lambda'' \subset \Lambda \cdot \Lambda'''}^{\Lambda'' \neq \varnothing} (-1)^{|\Lambda''-\Lambda'|} = \delta_{\Lambda \cdot \Lambda''', \Lambda'}(1 - \delta_{\Lambda', \varnothing}) - \delta_{\Lambda', \varnothing} \tag{4.15}$$

so that (4.14) becomes

$$\begin{aligned} \text{“}\beta\phi^{T}_{\Lambda'''}[\alpha''']\text{”} = {} & \sum_{\substack{\alpha' \subset \alpha'' \\ |\Lambda| = p, p+1 \\ \Lambda \cdot \Lambda''' \neq \varnothing}}^{\Lambda} (-1)^{p+|\Lambda|} \ln n_{\Lambda \cdot \Lambda'', \Lambda - \Lambda \cdot \Lambda'''}[\alpha', 0] \\ & - \sum_{\substack{|\Lambda| = p; p+1 \\ \Lambda \cdot \Lambda''' \neq \varnothing}} (-1)^{p+|\Lambda|} \ln n_{\Lambda}[0] \end{aligned} \tag{4.16}$$

identical with (4.9), and hence verifying (4.11).

If the lattice is not one-dimensional, but at least simply connected, e.g., a Bethe lattice, very similar considerations apply. The crucial generalization is that of (4.7), which, on similarly nibbling away from the outer vertices, now says that, if $d(\Lambda) \geqslant p+2$, Λ connected, then

$$n_{\Lambda}[\alpha] = \prod_{\substack{\alpha' \subset \alpha \\ d(\Lambda') = p+1}}^{\Lambda' \subset \Lambda} n_{\Lambda'}[\alpha'] \Big/ \prod_{\substack{\alpha' \subset \alpha \\ d(\Lambda) = p}}^{\Lambda' \subset \Lambda - \partial\Lambda} (n_{\Lambda'}[\alpha'])^{(q_{\Lambda'} - 1)} \tag{4.17}$$

running over maximal connected Λ_i'. Maximal denotes the inclusion of all vertices which do not change the diameter, $\partial\Lambda$ is the set of boundary points of Λ, and $q_{\Lambda'}$ is the number of $(p+1)$-diameter maximal connected Λ'' to which Λ' belongs Equation (4.8) generalizes in the obvious way, and if all subsets satisfying $d(\Lambda) \leqslant p+1$ occur in the interaction pattern—which need not be translation-invariant—then the extension

$$S = \sum_{\alpha} \sum_{d(\Lambda) = p,\, p+1}^{\Lambda \text{ max conn}} (-1)^{p+d(\Lambda)} (q_\Lambda - 1)\, n_\Lambda[\alpha] \ln n_\Lambda[\alpha] \tag{4.18}$$

following the path from (4.12) to (4.16), serves once more as the common generating functional in n_Λ space.

5. INTERACTION SUBPATTERNS I

The simplicity of the result (4.18) is of course due to the fact that the interaction pattern is closed in the sense that the inclusion of a subset Λ_i requires that of the subset $\bar{\Lambda}_i$ containing all paths of diameter $\leqslant p+1$ between two sites in Λ_i, as well as any subset of $\bar{\Lambda}_i$. This condition is required in order that the crucial interrelation (3.9) utilize available multisite densities alone, the insertion of empty sites implying, according to $\delta_{\nu,0} = 1 - \sum_{\alpha>0} \delta_{\nu,\alpha}$, that of sites of arbitrary occupation. In principle, any description between that of the grand potential, a functional of the ϕ_Λ alone, and entropy, a functional of the n_Λ alone, is available by Legendre transform, but the entropy picture, when available, is certainly the simplest.

