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Renormalized Equilibria of a Schlögl Model Lattice Gas

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A lattice gas model for Schlögl's second chemical reaction is described and analyzed. Because the lattice gas does not obey a semi-detailed-balance condition, the equilibria are non-Gibbsian. In spite of this, a self-consistent set of equations for the exact homogeneous equilibria are described, using a generalized cluster-expansion scheme. These equations are solved in the two-particle BBGKY approximation, and the results are compared to numerical experiment. It is found that this approximation describes the equilibria far more accurately than the Boltzmann approximation. It is also found, however, that it can give rise to spurious solutions to the equilibrium equations.

KEY WORDS: Lattice gases; Schlögl model; reaction–diffusion equations; correlations; renormalization.

1. INTRODUCTION

Lattice gas automata have been widely used as models of nonequilibrium statistical systems since it was shown in 1986 that they could be used to model Navier–Stokes fluids.(1) Lattice gases consist of particles moving about and colliding on a lattice in such a way that their macroscopic behavior satisfies hydrodynamic partial differential equations. Like the Ising model, they are simple discrete systems which are well suited both to computer implementation and to elegant analytic techniques; unlike the Ising model, however, they can be used to study phenomena far from equilibrium.

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All of the usual tools of kinetic theory can be used for the analysis of lattice gases. Lattice gases whose collisions obey a condition known as *semi-detailed balance* (SDB) can be shown(2) to have a Gibbsian (product) equilibrium distribution. As the lattice spacing goes to zero, expansion about this equilibrium yields the hydrodynamic equations satisfied by the system; this is a discrete version of the usual Chapman–Enskog procedure.(3)

To date, most analyses of lattice gases have been done using the Boltzmann molecular chaos approximation. The kinetic ring approximation has been used to improve this analysis for SDB lattice gases.(4, 5) We have recently used cluster expansion methods to develop an exact description of SDB lattice gases.(6) In such lattice gases, the exact equations of motion include the effects of correlations which renormalize the lattice-gas transport coefficients. In this paper, we extend these methods to describe a particular non-semi-detailed-balance (NSDB) lattice gas. Related work on exact equations for NSDB lattice gases has recently been done by Bussemaker *et al.*(7)

It has been known for decades that chemically reacting systems far from equilibrium can exhibit fascinating phenomenology, including pattern formation(8) and symmetry breaking.(9) Such complicated phenomenology can arise from very simple chemical reactions, and idealized model reactions have been developed to illustrate these phenomena. For example, the simple model reaction proposed by Schlögl in 1972,(10)

$$2X + A \rightleftharpoons 3X$$

where X is the reactant species and A is a background species of fixed density, can possess two stable equilibrium concentrations of the species X. In that case, the system can excibit spontaneous pattern formation as it breaks into domains of each concentration. Because kinetic fluctuations are important in the dynamics of such systems, it is natural that lattice gas automata be applied to their study, and this has been done with great success over the past 5 years.(11–14)

Reaction–diffusion lattice-gas models typically allow reactant particles to diffuse for some number of timesteps k between reactions. The diffusion steps obey SDB, while the reaction steps usually do not. It is remarkable that while natural chemically reacting systems seem to be able to generate spontaneously patterns with microscopically reversible laws of motion, all lattice-gas models of such systems to date have found it necessary to violate SDB. There is no doubt that it is easier to generate nontrivial structure in NSDB lattice gases. Violations of SDB can lead to the spontaneous generation of patterns and correlations, and hence non-Gibbsian equilibria.(15) In such situations, however, the Boltzmann molecular chaos assumption is particularly suspect, and the theoretical analysis of the system becomes difficult or impossible. Only in the limit of large k has analytic progress been made; at low k the Boltzmann theory is known to be seriously in error.(14)

In this paper, we describe a simple lattice-gas model for Schlögl's second chemical reaction. Because the reaction steps of this lattice gas do not obey SDB, the equilibria are non-Gibbsian. We derive a self-consistent set of equations for the exact homogeneous equilibria using cluster-expansion methods. We solve these equations in the two-particle BBGKY approximation; in this approximation these equations are similar to those arising from the method recently developed by Bussemaker *et al.*(7) Comparing our results to numerical experiment, we find that this approximation describes the equilibria far more accurately than the Boltzmann approximation. We also find that spurious solutions to the equilibrium equations appear; these solutions are unstable, however, and can be removed by including effects due to three-particle correlations.

2. DESCRIPTION OF THE SCHLÖGL MODEL LATTICE GAS

2.1. Schlögl's Second Chemical Reaction

Our starting point is the following generalization of Schlögl's second chemical reaction(10):

$$2X+A \overset{k_2^\pm}{\rightleftharpoons} 3X$$

$$X+B \overset{k_1^\pm}{\rightleftharpoons} 2X$$

$$C \overset{k_0^\pm}{\rightleftharpoons} X$$

where X is the reactant species, A, B, and C are background species of fixed density, and the $k_j^\pm$ are the forward ($+$) and reverse ($-$) rates for the reaction with j reactant molecules on the left. Denoting the density of species Y by N_Y, we obtain the stoichiometric equation for this reaction

$$\begin{aligned}\frac{dN_X}{dt} &= k_2^+ N_A N_X^2 - k_2^- N_X^3 + k_1^+ N_B N_X - k_1^- N_X^2 + k_0^+ N_C - k_0^- N_X \\ &= \kappa_0 - \kappa_1 N_X + \kappa_2 N_X^2 - \kappa_3 N_X^3\end{aligned}$$

where we have defined the stochiometric coefficients

$$\kappa_0 = k_0^+ N_C$$

$$\kappa_1 = k_0^- - k_1^+ N_B$$

$$\kappa_2 = k_2^+ N_A - k_1^-$$
$$\kappa_3 = k_2^-$$

Finally, to model the stochastic motion of the reactant X between reactions, we add a diffusive term to obtain the reaction–diffusion equation,

$$\frac{\partial N_X}{\partial t} = D\nabla^2 N_X + \kappa_0 - \kappa_1 N_X + \kappa_2 N_X^2 - \kappa_3 N_X^3 \tag{1}$$

Note that Eq. (1) allows for up to three spatially uniform equilibria, corresponding to the roots of the cubic. When there are three roots and $\kappa_3 > 0$, the low-density and high-density roots, denoted by N_X^- and N_X^+, respectively, are easily seen to be stable to small fluctuations, while the middle root, N_X^0, is unstable. The evolution of Eq. (1) from generic initial conditions thus yields domains of constant density N_X^- and N_X^+, separated by sharp gradients whose widths are governed by the diffusive term in Eq. (1). (See Fig. 2).

