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Inhomogeneous Glauber Dynamics and the Process of Crystallization of a Lattice Gas

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The model under consideration is a hard-core lattice gas in an external potential on a Bethe lattice with nonequilibrium time evolution governed by Glauber dynamics. A hierarchical decoupling of nonequilibrium correlations, motivated by and asymptotically providing the exact form of equilibrium multisite correlations in the inhomogeneous potential regime, is proposed. Application is made to the process of lattice gas crystallization, at high activity, from a spatially homogeneous fluid phase to an equilibrium crystal phase with unequal sublattice densities. The first few levels of the hierarchical decoupling give a consistent picture of two kinds of nonequilibrium instabilities—one leading to a sublattice density bifurcation, the other associated with an abrupt increase in densities and correlations in time.

KEY WORDS: Lattice gas; Glauber dynamics; inverse profile equation; density bifurcation.

1. INTRODUCTION

Owing to the lack of an explicit canonical formalism, nonequilibrium phenomena remain obscure in many relevant aspects. Attempts have been made to apply directly the standard methods of equilibrium thermodynamics, within the framework of Kirkwood–Salsburg equations(1) and the liquid-state replica method,(2,3) to irreversible processes such as random sequential adsorption. On the other hand, for much more complicated reversible nonconservative stochastic dynamics, say of Glauber type,(4) the

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guaranteed asymptotic time evolution of the system to its equilibrium state with nontrivial spatial and correlation structure can restrict and/or suggest the form of time-dependent quantities.

Rigorous approaches to systems with time evolution governed by local Glauber dynamics are usually based on an infinite hierarchy of "equations of motion" for time-dependent correlations. This hierarchy can be exactly decoupled at some level only in very special cases: 1D zero-field Ising model with cell-interaction structure,(5) the zero-field Potts chain(6,7) (both systems exhibit a nonuniversal dynamic critical exponent z), the voter model(8,9) lacking detailed balance. From a macroscopic point of view, the hierarchy provides a natural way of generating realistic hydrodynamic-type equations describing diffusion phenomena in spatially inhomogeneous systems, such as the phase segregation.(9)

A different class of nonequilibrium phenomena is associated with inhomogeneity on a microscopic scale, like the process of crystallization (for a recent review of spatiotemporal pattern formation in systems away from equilibrium, see ref. 10). Even with homogeneous external conditions, the system has to be treated from the beginning as inhomogeneous in order to describe consistently densities and correlations inside the cell-structured crystal phase. The aspect of inhomogeneity is especially important in the nonequilibrium phase transition from a homogeneous fluid to a solid phase. In order to obtain a consistent picture of this phase transition, it is important to ensure, at every level of an unavoidable approximation hierarchy, the correct approach of the system to its exact equilibrium crystal state characterized not only by a position-dependent density profile, but also by the whole set of position-dependent multisite correlations. The fact that this task is far from being simple is better seen when we recall that even the equilibrium statistics of an inhomogeneous system is not well understood at present. The only exceptions are models on simply connected lattices(11-14) which possess, within the density functional formalism, local forms of the inverse profile relation, i.e., the dependence of the external potential on the evoked density profile.

In this paper, we consider a hard-core lattice gas model on a Bethe lattice with NN exclusion in an external potential. At sufficiently high activity, this model exhibits as the only stable equilibrium solution a symmetry-broken phase with different particle densities on the two adjacent sublattices,(14) an apparent Bethe-lattice counterpart of the crystal phase in 2D hard-square(15,16) or hard-hexagon(16,17) models. The nonequilibrium adsorbtion and deadsorbtion of gas particles is governed by Glauber dynamics. Our aim is to describe consistently the process of lattice gas crystallization from a homogeneous fluid phase to an inhomogeneous solid phase. Emphasis is put on the study of instability leading to the sublattice densities bifurcation.

The paper is organized as follows. In Section 2, we review the formalism of Glauber dynamics for the lattice gas under study in a site-dependent external potential, and formulate a simplified hierarchy of "equations of motion" for special time-dependent correlations defined on connected clusters of sites. In Section 3, we propose a hierarchical decoupling of these correlations, motivated by their exact form found in the equilibrium *inhomogeneous* regime. In Sections 4 and 5, we study the stability of a homogeneous fluid phase with respect to the sublattice density bifurcation, deduced from "equations of motion" at different decoupling levels.