We will want to apply two types of constraints to the closed interaction pattern. Indeed, the entropy formulation gracefully absorbs constraints either at the $\{\phi\}$ level or at the $\{n\}$ level. To see this most economically, we divide the interactions into two subclasses, say $\{\phi_1, \phi_2\}$, and correspondingly divide the densities into $\{n_1, n_2\}$, so that, in obvious shorthand,

$$dS\{n_1, n_2\} = \phi_1\{n_1, n_2\} \cdot dn_1 + \phi_2\{n_1, n_2\} \cdot dn_2 \tag{5.1}$$

Suppose first that the constraint set $\{n_2\} = 0$ is to be imposed. It is clear from (5.1) that

$$dS\{n_1, 0) = \phi_1\{n_1, 0\} \cdot dn_1 \tag{5.2}$$

so that

$$\bar{S}\{n_1\} = S\{n_1, 0\} \tag{5.3}$$

serves as constrained generating functional. Conversely, let us impose $\{\phi_2\}=0$, with the solution

$$n_2 = m\{n_1\} \tag{5.4}$$

Now, from (5.1),

$$dS\{n_1, m\{n_1\}\} = \phi_1\{n_1, m\{n_1\}\}\cdot dn_1 \tag{5.5}$$

showing that

$$\bar{S}\{n_1\} = S\{n, m\{n_1\}\} \tag{5.6}$$

is the constrained generating functional. In either case, it suffices to substitute the constraint into the entropy.

One extreme subpattern now is that of a single species with hard-core interaction of range p. Hence $\alpha=0$, 1 and $n_A(1)=0$ for $2\leqslant d(A)\leqslant p+1$. It follows that for $A'\subset A$,

$$\begin{aligned} n_{A',A-A'}[1,0] &= \sum_{A''\subset A-A'} (-1)^{|A''|} n_{A'+A''}[1] \\ &= 1-\sum_{x\in A} n_x(1) \qquad \text{for} \quad |A'|=0 \\ &= n_{A'}(1) \qquad\qquad\quad\ \text{for} \quad |A'|=1 \\ &= 0 \qquad\qquad\qquad\quad\ \ \text{for} \quad |A'|>1 \end{aligned} \tag{5.7}$$

Consequently, (4.18) now becomes

$$\begin{aligned} S = &-\sum n_x \ln n_x + \sum_{d(A)=p}^{A\,\text{max conn}} \left(1-\sum_{x\in A} n_x\right)\ln\left(1-\sum_{x\in A} n_x\right) \\ &-\sum_{d(A)=p+1}^{A\,\text{max conn}} \left(1-\sum_{x\in A} n_x\right)\ln\left(1-\sum_{x\in A} n_x\right) \end{aligned} \tag{5.8}$$

In this case[11–13] the internal energy $U=0$, so course $\beta\bar{F}=-S$. Note, too, that combinations of hard and soft interactions proceed similarly.

A more complex class of subpatterns is that in which only some subcollection $B\subset A=\{A_i\}$ is to contribute to the interaction pattern, i.e., interactions within $A-B$ are to vanish. The simplest transcription from the entropy viewpoint is that, whereas

$$\beta\phi_{x+A_i}[\alpha] = \partial S/\partial n_{x+A_i}[\alpha] \qquad \text{for} \quad A_i\subset B, \quad \alpha<0 \tag{5.9a}$$

the remaining conjugate interactions are to vanish,

$$0=\partial S/\partial n_{x+A_i}[\alpha] \qquad \text{for} \quad A_i \subset A-B, \quad \alpha>0 \tag{5.9b}$$

While (5.9) is very neat, and in accord with the structure of collective modes uncovered in a free energy format,[8] explicit profile equations for this system require the explicit elimination of the n_{x+A_i} for $A_i \subset A-B_i$. According to (5.6), the elimination can be done directly in the entropy expression.