2.2. Lattice Gas Model

We model the kinetics of the generalized Schlögl reaction by a lattice gas automaton. This consists of a regular lattice $\mathscr{L}$ with n lattice vectors at each site; we denote the lattice vectors by $\mathbf{c}_i$, where $i \in \{1,..., n\}$. The state of the system at time t is then completely specified by the quantities $n^i(\mathbf{x}, t) \in \{0, 1\}$, where $i \in \{1,..., n\}$ and $\mathbf{x} \in \mathscr{L}$. We have $n^i(\mathbf{x}, t) = 1$ if there is a particle with velocity $\mathbf{c}_i$ at position $\mathbf{x}$ at time t, and $n^i(\mathbf{x}, t) = 0$ otherwise.

The evolution of the lattice gas for one timestep takes place in two substeps. In the *propagation* substep, the particles simply move along their corresponding lattice vectors,

$$n^i(\mathbf{x} + \mathbf{c}_i, t + \Delta t) \leftarrow n^i(\mathbf{x}, t)$$

This is followed by the *collision* substep, in which the newly arrived particles change their state. The collisions are chosen to model the reactive and diffusive dynamics of species X. Their effect is captured in the collision operator ω^i, which gives the increase in the number of particles moving along direction i due to collisions. In terms of this collision operator, the full equation of evolution of the lattice gas may be written

$$n^i(\mathbf{x} + \mathbf{c}_i, t + \Delta t) = n^i(\mathbf{x}, t) + \omega^i(n^*(\mathbf{x}, t)) \tag{2}$$

where the dependence of ω^i on $n^*(\mathbf{x}, t)$ indicates that each component of the collision operator can depend on all the components n^i at the local site.

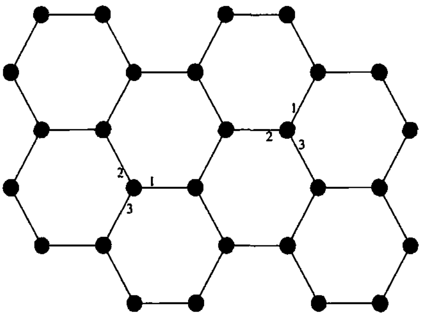

Fig. 1. The hexagonal lattice, with the checkerboard coloring and the enumeration of the three bits at each site.

In this work, we restrict our attention to the Schlögl model in two dimensions. We use a hexagonal (honeycomb) lattice because it has only three bits of state at each site ($n = 3$), thereby greatly simplifying the analysis; at the same time, it is sufficiently symmetric to ensure the isotropic form of the density balance equation, Eq. (1). This lattice is illustrated in Fig. 1. Note that such a lattice can be colored like a checkerboard; note also that the correspondence between the bits and the lattice vectors is rotated by $\pi/3$ for the differently colored sites.

2.3. The Collision Operator

Following previous work on the modeling of chemical reactions by lattice gases,(11–14) we define two types of interparticle collisions. The chemical reactions take place in *reactive collisions* in which particle number does not need to be conserved. Between reactions, the particles execute *diffusive collisions* in which particle number is conserved. Both types of collision processes are *stochastic*; that is, the outgoing state of a collision depends on one or more random bits that must be generated at each site at each timestep, as well as on the incoming state. Reactive collisions occur once every k timesteps; the remainder of the collisions are diffusive.

We need to define carefully the dynamics of the reactive and diffusive collisions, and thence the form of the respective collision operators, ω_R and ω_D. Because there are three bits per site, each site can be in one of eight states. We enumerate these states by specifying the three bit values, i.e., 000, 001,..., 111. The collision process can then be completely determined by specifying the outgoing state corresponding to each incoming state. Since the lattice gas is stochastic, this specification may depend on one or more random bits.

Let $a(s \to s')$ be 1 if a collision takes state s to state s', and 0 otherwise. Clearly, for each incoming state s, $a(s \to s')$ can equal 1 for exactly one s', and must equal 0 for all others. In terms of this *transition matrix*, the collision operator can be written

$$\omega^i(n^*) = \sum_{s,\,s'} a(s \to s')(s'^i - s^i) \prod_{j=1}^{n} \delta_{n^j,\,s^j} \tag{3}$$

where $\delta_{ij} \equiv 1 - i - j + 2ij$ is the Kronecker delta of the two bits i and j. Together, Eqs. (2) and (3) are a complete specification of the dynamics of the lattice gas in terms of the transition matrix $a(s \to s')$, which will be defined through its ensemble average in the following section. Note that $a(s \to s')$ may depend on random bits.

2.4. The Boltzmann Equation

We now suppose that we have prepared an ensemble of lattice-gas simulations, on grids of the same size, with initial conditions that are sampled from some distribution. We may take averages across this ensemble. Denoting $N^i(\mathbf{x}, t) \equiv \langle n^i(\mathbf{x}, t)\rangle$, the ensemble average of Eq. (2) is

$$N^i(\mathbf{x} + \mathbf{c}_i,\, t + \Delta t) = N^i(\mathbf{x}, t) + \langle \omega^i(n^*(\mathbf{x}, t))\rangle$$

We are hampered from taking the ensemble average of the collision operator, Eq. (3), by the fact that it is generally a nonlinear function of the $n^i(\mathbf{x}, t)$, and the average of the product is not equal to the product of the averages unless the quantities involved are uncorrelated. The simplest approximation to make is the *Boltzmann molecular chaos* assumption that the particles entering a collision are uncorrelated; in this case, the ensemble average of ω^i yields the *Boltzmann collision operator*,

$$\Omega^i(N^*) = \sum_{s,\,s'} A(s \to s')(s'^i - s^i) \prod_{j=1}^{n} (N^j)^{s^j}(1 - N^j)^{1 - s^j}$$

where $A(s \to s') \equiv \langle a(s \to s')\rangle \in [0, 1]$ is the *ensemble-averaged transition matrix*. The evolution equation in this approximation is the *Boltzmann equation*,

$$N^i(\mathbf{x} + \mathbf{c}_i,\, t + \Delta t) = N^i(\mathbf{x}, t) + \Omega^i(N^*(\mathbf{x}, t)) \tag{4}$$

Note that there are three one-particles states (001, 010, 100), three two-particle states (100, 101, 011), one zero-particle state (000), and one three-particle state (111). Let $|s|$ denote the number of particles in state s, so, for example, $|101| = 2$. For the lattice gas considered here, the mean outcome of both diffusive and reactive collisions depends only on the total

Table I. Ensemble-Averaged Transition Matrix

	$A(s \rightarrow s')$			
$\lvert s'\rvert$	$\lvert s\rvert = 0$	$\lvert s\rvert = 1$	$\lvert s\rvert = 2$	$\lvert s\rvert = 3$
0	P_0^0	$P_1^0/3$	$P_2^0/3$	P_3^0
1	P_0^1	$P_1^1 \vert 3$	$P_2^1/3$	P_3^1
2	P_0^2	$P_1^2/3$	$P_2^2/3$	P_3^2
3	P_0^3	$P_1^3/3$	$P_2^3/3$	P_3^3

number of incoming particles, and is always uniformly distributed over the states of the outgoing particle number. Mathematically, this means that the $A(s \rightarrow s')$ can depend only on $|s|$ and $|s'|$, and can thus be tabulated as in Table I, where P_j^i is the probability that a collision will take a state with j particles into a state with i particles.