2. GLAUBER DYNAMICS FOR INHOMOGENEOUS LATTICE GAS

The model under consideration is a lattice gas on a Bethe lattice with an arbitrary coordination number q, with a hard-core exclusion for the occupancy of NN sites, and in an inhomogeneous potential u_x.

At thermodynamic equilibrium, the probability that a site is empty ($\sigma_x = 0$) or occupied ($\sigma_x = 1$) is given, to within a σ_x-independent proportionality factor, by

$$p_x(\sigma_x) \sim \exp(-\beta u_x \sigma_x) \prod_{a=1}^{q} (1 - \sigma_x \sigma_{x+a}) \tag{1}$$

where β is the inverse temperature and the product runs over all NN's of site x.

The nonequilibrium time evolution of the system of adsorbing and deadsorbing gas particles is considered to be governed by Glauber dynamics. Namely, the probability function $p(\boldsymbol{\sigma}, t)$ that the state variables take on values $\boldsymbol{\sigma} = \{\sigma_x\}$ at time t satisfies the master equation

$$\frac{d}{dt} p(\boldsymbol{\sigma}; t) = -\sum_x w_x(\boldsymbol{\sigma})\, p(\boldsymbol{\sigma}; t) + \sum_x w_x\,(\boldsymbol{\sigma} \,|\, \sigma_x \to \bar{\sigma}_x)\, p\,(\boldsymbol{\sigma} \,|\, \sigma_x \to \bar{\sigma}_x; t) \tag{2}$$

Here, we use the notation $\bar{\sigma}_x = 1 - \sigma_x$ for reversed site occupation and $w_x(\boldsymbol{\sigma})$ is the probability per unit time that the occupancy at site x changes from σ_x to $\bar{\sigma}_x$. In order to ensure that the system will reach equilibrium at $t \to \infty$, the transition probabilities have to satisfy the detailed balance condition

$$\frac{p_x(\sigma_x = 1)}{p_x(\sigma_x = 0)} = \frac{w_x(\sigma_x = 0)}{w_x(\sigma_x = 1)} \tag{3}$$

which, by virtue of (1), is equivalent to

$$w_x(\sigma_x) \sim \sigma_x + z_x(1-\sigma_x) \prod_{a=1}^{q} (1-\sigma_{x+a}) \tag{4}$$

where $z_x = \exp(-\beta u_x)$; the σ_x-independent proportionality factor is not irrelevant, but if it is a constant, it only determines time scale. The master equation (2) can then be written in a compact form as follows:

$$\frac{d}{dt} p(\boldsymbol{\sigma}; t) = \sum_{x, \{\sigma'_x = 0, 1\}} (2\sigma_x - 1) \left[z_x \prod_{a=1}^{q} (1-\sigma_{x+a})(1-\sigma'_x) - \sigma'_x \right] \times p\,(\boldsymbol{\sigma} \,|\, \sigma_x \to \sigma'_x; t) \tag{5}$$

To obtain a system of differential equations for the expectation values of the occupation numbers and higher-order density correlations,

$$\langle \sigma_x \rangle_t = \sum_{\{\sigma\}} \sigma_x p(\boldsymbol{\sigma}; t), \qquad \langle \sigma_x \sigma_y \cdots \rangle_t = \sum_{\{\sigma\}} \sigma_x \sigma_y \cdots p(\boldsymbol{\sigma}; t)$$

we proceed in the standard way, i.e., multiply both sides of (5) by the corresponding state variables and then sum over all $\boldsymbol{\sigma}$, taking into account the equality $\sum_{\sigma=0,1} (2\sigma - 1) = 0$ for all remaining state variables. For tactical reasons, we take advantage of the exclusion character of the NN interaction and construct in this way a chain of coupled equations for one-site densities $\rho_x = \langle \sigma_x \rangle_t$ and the probabilities of connected clusters of vacant one, two, ... sites at time t,

$$\frac{d}{dt} \rho_x = z_x \left\langle \bar{\sigma}_x \prod_a \bar{\sigma}_{x+a} \right\rangle_t - \rho_x \tag{6a}$$

$$\frac{d}{dt} \langle \bar{\sigma}_x \bar{\sigma}_{x+a} \rangle_t = -z_x \left\langle \bar{\sigma}_x \prod_b \bar{\sigma}_{x+b} \right\rangle_t - z_{x+a} \left\langle \bar{\sigma}_{x+a} \prod_b \bar{\sigma}_{(x+a)+b} \right\rangle_t + \rho_x + \rho_{x+a} \tag{6b}$$