The structure of the entropy functional for simply connected lattices with closed interaction pattern is, as we have seen, local to within the range of the interaction. If the closure condition is broken, as is in what are regarded as realistic patterns, the topology of the connection network no longer mirrors that of the lattice, and the resulting feedback loops may conceivably impose nonlocality on the entropy structure (see ref. 14 for this phenomenon in a free energy context). Let us investigate this possibility for some familiar interaction patterns of a simple (one-component) lattice gas. Since only $\alpha_x=1$ is nonempty, we can here use the abbreviation

$$n_A[1,\dots,1]=n_A \tag{5.10}$$

and consequently

$$n_{A-A',A'}[1,0]=\sum_{A''\subset A'}(-1)^{|A'-A''|}n_{A-A''}, \qquad \text{where} \quad A\cdot A'=\varnothing \tag{5.11}$$

The one-dimensional integer lattice serves as a suitable framework for our discussion, and for closed range p interaction, (4.18) then reduces to

$$\begin{aligned}
S&=\sum_{x,\alpha} n_{x+A^p}[\alpha]\ln n_{x+A^p}[\alpha]\\
&\quad-\sum_{x,\alpha} n_{x+A^{p+1}}[\alpha]\ln n_{x+A^{p+1}}[\alpha]\\
&=\sum_{x}\sum_{A\subset A^p}\left(\sum_{A'\subset A}(-1)^{|A-A'|}n_{A^p-A}\right)\ln\left(\sum_{A'\subset A}(-1)^{|A-A'|}n_{A^p-A}\right)\\
&\quad-\sum_{x,A\subset A^{p+1}}\left(\sum_{A'\subset A}(-1)^{|A-A'|}n_{A^{p+1}-A}\right)\ln\left(\sum_{A'\subset A}(-1)^{|A-A'|}n_{A^{p+1}-A}\right)
\end{aligned} \tag{5.12}$$

Consider now the simplest nontrivial case, $p=2$, or next-nearest-neighbor (NNN) interaction. The interactions are represented schematically, and then mapped onto a two-row triangular lattice with 3-site interaction, in Fig. 1a. The entropy is local,

$$
\begin{aligned}
S = {} & \sum n_{x,x+1} \ln n_{x,x+1} + \sum (n_x - n_{x,x+1}) \ln(n_x - n_{x,x+1}) \\
& + \sum (n_{x+1} - n_{x,x+1}) \ln(n_{x+1} - n_{x,x+1}) \\
& + \sum (1 - n_x - n_{x+1} + n_{x,x+1}) \ln(1 - n_x - n_{x+1} + n_{x,x+1}) \\
& - \sum n_{x-1,x,x+1} \ln n_{x-1,x,x+1} \\
& - \sum (n_{x-1,x} - n_{x-1,x,x+1}) \ln(n_{x-1,x} - n_{x-1,x,x+1}) \\
& - \sum (n_{x,x+1} - n_{x-1,x,x+1}) \ln(n_{x,x+1} - n_{x-1,x,x+1}) \\
& - \sum (n_{x-1,x+1} - n_{x-1,x,x+1}) \ln(n_{x-1,x+1} - n_{x-1,x,x+1}) \\
& - \sum (n_x - n_{x-1,x} - n_{x,x+1} + n_{x-1,x+1}) \\
& \times \ln(n_x - n_{x-1,x} - n_{x,x+1} + n_{x-1,x,x+1}) \\
& - \sum (n_{x-1} - n_{x-1,x} - n_{x-1,x+1} + n_{x-1,x,x+1}) \\
& \times \ln(n_{x-1} - n_{x-1,x} - n_{x-1,x+1} + n_{x-1,x,x+1}) \\
& - \sum (n_{x+1} - n_{x-1,x+1} - n_{x,x+1} + n_{x-1,x,x+1}) \\
& \times \ln(n_{x+1} - n_{x-1,x+1} - n_{x,x+1} + n_{x-1,x,x+1}) \\
& - (1 - n_{x-1} - n_x - n_{x+1} + n_{x-1,x} + n_{x-1,x+1} \\
& + n_{x,x+1} - n_{x-1,x,x+1}) \\
& \times \ln(1 - n_{x-1} - n_x - n_{x+1} + n_{x-1,x} \\
& + n_{x-1,x+1} + n_{x,x+1} - n_{x-1,x,x+1})
\end{aligned}
\tag{5.13}
$$