For the diffusive collisions, we must have

$$P_j^i = \delta_j^i$$

where δ_j^i is the Kronecker delta. Thus, a diffusive collision is nothing more than a random permutation of the three incoming bits. Calculation of the corresponding Boltzmann collision operator is straightfoward, yielding

$$\Omega_D^i(N^*) = -\tfrac{2}{3}N^i + \tfrac{1}{3}N^{i+1} + \tfrac{1}{3}N^{i+2} \tag{5}$$

where the superscript of N is understood to be taken modulo 3.

To simplify the algebra for the reaction step, we henceforth restrict our attention to the following specific values for the particle transition probabilities:

$$P_j^i = \begin{pmatrix} \tau & 1-\tau & 0 & 0 \\ \tau & 1-\tau & 0 & 0 \\ 0 & 0 & 1-\sigma & \sigma \\ 0 & 0 & 1-\sigma & \sigma \end{pmatrix}_j^i \tag{6}$$

for $i, j \in \{0, 1, 2, 3\}$, and we choose $\sigma = \tau = 2/3$. Calculation of the corresponding Boltzmann collision operator yields

$$\Omega_R^i(N^*) = \tfrac{1}{9} - N^i + \tfrac{7}{9}(N^0N^1 + N^0N^2 + N^1N^2) - \tfrac{14}{9}N^0N^1N^2 \tag{7}$$

A complete Boltzmann description of the system is given by Eq. (4), using Eq. (7) once every k timesteps and Eq. (5) otherwise.

2.5. Boltzmann Equilibria

Note that the Boltzmann equation, Eq. (4), admits homogeneous, isotropic equilibria, $N^0 = N^1 = N^2 = f$, where f obeys $\Omega(f) = 0$. Note also that the diffusive collision operator, Eq. (5), satisfies $\Omega_{\mathrm{D}}(f) = 0$ identically. We thus find homogeneous, isotropic equilibria by demanding that the reaction step do likewise,

$$\begin{aligned} 0 &= \Omega^i_{\mathrm{R}}(f) \\ &= \tfrac{1}{9} - f + \tfrac{7}{3} f^2 - \tfrac{14}{9} f^3 \\ &= \tfrac{1}{9}(1 - 2f)(7f^2 - 7f + 1) \end{aligned} \tag{8}$$

This has roots at $f = \frac{1}{2}$ and $f = \frac{1}{2}(1 \pm \sqrt{\frac{3}{7}})$. Figure 2 displays the evolution of the lattice gas model for the parameters given above, with the initial condition $f = \frac{1}{2}$ everywhere.

3. EXACT EQUATIONS OF MOTION

The exact microscopic equations of motion for any lattice gas are easily described in terms of the multiparticle means N^α (following the notation of our previous paper,(6) we denote by α an arbitrary subset of the bits (particles) in the system, and by N^α the ensemble average of the product of those bits). In terms of these means, the exact time-development equation is

$$N^\alpha(t + \Delta t) = \mathscr{A}^\alpha_\beta K^\beta_\gamma N^\gamma(t) \tag{9}$$

where we use the convention of summing over any index which appears twice on one side of an equation and not at all on the other side. In this equation, $\mathscr{A}^\alpha_\beta$ is an advection operator, described by a permutation matrix on the set of bit sets α, which carries each bit of the system forward along its associated velocity vector. The operator K^β_γ describes the collision process. It can be factorized into contributions from each lattice site,

$$K^\beta_\gamma = \prod_{\mathbf{x} \in L_\beta} V^{\beta_{\mathbf{x}}}_{\gamma_{\mathbf{x}}} \tag{10}$$

where L_β is the set of vertices associated with bits in β and $\beta_{\mathbf{x}}$ is the set of bits in β at the lattice site $\mathbf{x}$. The mean vertex coefficients V^β_γ are related to the state transition probabilities $A(s \to s')$ through

$$V^\mu_\nu = \sum_{s' \supseteq \mu} \sum_{s \subseteq \nu} (-1)^{|\nu| - |s|} A(s \to s') \tag{11}$$

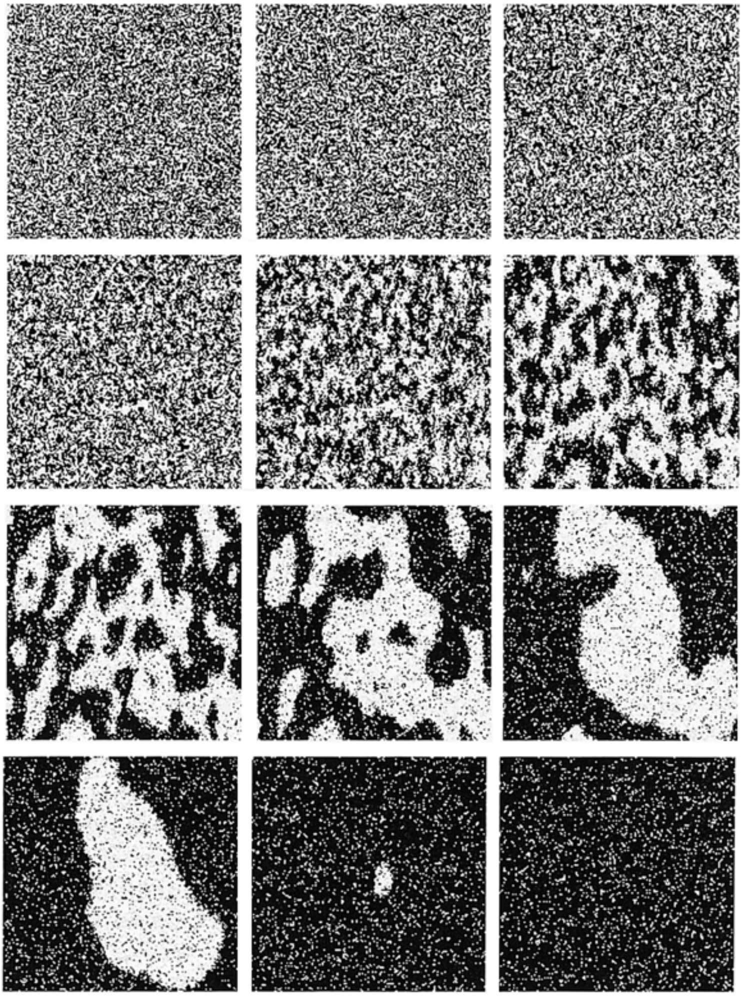

Fig. 2. Evolution of the Schlögl model on a 512×512 grid, from an initial density of 0.5, yields domains of both low and high equilibrium densities, separated by sharp gradients whose width is governed by the diffusive term in the rate equation. Beginning at the upper left, the frames show the evolution at times 1, 3, 10, 30, 100, 300, 1000, 3000, 10000, 30000, 100000, and 300000.

The exact time-development Eq. (9) can be rewritten in terms of connected correlation functions (CCFs) using the standard cluster expansion. The means are expressed in terms of the CCFs through

$$N^{\alpha}=f^{\alpha}(\Gamma^{*})=\sum_{\zeta\in\pi(\alpha)}\Gamma^{\zeta_1}\Gamma^{\zeta_2}\dots\Gamma^{\zeta_q} \tag{12}$$

where $\pi(\alpha)$ is the set of all partitions of α into disjoint subsets, $\zeta_1,\dots,\zeta_q$. For example, we have $N^a=\Gamma^a$, $N^{ab}=\Gamma^{ab}+\Gamma^a\Gamma^b$. This relation can be inverted to express the CCFs in terms of the means, $\Gamma^{\alpha}=g^{\alpha}(N^{*})$.

We can now rewrite (9) as

$$\Gamma^{\alpha}(t+\Delta t)=\mathscr{A}^{\alpha}_{\beta}g^{\beta}(K^{*}_{\gamma}f^{\gamma}(\Gamma^{*})) \tag{13}$$

This exact equation has been used as a starting point in previous works.(6, 7) It has been applied to SDB lattice gases,(6) where the equilibria have no correlations and the expression on the right-hand side can be linearized in terms of the CCFs Γ^{α} with $|\alpha|\geqslant 2$. Equation (13) has also been applied to NSDB lattice gases by Bussemaker *et al.*,(7) who neglected CCFs Γ^{α} with $|\alpha|\geqslant 3$, and thereby derived the two-particle BBGKY equations for NSDB lattice gases.

It has been shown(6) that the linearized form of (13) can naturally be expressed in terms of a sum over diagrams, each of which is weighted by a product of factors associated with each vertex at each timestep. There is a finite number of possible vertices, so that a complete formulation of the dynamics of a SDB lattice gas can be given in terms of a set of "Feynman rules" for allowed diagrams and vertex weights.

An analogous diagrammatic description can be given for the exact nonlinear equations (13). The nonlinear diagrammatic expansion can be derived by proving a general factorization theorem for the time development of CCFs including particles at different vertices. The essential ingredient in proving this factorization is the observation that if a set of variables α depends stochastically on another set of variables β, so that the CCF Γ^{α} is given by

$$\Gamma^{\alpha}=\mathscr{K}^{\alpha}_{\xi}\prod_{\xi_i\in\xi}\Gamma^{\xi_i} \tag{14}$$

where $\xi=\{\xi_1,\dots,\xi_m\}$ is a set of (not necessarily disjoint) subsets of β, then the CCF of α joined with a set of variables γ which are not dependent on β is given by

$$\Gamma^{\alpha\cup\gamma}=\mathscr{K}^{\alpha}_{\xi}\prod_{\zeta\in\pi_m(\gamma)}\prod_{i}\Gamma^{\xi_i\cup\zeta_i} \tag{15}$$

where $\zeta = \{\zeta_1, ..., \zeta_m\}$ is summed over all partitions of γ into precisely m distinct sets. This result essentially states that once we know an expression for the outgoing CCFs at a particular vertex of a lattice gas in terms of the incoming CCFs, we can calculate the CCF of a set of particles at multiple lattice sites by applying (15) at each vertex separately. The general expression for an outgoing CCF at one vertex can be written by expanding

$$\Phi^\beta(\Gamma^*) \equiv g^\beta(K^*_\gamma f^\gamma(\Gamma^*))$$

as an explicit polynomial in the CCFs; i.e.,

$$\Phi^\beta(\Gamma^*) = \mathscr{K}^\beta_\xi \prod_{\xi_i \in \xi} \Gamma^{\xi_i} \tag{16}$$

where $\xi = \{\xi_1, ..., \xi_k\}$ is summed over all sets of CCFs with nonzero coefficients. Each time Eq. (15) is applied at a particular vertex, the correlated quantities at the other vertices are carried along and divided up in all possible ways among the incoming CCFs. A simple example of this result is that when a is an outgoing particle from a vertex with incoming particles b_1, b_2, b_3 and c is an outgoing particle from a different vertex at the same timestep, we have (for a general lattice gas)

$$\Gamma^a = F(\{\Gamma^{b_i}\}, \{\Gamma^{b_i b_j}: i \neq j\}, \Gamma^{b_1 b_2 b_3})$$

and

$$\Gamma^{ac} = \sum_i \frac{\partial F}{\partial \Gamma^{b_i}} \Gamma^{b_i c} + \frac{1}{2} \sum_{i \neq j} \frac{\partial F}{\partial \Gamma^{b_i b_j}} \Gamma^{b_i b_j c} + \frac{\partial F}{\partial \Gamma^{b_1 b_2 b_3}} \Gamma^{b_1 b_2 b_3 c} \tag{17}$$

The proof of (15) follows fairly easily by induction. The details of this proof and the general factorization theorem in the nonlinear case will be given in a separate publication.(16) The result (17), which follows directly from (12), will be sufficient for our purposes in this paper.