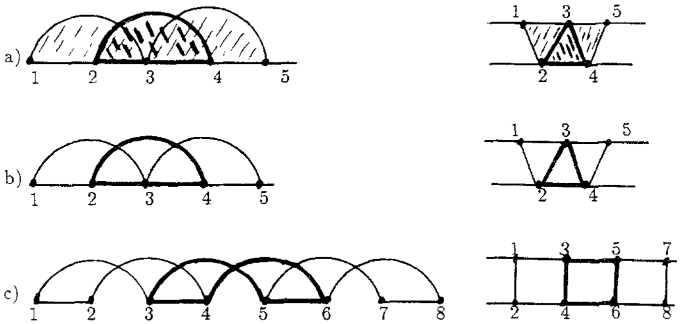

Fig. 1. Reduction of NNN pattern.

which is a function of the $\{n_x, n_{x,x+1}, n_{x-1,x+1}, n_{x-1,x,x+1}\}$, and of course so are the profile and the various direct correlations, i.e., $\partial\phi_A/\partial n_{A'}$.

To reduce (5.13) to the bond and site interaction triangular lattice (Fig. 1b), we must eliminate the 3-site interaction. Since

$$\begin{aligned}
0 &= \beta\phi_{x-1,x,x+1} \\
&= -\ln n_{x-1,x,x+1} + \ln(n_{x,x+1} - n_{x-1,x,x+1}) \\
&\quad + \ln(n_{x-1,x+1} - n_{x-1,x,x+1}) \\
&\quad + \ln(n_{x-1,x} - n_{x-1,x,x+1}) - \ln(n_{x+1} - n_{x,x+1} - n_{x-1,x+1} + n_{x-1,x,x+1}) \\
&\quad - \ln(n_x - n_{x-1,x} - n_{x,x+1} + n_{x-1,x,x+1}) \\
&\quad - \ln(n_{x-1} - n_{x-1,x} - n_{x-1,x+1} + n_{x-1,x,x+1}) \\
&\quad + \ln(1 - n_{x-1} - n_x - n_{x+1} + n_{x-1,x} + n_{x-1,x+1} + n_{x,x+1} - n_{x-1,x,x+1})
\end{aligned} \tag{5.14}$$

this involves "only" the algebraic solultion of (5.14) for $n_{x-1,x,x+1}$ and substitution back into (5.13); locality still obtains.

A further reduction to two-row square lattice (Fig. 1c) then requires the elimination of alternate nearest neighbor bonds as well, and hence that of $n_{2x,2x+1}$. And of course, the associated 3-site densities $n_{2x-1,2x,2x+1}$, $n_{2x,2x+1,2x+2}$ must also be eliminated. A glance at (5.13) shows that the equations $\beta\phi_{2x,2x+1} = 0$, $\beta\phi_{2x-1,2x,2x+1} = 0$, and $\beta\phi_{2x,2x+1,2x+2} = 0$ indeed allow one to solve for $n_{2x,2x+1}$, $n_{2x-1,2x,2x+1}$, and $n_{2x,2x+1,2x+2}$—in principle—in terms of the relevant n_{2x-1}, n_{2x}, n_{2x+1}, n_{2x+2}, $n_{2x,2x+1}$, $n_{2x-1,2x}$, $n_{2x,2x+2}$, and $n_{2x-1,2x+1}$, and so the locality of the 2-row square lattice entropy folows.

6. INTERACTION SUBPATTERNS II

A more usual technique(14) for constructing a higher dimensional lattice from a one-dimensional one is that of maintaining nearest neighbor pair interaction, but combining several sites into a "higher-spin" supersite. This procedure can be carried out in different ways, all of which must be equivalent to the formulation of Section 5, but may nonetheless have notational advantages. In particular, it might appear from the examples of Section 5 that the entropy will always be local. This is hardly the case, but its investigation does require more complex interaction patterns, for which purpose notation can be important.