We conclude this section with a derivation of a simple form of the factorization theorem which we will need in the sequel. Assume that at one vertex we have an outgoing particle A and incoming particles a, b, c, and that at another vertex we have an outgoing particle $\bar{A}$ and incoming particles $\bar{a}$, $\bar{b}$, $\bar{c}$. We wish to find the dependence of the outgoing CCF $\Gamma^{A\bar{A}}$ on the incoming correlations, neglecting all CCFs between three or more particles. It will suffice for us to know the dependence of the outgoing one-particle means on the incoming one- and two-particle CCFs at each vertex. Thus, we can write

$$\Gamma^A = F(\Gamma^a, \Gamma^b, \Gamma^c, \Gamma^{ab}, \Gamma^{bc}, \Gamma^{ac}) + \mathcal{O}(C_3)$$

and

$$\Gamma^{\bar{A}} = F(\Gamma^{\bar{a}}, \Gamma^{\bar{b}}, \Gamma^{\bar{c}}, \Gamma^{\bar{a}\bar{b}}, \Gamma^{\bar{b}\bar{c}}, \Gamma^{\bar{a}\bar{c}}) + \mathcal{O}(C_3)$$

where by $\mathcal{O}(C_i)$ we denote quantities dependent on CCFs of i or more variables. Applying (17) once, we have

$$\Gamma^{A\bar{A}} = \frac{\partial F}{\partial \Gamma^{a}} \Gamma^{a\bar{A}} + \frac{\partial F}{\partial \Gamma^{b}} \Gamma^{b\bar{A}} + \frac{\partial F}{\partial \Gamma^{c}} \Gamma^{c\bar{A}} + \mathcal{O}(C_3)$$

Applying (17) again, we have

$$\Gamma^{A\bar{A}} = \frac{\partial F}{\partial \Gamma^{\alpha}} \frac{\partial \bar{F}}{\partial \Gamma^{\bar{\alpha}}} \Gamma^{\alpha\bar{\alpha}} + \mathcal{O}(C_3) \tag{18}$$

where α, $\bar{\alpha}$ are summed over $\{a, b, c\}$ and $\{\bar{a}, \bar{b}, \bar{c}\}$, respectively, and where $\bar{F}$ is shorthand for F evaluated at the barred variables. Note that this equation has a diagrammatic interpretation because the coefficient associated with the propagation of a pair of correlated quantities at different vertices factorizes into contributions from each vertex separately. We will use this simple factorization result in the next section to compute the exact two-particle BBGKY equations for the equilibria of the Schlögl model lattice gas.

4. EQUILIBRIA OF SCHLÖGL MODEL

We will now consider the exact equations of motion for the Schlögl model lattice gas defined in Section 2. By neglecting correlations between more than two-particles, we arrive at the two particle BBGKY equations, which we then solve using the diagrammatic method. The two-particle BBGKY equations were described for a general NSDB lattice gas by Bussemaker *et al.*,(7) who gave an iterative method for finding solutions to these equations. Although the equations we are solving here are essentially equivalent to those which would be found by applying the methods of these authors to the Schlögl model lattice gas, our diagrammatic method of solution of these equations is rather different. Using the diagrammatic formalism, there is no issue of convergence as there is with the iterative methods; furthermore, in our analysis, there is no question of uniqueness of solutions—we can identify directly all distinct solutions of the two-particle equations. In fact, we find that the two-particle BBGKY equations have spurious solutions for the lattice gas considered here.

The first step in writing the exact equations for the Schlögl model lattice gas is to write the exact equation for CCFs at a single vertex. There

Table II. Vertex Coefficients for Diffusive Vertices

$\|\alpha\|$	V^{α}_{β}			
	$\|\beta\|=0$	$\|\beta\|=1$	$\|\beta\|=2$	$\|\beta\|=3$
0	1	0	0	0
1	0	1/3	0	0
2	0	0	1/3	0
3	0	0	0	1

are two sets of such equations, corresponding to the diffusive and reactive vertices, respectively. The mean vertex coefficients V^{α}_{β} for both of these vertex types are symmetric with respect to permutations of incoming and outgoing bits separately, and therefore are only functions of the numbers of bits in α and β. These vertex coefficients are easily calculated and are tabulated in Tables II and III.

From these vertex coefficients, we can use (13) to write the exact equations for the outgoing CCFs from a diffusive or reactive vertex in terms of the incoming CCFs. These equations are again invariant under arbitrary independent permutations of the incoming and outgoing bits. Labeling the outgoing particles by A, B, C and the incoming particles by a, b, c, we obtain the equations for a diffusive vertex as

$$\begin{aligned}\Gamma^{A} &= \tfrac{1}{3}(\Gamma^{a}+\Gamma^{b}+\Gamma^{c})\\ \Gamma^{AB} &= \tfrac{1}{3}(\Gamma^{ab}+\Gamma^{ac}+\Gamma^{bc})\\ \Gamma^{ABC} &= \Gamma^{abc}\end{aligned} \tag{19}$$

The one-particle equation for a reactive vertex is

$$\begin{aligned}\Gamma^{A} = \tfrac{1}{9}+\tfrac{7}{9}(&\Gamma^{a}\Gamma^{b}+\Gamma^{a}\Gamma^{c}+\Gamma^{b}\Gamma^{c}-2\Gamma^{a}\Gamma^{b}\Gamma^{c}+\Gamma^{ab}-2\Gamma^{c}\Gamma^{ab}\\ &+\Gamma^{ac}-2\Gamma^{b}\Gamma^{ac}+\Gamma^{bc}-2\Gamma^{a}\Gamma^{bc}-2\Gamma^{abc})\end{aligned} \tag{20}$$

Table III. Vertex Coefficients for Reactive Vertices

$\|\alpha\|$	V^{α}_{β}			
	$\|\beta\|=0$	$\|\beta\|=1$	$\|\beta\|=2$	$\|\beta\|=3$
0	1	0	0	0
1	1/9	0	7/9	−14/9
2	0	0	7/9	−14/9
3	0	0	2/3	−4/3

The equations for two- and three-particle outgoing CCFs are straightforward to calculate but are algebraically more complicated than Eq. (20). Note that setting the two- and three-particle correlations to zero in this equation, and setting all one-particle correlations to the mean occupation number $f = \Gamma^a = \Gamma^b = \Gamma^c$, reproduces the Boltzmann equilibrium, Eq. (8).

Henceforth, we will restrict attention to uniform equilibria, so that the correlations are independent of spatial coordinate or orientation. We denote the equilibrium values of the one-, two-, and three-particle CCFs *entering* a reactive vertex by I_1, I_2, and I_3, respectively. Similarly, we denote the CCFs *leaving* a reactive vertex by O_1, O_2, and O_3. The exact equations of motion for the one- and two-particle CCFs leaving a reactive vertex are

$$
\begin{aligned}
O_1 &= \frac{1}{9} + \frac{7I_1^2}{3} - \frac{14I_1^3}{9} + \frac{7I_2}{3} - \frac{14I_1I_2}{3} - \frac{14I_3}{9} \\
O_2 &= \frac{-1}{81} + \frac{49I_1^2}{27} - \frac{98I_1^3}{81} - \frac{49I_1^4}{9} + \frac{196I_1^5}{27} \\
&\quad - \frac{196I_1^6}{81} + \frac{49I_2}{27} - \frac{98I_1I_2}{27} - \frac{98I_1^2I_2}{9} \\
&\quad + \frac{784I_1^3I_2}{27} - \frac{392I_1^4I_2}{27} - \frac{49I_2^2}{9} + \frac{196I_1I_2^2}{9} \\
&\quad - \frac{196I_1^2I_2^2}{9} - \frac{98I_3}{81} + \frac{196I_1^2I_3}{27} - \frac{392I_1^3I_3}{81} \\
&\quad + \frac{196I_2I_3}{27} - \frac{392I_1I_2I_3}{27} - \frac{196I_3^2}{81}
\end{aligned}
\tag{21}
$$

The equation for O_3 can be similarly written, but is slightly more complicated and will not be used here. Recall that, as was demonstrated in the previous section, the exact dynamical equation of an arbitrary number of correlated quantities can be described in terms of the exact equations for the CCFs at a single vertex. Thus, Eq. (21), along with the corresponding equation for O_3, gives a complete description of the equations of motion of *all* CCFs at a reactive timestep.

To complete the equilibrium equations (1), we must determine the relations between the outgoing correlations O_i from a reactive vertex and the incoming correlations I_i. Referring back to Eqs. (13) and (19), we see that at diffusive timesteps, the correlations essentially perform random walks on the honeycomb lattice. Thus, the correlation I_1 entering a fixed reactive vertex at some timestep is a weighted sum of outgoing correlations O_1 from vertices at the previous reactive timestep, with total weight 1. Since we have assumed an isotropic equilibrium, we have an equilibrium density f satisfying

$$f = I_1 = O_1 \tag{22}$$

It is interesting to note that by using this equality in the first equation in (21) we can write an exact expression for I_3 in terms of I_2 and I_1. Inserting this expression into the second equation of (21), we find that the terms in I_2 cancel and we have the result

$$O_2 = -\tfrac{1}{9} + f - f^2 \tag{23}$$

Note that this equation is *exact*, and must be satisfied by any isotropic equilibrium of the system.

More generally, if we choose any values for σ and τ in Eq. (6), we may derive the exact equation,

$$O_2 = \frac{(-1 + \tau - 2\sigma + 2\tau\sigma) + 3(1 + 2\sigma) I_1 - 3(1 + \tau + \sigma) I_1^2}{3(1 + \tau + \sigma)}$$

which reduces to Eq. (23) when $\tau = \sigma = 2/3$. The existence of such a simple equation for O_2 is a feature of the specific form chosen for Eq. (6); for example, if P_0^0 and P_0^1 are not equal, the right-hand side of the above equation for O_2 will involve I_2.

In principle, we would now like to find an exact set of expressions relating the quantities I_2, I_3 to outgoing quantities O_2, O_3 by iterating the exact equations of motion. However, this is technically infeasible since such a calculation would involve a sum over diagrams involving arbitrary numbers of correlated quantities. Thus, we shall now restrict ourselves to the two-particle BBGKY equations by neglecting correlations of more than two particles. By making this simplification, we derive a simple set of equations whose solutions give the equilibria of the lattice gas in the two-particle BBGKY approximation.

Neglecting three-particle correlations, and setting $f = O_1 = I_1$, we find that the exact equations for the CCFs at a reactive vertex become

$$\begin{aligned} f &= \frac{1}{9} + \frac{7f^2}{3} - \frac{14f^3}{9} + \frac{7I_2}{3} - \frac{14fI_2}{3} \\ &= f + \frac{1}{9}(1 - 2f)(1 - 7f + 7f^2 + 21I_2) \end{aligned} \tag{24}$$

$$
\begin{aligned}
O_2 = & \frac{-1}{81} + \frac{49f^2}{27} - \frac{98f^3}{81} - \frac{49f^4}{9} + \frac{196f^5}{27} - \frac{196f^6}{81} + \frac{49I_2}{27} \\
& - \frac{98fI_2}{27} - \frac{98f^2I_2}{9} + \frac{784f^3I_2}{27} - \frac{392f^4I_2}{27} \\
& - \frac{49I_2^2}{9} + \frac{196fI_2^2}{9} - \frac{196f^2I_2^2}{9}
\end{aligned}
\tag{25}
$$

The first of these equations is satisfied whenever either

$$f = \tfrac{1}{2}$$

or

$$I_2 = -\tfrac{1}{21}(1 - 7f + 7f^2) \tag{26}$$

The solution $f = 1/2$ corresponds to the unstable equilibrium of the Boltzmann theory, and shows that this unstable equilibrium still exists in the two-particle BBGKY approximation. Inserting (26) into (25), we again derive the identity (23), so this identity still holds in the two-particle BBGKY approximation.

To find all solutions to the two-particle BBGKY equilibrium equations, it remains for us to find a relation between I_2 and O_2. This is the type of relation which was analyzed by Bussemaker *et al.*(7) using an iterative method. Here, we describe this relation using an explicit sum over diagrams which allows an analytic study of the resulting equilibria. The analysis of the flow of two-particle correlations is slightly more subtle than that of the one-particle density. Tracing back a given incoming correlation I_2 to the previous reactive vertex (k timesteps earlier), we find that with some probability $\phi_k(1)$ the random walks of the correlated quantities lead back to a pair of outgoing particles from a single vertex associated with an outgoing correlation O_2. However, the remaining random walks [with probability $1 - \phi_k(1)$] lead to a pair of correlated quantities at different vertices. For a fixed pair of vertices, we denote such an outgoing correlation from a reactive step by $O_{1,1}$. Using Eqs. (20) and (18), we can expand $O_{1,1}$ in terms of incoming CCFs of the six particles associated with the two vertices in question. Making the two-particle BBGKY approximation, we have

$$O_{1,1} = \lambda^2 \left(\sum_{\text{pairs}} I_{1,1} \right) \tag{27}$$

where the sum is taken over all nine possible pairs of incoming particles, one from each vertex, which may be correlated, and where we can compute the "bounce probability" λ, as in Eq. (18), by taking the derivative of the right-hand side of Eq. (24),

$$\lambda = \lambda(f, I_2) = \tfrac{14}{9}(f - f^2 - I_2) = \tfrac{2}{27}(1 + 14f - 14f^2) \tag{28}$$

Note that $\lambda \leqslant 1/3$, with equality only when $f = 1/2$. We can repeat the above steps for the particles correlated in each term $I_{1,1}$. Moving back through $k-1$ diffusive vertices, associated with random walks of the correlated quantities, we again have some set of diagrams where the correlation originates in a pair of outgoing particles from a single previous reactive vertex, and some other set of diagrams where the correlated quantities are still separate. Repeating this analysis indefinitely, we find that the equilibrium correlations I_2 and O_2 can be related by

$$I_2 = \alpha(f)\, O_2 \tag{29}$$

where

$$\alpha(f) \equiv \sum_{t=1}^{\infty} \phi_k(t)(3\lambda)^{2t-2} \tag{30}$$

is the operator associated with ring diagrams, and where $\phi_k(t)$ is the weighted sum over all diagrams describing random walks of two particles for kt timesteps on the honeycomb lattice, where the particles leave a particular vertex on the first step in a fixed pair of directions and arrive together at some possibly different vertex at the final step. In these diagrams, the particles are not allowed to visit the same vertex at any timestep divisible by k (reactive vertices), and when they visit the same vertex at any other timestep (diffusive vertices), they exit in different directions with each possible pair of outgoing directions having equal probability [corresponding to (19)]. Note that the factor of 3 appears because the usual probability 1/3 of a given random bounce is replaced by the weight λ.