For nearest neighbor interaction, (5.10) reduces to the obvious mixed species generalization of (2.12):

$$S=\sum_{x,\alpha} n_x(\alpha)\ln n_x(\alpha)-\sum_{x,\alpha,\alpha'} n_{x,x+1}(\alpha,\alpha')\ln n_{x,x+1}(\alpha,\alpha') \tag{6.1}$$

where

$$\begin{aligned}
n_x(0)&=1-\sum_{\alpha>0} n_x(\alpha)\\
n_{x,x+1}(\alpha,0)&=n_x(\alpha)-\sum_{\alpha'>0} n_{x,x+1}(\alpha,\alpha')\\
n_{x,x+1}(0,\alpha)&=n_{x+1}(\alpha)-\sum_{\alpha'>0} n_{x,x+1}(\alpha',\alpha)\\
n_{x,x+1}(0,0)&=1-\sum_{\alpha>0} n_x(\alpha)-\sum_{\alpha'>0} n_{x+1}(\alpha)+\sum_{\substack{\alpha>0\\ \alpha'>0}} n_{x,x+1}(\alpha,\alpha')
\end{aligned} \tag{6.2}$$

In conformity with our intended application, we imagine that each location x is in fact a collection of D sites (where D can also depend upon x). Thus, α now denotes a subset $\Lambda\subset 2^D=(1,\ldots,s)$, and the argument 0 refers to the empty set $\varnothing$. On differentiating (6.1) with respect to $n_x(\Lambda)$ and $n_{x,x+1}(\Lambda,\Lambda')$ for $\Lambda,\Lambda'\neq\varnothing$, and using the explicit form of (6.2), we now find the corresponding profile equations

$$\begin{aligned}
\beta\phi_x(\Lambda_1)=&\ln n_x(\Lambda_1)-\ln n_x(\varnothing)\\
&+\ln n_{x,x+1}(\alpha,\varnothing)+\ln n_{x-1,x}(\varnothing,\varnothing)\\
&-\ln n_{x,x+1}(\Lambda_1,\varnothing)-\ln n_{x-1,x}(\varnothing,\Lambda_1)
\end{aligned} \tag{6.3a}$$

$$\begin{aligned}
\beta\phi_{x,x+1}(\Lambda_1,\Lambda_2)=&-\ln n_{x,x+1}(\varnothing,\varnothing)\\
&+\ln n_{x,x+1}(\varnothing,\Lambda_2)+\ln n_{x,x+1}(\Lambda_1,\varnothing)\\
&-\ln n_{x,x+1}(\Lambda_1,\Lambda_2)
\end{aligned} \tag{6.3b}$$

In (6.3), $\phi_x(\Lambda_1)$ represents a full $|\Lambda_1|$-site "self"-interaction at location x, and $\phi_{x,x+1}(\Lambda_1,\Lambda_2)$ a $|\Lambda_1|\cdot|\Lambda_2|$-site "mutual" interaction. If we have in mind a lattice of vertices interacting across bonds, only singlet and pair interactions are nonvanishing, and any interaction is a superposition of these. In other words, we will have

$$\phi_x(\Lambda)=\sum_{\lambda\in\Lambda}\phi_x(\lambda)+\sum_{\lambda<\lambda'\in\Lambda}\phi_x(\lambda,\lambda') \tag{6.4a}$$

$$\phi_{x,x+1}(\Lambda,\Lambda')=\sum_{\substack{\lambda\in\Lambda\\ \lambda'\in\Lambda'}}\phi_{x,x+1}(\lambda,\lambda') \tag{6.4b}$$

with at most the set $\phi_1 = \{\phi_x(\lambda), \phi_x(\lambda, \lambda'), \phi_{x,x+1}(\lambda, \lambda')\}$ as independent interactions. Thus, all but the corresponding set $n_1 = \{n_x(\lambda), n_x(\lambda, \lambda'), n_{x,x+1}(\lambda, \lambda')\}$ are to be eliminated from the entropy.

Since combinations of $\{\phi\}$ are to be constrained to vanish, (5.6) would be applicable only if we were willing to introduce the associated conjugate densities. But we want to retain the set n_1 as independent variables, and so it is not correct to merely eliminate the n_2 in the entropy. However, from the fact that the microscopic n_1 occurs as the coefficient set of ϕ_1 in the energy, we know that there exists an entropy function on the space n_1, with ϕ_1 as conjugates. Thus, if the constraints allow us to write

$$n_1 = m\{n_1\} \tag{6.5}$$

as in (5.4), the resulting profile

$$\beta\phi_1 = \frac{\partial S\{n_1, n_2\}}{\partial n_1}\bigg|_{n_2 = m\{n_1\}} \tag{6.6}$$

can be "integrated back" to produce

$$\beta\phi_1 = \frac{\partial \bar{S}\{n_1\}}{\partial n_1} \tag{6.7}$$

by simply turning up all densities n_1 from 0:

$$\begin{aligned}\bar{S}\{n_1\} &= \int_0^1 \frac{\partial}{\partial\lambda}\bar{S}\{\lambda n_1\}\,d\lambda\\ &= \int_0^1 n_1\cdot\frac{\partial \bar{S}\{\lambda n_1\}}{\partial \lambda n_1}\,d\lambda\\ &= \int_0^1 n_1\cdot\frac{\partial}{\partial n_1} S\{\lambda n_1, n_2\}\bigg|_{n_2 = m\{\lambda n_1\}}\frac{d\lambda}{\lambda}\end{aligned} \tag{6.8}$$

The only problem is that of finding $n_2 = m\{n_1\}$ explicitly, and this then determines the structure of $\bar{S}$.

Let us start our in-principle elimination with the $(x, x+1)$ interaction terms. According to (6.3b) and (6.4b), which are valid for all Λ_1, Λ_2, there are $(2^D - 1)^2$ independent relations

$$\frac{n_{x,x+1}(\Lambda_1, \Lambda_2)\, n_{x,x+1}(\varnothing, \varnothing)}{n_{x,x+1}(\Lambda_1, \varnothing)\, n_{x,x+1}(\varnothing, \Lambda_2)} = \prod_{\substack{\lambda_1\in\Lambda_1\\ \lambda_2\in\Lambda_2}} \frac{n_{x,x+1}(\lambda_1, \lambda_2)\, n_{x,x+1}(\varnothing, \varnothing)}{n_{x,x+1}(\lambda_1, \varnothing)\, n_{x,x+1}(\varnothing, \lambda_2)} \tag{6.9}$$

Appending the pair equations of (6.20) in the form of $2\cdot 2^D-1$ independent relations

$$\begin{aligned}&\sum_{\Lambda_1} n_{x,x+1}(\Lambda_1,\Lambda_2)=n_{x+1}(\Lambda_2)\\ &\sum_{\Lambda_2} n_{x,x+1}(\Lambda_1,\Lambda_2)=n_x(\Lambda_1)\end{aligned}\tag{6.10}$$

we can solve the 2^{2D} quantities $n_{x,x+1}(\Lambda_1,\Lambda_2)$ in terms of the two-site densities $n_{x,x+1}(\lambda_1,\lambda_2)$. The solution is complicated, but this is a *local* expression,

$$n_{x,x+1}(\Lambda_1,\Lambda_2)=f_{\Lambda_1,\Lambda_2}\{n_{x,x+1}(\lambda,\lambda');n_x(\Lambda),n_{x+1}(\Lambda)\}\tag{6.11}$$

Elimination of any further bonds, $\phi_{x,x+1}(\lambda,\lambda')=0$ for some subset $(\lambda,\lambda')\in\Lambda_2\subset 2^D\otimes 2^D$, would not alter the result.

We proceed next to the (x) interaction terms. Combining (6.3a) and (6.4a), we have the 2^D-1

$$\begin{aligned}\frac{n_x(\Lambda)}{n_x(\varnothing)}&=\frac{n_{x,x+1}(\Lambda,\varnothing)\,n_{x-1,x}(\varnothing,\Lambda)}{n_{x,x+1}(\varnothing,\varnothing)\,n_{x-1,x}(\varnothing,\varnothing)}\\ &\quad\times\prod_{\Lambda}\frac{n_x(\lambda)}{n_x(\varnothing)}\,\frac{n_{x,x+1}(\varnothing,\varnothing)\,n_{x-1,x}(\varnothing,\varnothing)}{n_{x,x+1}(\lambda,\varnothing)\,n_{x-1,x}(\varnothing,\lambda)}\\ &\quad\times\prod_{\lambda<\lambda'\in\Lambda}\frac{n_x(\lambda\lambda')}{n_x(\varnothing)}\,\frac{n_{x,x+1}(\varnothing,\varnothing)\,n_{x-1,x}(\varnothing,\varnothing)}{n_{x,x+1}(\lambda\lambda',\varnothing)\,n_{x-1,x}(\varnothing,\lambda\lambda')}\end{aligned}\tag{6.12}$$