As an example of a coefficient $\phi_k(t)$, it is easy to calculate

$$\phi_2(1) = \tfrac{1}{9}$$

since the unique diagram which contributes is as shown in Fig. 3. Similarly, since at $t = 2$ there are 30 diagrams which each contribute $(1/3)^6$, one finds that

$$\phi_2(2) = 30(\tfrac{1}{3})^6 = \tfrac{10}{243}$$

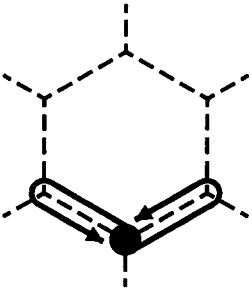

Fig. 3. Unique diagram contributing to $\phi_2(1)$.

It follows from the random walk interpretation of $\phi_k(t)$ that

$$\sum_{t=1}^{\infty} \phi_k(t) = 1$$

since the probability that two random walkers in 2D will eventually collide is 1. An immediate consequence is that the series

$$\sum_{t=1}^{\infty} \phi_k(t)(3\lambda)^{2t-2}$$

converges whenever $\lambda \leqslant 1/3$. Furthermore, for λ satisfying this condition, we can calculate the above series to arbitrary accuracy; given any ε, when $\lambda \leqslant 1/3$ we can choose T such that $\sum_{t=1}^{T} \phi_k(t) > 1 - \varepsilon$, and it follows immediately that

$$\sum_{t>T} \phi_k(t)(3\lambda)^{2t-2} < \varepsilon$$

Thus, to calculate the sum to within an accuracy of ε we need only calculate a finite number of coefficients $\phi_k(t)$, a task which is easily performed numerically by a computer.

We may now use (23), (26), and (29) to derive a single equation for the two-particle BBGKY equilibrium density f,

$$\zeta(f) \equiv \tfrac{1}{9}(1-2f)[1-7f+7f^2-\tfrac{7}{3}(1-9f-9f^2)\,\alpha(f)] = 0 \qquad (31)$$

As defined above, $\zeta(f)$ is the rate of change of f as it appears on the right-hand side of Eq. (24). Since, as mentioned above, we can calculate $\alpha(f)$ to an arbitrary degree of accuracy, it is a straightforward process to determine

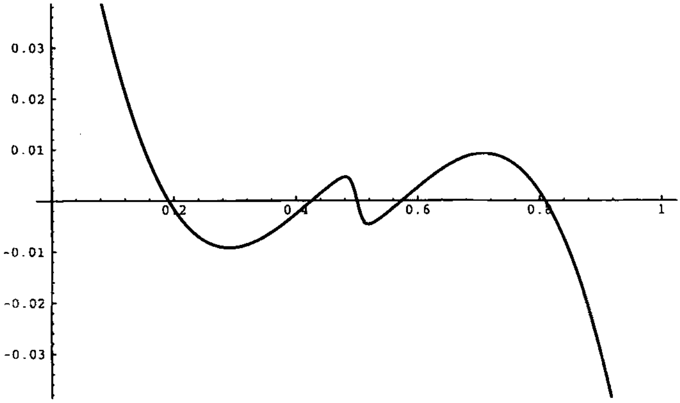

Fig. 4. Plot of $\zeta(f)$ versus f for $k = 3$.

numerically the values of f which satisfy Eq. (31) to an arbitrary degree of accuracy. We have performed such a numerical analysis for k ranging from 2 to 7. For each value of k, we find not three, but rather *five* distinct equilibria satisfying $\zeta(f) = 0$. As an example, we graph in Fig. 4 the function $\zeta(f)$ for $k = 3$. This function has two zeros at $f \approx 0.1903$ and $f \approx 0.8097$, which correspond to stable equilibria of the system. We will refer to these zeros as "primary" solutions. In addition, however, the function has two unstable zeros near $f = 1/2$, which we will call "secondary" solutions. Furthermore, the root at $f = 1/2$ appears to be stable in this approximation. Because the series for $\alpha(f)$ converges very slowly in the vicinity of $f = 1/2$, one might be suspicious of the secondary solutions. To see that such solutions must exist, however, we can observe that at $f = 1/2$ we have $\alpha(1/2) = 1$ and $\alpha'(1/2) = 0$, and therefore $\zeta'(1/2) = -13/27 < 0$ for any k. So there must be a secondary pair of solutions, just as we see in the graph.

Comparison of the primary equilibrium solutions with numerical results from simulations of the lattice gas with various values of k shows that these solutions of the two-particle BBGKY equations predict the exact equilibria of the lattice-gas system remarkably well. This comparison is given in Fig. 5 for the larger of the stable equilibria. We see that the two-particle BBGKY aproximation gives an excellent numerical prediction of the equilibria of the Schlögl model lattice gas. However, the existence of the spurious secondary equilibria demonstrates that one must be careful when dealing with truncations of the exact equations for a lattice gas.