to be coupled of course with the single

$$\sum_{\Lambda} n_x(\Lambda)=1\tag{6.13}$$

Equations (6.12) and (6.12) can then be solved in the form

$$n_x(\Lambda)=g_\Lambda\{n_x(\lambda)\,n_x(\lambda\lambda');n_{x,x+1}(\Lambda',\Lambda''),n_{x-1,x}(\Lambda',\Lambda'')\}\tag{6.14}$$

But consider now the joint solvability of (6.11) and (6.14). If $D=2$, all $n_x(\Lambda)$ refer to vertices and bonds; since these are indeed our independent variables, the set (6.14) is irrelevant, and (6.11) yields, via (6.8), a local entropy, as in Fig. 1b. If $D>2$, substitution of (6.11) into (6.14) allocates both n_{x+1} and n_{x-1} to n_x, so that a difference equation results, with of course a nonlocal solution. Locality is therefore broken at this level.

7. DISCUSSION

In summary, we have seen that the entropy functional serves as an effective tool in the analysis of lattice gases on simply connected lattices, as well as on non-simply-connected ones which are closely related. The hallmark of the entropy in these cases is that it is expressible in terms of an entropy density which is local in that it covers only a finite range of sites. This expression may be complicated, but it is strictly algebraic. Locality is convenient when it exists, but does imply a rather sparse phenomenology, as opposed to that of more common non-simply-connected lattices, in which feedback loops exert a crucial influence on the structural thermodynamics.

While the development reported here does not bear directly upon problems encountered in such realistic lattices, it does suggest approximations, largely well known in the literature. Simplest is a direct transcription of (4.18), totally in the spirit of Bethe's original Ising model approximation,$^{(15)}$ in which a lattice is matched locally to an appropriate Bethe lattice. In other words, we now reproduce (4.18), but choose the sets Λ of the lattice in question. For example, for a nearest neighbor interacting square lattice, (4.18) would transcribe to the approximation

$$S = 3 \sum_{x}^{\alpha} n_x(\alpha) \ln n_x(\alpha) - \frac{1}{2} \sum_{\langle x, y\rangle}^{\alpha, \alpha'} n_{xy}(\alpha, \alpha') \ln n_{xy}(\alpha, \alpha') \tag{7.1}$$

while expressions of the Kikuchi type result$^{(16)}$ from choosing a nominal range $p > 1$ and eliminating the unwanted (two- and) multisite interactions. It is also to be noted that, in the form

$$\begin{aligned} S = & -\sum_{x}^{\alpha} n_x(\alpha) \ln n_x(\alpha) \\ & -\frac{1}{2} \sum_{\langle x, y\rangle}^{\alpha, \alpha'} n_x(\alpha)\, n_y(\alpha')\, g_{xy}(\alpha, \alpha') \ln g_{xy}(\alpha, \alpha') \end{aligned} \tag{7.2}$$

where

$$g_{xy}(\alpha, \alpha') = n_{xy}(\alpha, \alpha')/n_x(\alpha)\, n_y(\alpha)$$

(7.1) and its descendants have suggestive extensions to continuum fluids (see, e.g., ref. 5).

The approximations typified by (7.1) are of course tentative, since they address the question of interaction loops in at most a primitive local fashion. A next stage is clearly the analysis of true multiloop networks. Some first steps in this direction have been taken$^{(8,17)}$ in the context of free energy density functionals, and preliminary evidence indicates that similar techniques will be effective in the entropy format, with similar qualitative consequences. This work will form the subject of a future publication.

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