Though the secondary roots can be dismissed as unstable, the prediction that the root at $f = 1/2$ is stable remains a disturbing feature of the

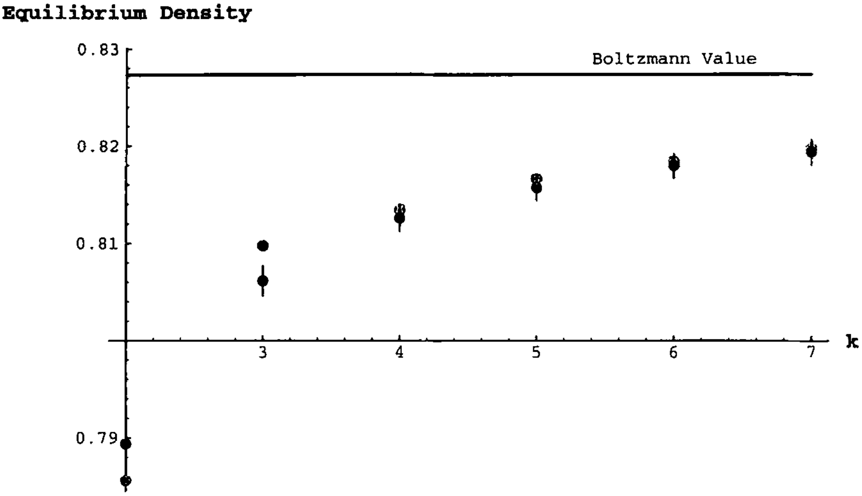

Fig. 5. Equilibrium density versus k. The black points with the error bars are from numerical experiment, the gray points without error bars are from the two-particle BBGKY theory, and the line across the top is the Boltzmann value. Only the larger of the two stable equilibria is plotted, since there is clearly a symmetry for $f \to 1 - f$.

two-particle BBGKY. approximation. We will now proceed to give a simple analytic argument which shows that the secondary solutions are highly sensitive to the introduction of three-particle CCFs, and thus that their existence is suspect on *a priori* grounds. First, let us observe that the introduction of a small amount of three-particle correlation in I_3 would change (26), which would then read

$$I_2 = -\frac{1}{21}(1 - 7f + 7f^2) + \frac{2I_3}{3(1-2f)}$$

If the correlation I_3 were small, this would cause a change in I_2 which would be small except in the region $f \approx 1/2$, where the change would be dramatic. A change in I_2 would in turn cause a comparable change in λ through (28). Since the sum (30) converges slowly in the region of $\lambda \approx 1/3$, the value of $\alpha(f)$ is highly sensitive to a slight change in λ in this region, which is precisely the region where $f \approx 1/2$. In fact, only a small change in λ is needed to lower α sufficiently that $\zeta'(1/2) > 0$, which would result in the disappearance of the spurious equilibria and the concomitant instability of the $f = 1/2$ root.

The composition of the two extreme sensitivities described here makes it clear that the existence of the spurious equilibria is highly dependent upon the vanishing of the three-particle CCF I_3. In fact, we have extended our analysis to include a simple class of three-particle diagrams and found that with this minor modification, the spurious equilibria completely disappear. Specifically, one can take the exact three-particle equations at a vertex, and solve using the additional condition that $I_3 = \mu O_3$, where μ is the weight of some simple class of diagrams involving three correlated particles. For the case $k = 2$, the simplest three-particle diagram is the one where three particles leave a vertex and bounce directly back on the subsequent advective step. This diagram gives $\mu = 1/27$. Exactly solving the resulting equations for the one-, two-, and three-particle CCFs, we find that there are precisely two stable solutions and an unstable solution at $f = 1/2$. Thus, it seems clear that the secondary equilibria generated by the two-particle BBGKY equations are spurious, since they can be removed by such a simple perturbation. Unfortunately, including an arbitrary set of three-particle diagrams, without performing the systematic three-particle BBGKY approximation, tends to reduce the effectiveness of the approximation; thus, although the spurious equilibria are removed, the analysis described here does not give more accurate predictions for the actual equilibria than the two-particle BBGKY analysis. To have a significantly improved approximation to the actual equilibria of the lattice gas, one would need to use a more complicated approximation scheme such as the complete three-particle BBGKY approximation.

We conclude this section with a brief discussion of finite-size effects. For any finite lattice, the complete equations of motion can have only a single equilibrium solution, corresponding to $f = 1/2$, since fluctuations can always drive a transition from one local equilibrium to another. Thus, if we have a lattice with l sites, the exact solution of the dynamical equations for all CCFs of $3l$ or fewer particles should only give a single solution. It is interesting to consider the effect that a finite lattice size would have on our discussion of the two-particle BBGKY equations. The only way in which a finite lattice size would modify the equations is to change the coefficients $\phi_k(t)$ to correspond to random walks on the finite lattice. A particularly simple example of this is the degenerate case where we have a lattice with only a single vertex. In this case, the outgoing particles from a collision return immediately to the same vertex. Thus, we have $\phi_k(1) = 1$ for all k, and of course $\phi_k(t) = 0$ for all $t > 1$. This modification of the coefficients has no effect on the exact equations at a vertex, Eqs. (24) and (25), so $f = 1/2$ is still a solution of the equilibrium equations. However, using the modified values for ϕ, we find that the two-particle BBGKY equation (31) becomes

$$\zeta(f) = \tfrac{1}{27}(1 - 2f)(-4 + 42f - 42f^2) = 0$$

This equation has three solutions, of which two are spurious equilibria analogous to those encountered previously on the infinite lattice. Thus, although the finite-size effects remove the extra physical equilibria, which we only expect to exist in the thermodynamic limit, these effects leave the spurious solutions of the BBGKY-truncated equilibrium equations intact. An interesting question, which we will address in future work, is at precisely what lattice size the thermodynamic equilibria first appear in the two-particle BBGKY approximation. An answer to this and related questions might shed light on the relationship between *i*-particle correlations and fluctuation scales.

5. CONCLUSIONS

We have described an NSDB lattice gas model for Schlögl's second chemical reaction. We derived a self-consistent set of equations for its exact homogeneous equilibria, solved these equations in the two-particle BBGKY approximation, and compared the results to numerical experiment. We found that this approximation describes the equilibria far more accurately than the Boltzmann approximation, but we also noted that it can give rise to spurious solutions to the equilibrium equations which can only be removed by including effects due to three-particle correlations.

The possibility of the existence of spurious solutions of the two-particle BBGKY equations was raised by Bussemaker *et al.*(7) The method they used to solve these equations was an iterative approximation method which was not well suited to recognizing the existence of multiple solutions. The use in this paper of a diagrammatic formalism to discribe the time development of the correlations made it possible to write the BBGKY-truncated equilibrium equations in a closed form which was amenable to numerical solution. It would be interesting to extend the diagrammatic analysis described here to higher order truncations of the BBGKY hierarchy. The diagrammatic method of analysis used here should also be directly applicable to the two-particle BBGKY approximations of other NSDB lattice gases; the set of diagrams to be summed over and their weights, however, will depend upon the specific lattice gas being studied. In general, rather than a single equation such as Eq. (31), one may end up with a system of coupled equations.

The physically meaningful solutions of these BBGKY-truncated equilibrium equations provide an accurate description of the non-Gibbsian equilibrium of this lattice gas. The next step in this program of study will be to expand about this non-Gibbsian equilibria in Knudsen number, thereby generalizing the usual Chapman–Enskog analysis. In this way, the full reaction–diffusion equation, Eq. (1) will be derived, including the renormalized diffusion coefficient. This work is in progress.(16)

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