$$\begin{aligned}\frac{d}{dt}\langle\bar{\sigma}_x\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\rangle_t = &-z_x\left\langle\bar{\sigma}_x\prod_c\bar{\sigma}_{x+c}\right\rangle_t\\ &-z_{x+a}\left\langle\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\prod_c\bar{\sigma}_{(x+a)+c}\right\rangle_t\\ &-z_{x+b}\left\langle\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\prod_c\bar{\sigma}_{(x+b)+c}\right\rangle_t\\ &-2\langle\bar{\sigma}_x\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\rangle_t\\ &+2-\rho_x-\rho_{x+a}-\rho_{x+b}\qquad (a\neq b)\end{aligned}\tag{6c}$$

and so on. Here, we have used the notation $(x+a)+c$ for the cth of the nearest neighbors of the ath of the nearest neighbors of site x (thus the whole set $\{(x+a)+c\}$ $c=1,\ldots,q$ contains site x itself) and take advantage of the fact that the time evolution from a correct initial state with no pair of occupied adjacent sites always retains $\langle\sigma_x\sigma_{x+a}\rangle_t=0$. Note that relations (6a) and (6b) are, due to the exclusion nature of the NN interaction, identical.

3. HIERARCHICAL DECOUPLING OF CORRELATIONS

3.1. Equilibrium Correlations

The chain of equations (6) provides an infinite set of interrelations between probabilities of connected empty clusters of various sizes at time t. To decouple it, we have to restrict ourselves, at a given approximation level l, to all multisite correlations of size $\leqslant l$ and to express all higher-order correlations of size $>l$ in terms of them. A reasonable approximation scheme of nonequilibrium correlations has to provide the *exact* equilibrium solutions to Eqs. (6),

$$\rho_x^* = \rho_x(t\to\infty),\qquad \langle\bar{\sigma}_x\bar{\sigma}_{x+a}\rangle^* = \langle\bar{\sigma}_x\bar{\sigma}_{x+a}\rangle_{t\to\infty}$$
$$\langle\bar{\sigma}_x\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\rangle^* = \langle\bar{\sigma}_x\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\rangle_{t\to\infty},\ldots$$

determined by the stationarity conditions

$$d\rho_x/dt=0,\qquad d\langle\bar{\sigma}_x\bar{\sigma}_{x+a}\rangle_t/dt=0,\qquad d\langle\bar{\sigma}_x\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\rangle_t/dt=0,\ldots$$

The equilibrium statistics of an inhomogeneous system is, in general, very complicated. However, for simply connected lattices like the Bethe lattice the articulation character of lattice points permits a local thermodynamic description of the system within the inverse formulation, with site-dependent densities ρ_x chosen as the independent controlling variables.[12,13] For the present system, the inverse profile equation

$$z_x = \frac{\rho_x^*(1-\rho_x^*)^{q-1}}{\prod_{a=1}^{q} (1-\rho_x^*-\rho_{x+a}^*)} \tag{7}$$

has been obtained by Robledo and Varea[14] using Widom's potential distribution theorem.[18] The introduction of the inverse format is very natural for the set of differential equations (6) provided that the explicit forms of all equilibrium multisite correlations in terms of $\{\rho_x^*\}$ are available. In what follows we will show that for the model considered this is the case.

As has been already mentioned, the inverse profile (7) is a special case of local inverse relations for simply connected lattices. It can be derived by using[12] the independence of the potential at a given site x from the densities inside lattice subsets which can be separated from site x via articulation points $\neq x$. In the case of the Bethe lattice, we can in this way reduce the original problem to the inverse problem of a finite cluster of sites $\{x, x+a\ (a=1,..., q)\}$ with the given density profile $\{\rho_x^*, \rho_{x+a}^*\ (a=1,..., q)\}$. The effect of the remaining part of the system is reflected through the modification of $z_{x+a} \to \tilde{z}_{x+a}$, but not of z_x itself. Within this local lattice structure the inverse relation (7) is straightforwardly available.

Let us now apply the above topological considerations to the calculation of the exact form of the equilibrium correlation $\langle \prod_{x \in \Omega_s} \bar{\sigma}_x \rangle^*$, i.e., the probability of a connected cluster $\Omega = \{\Omega_s; \Omega_b\}$ of empty sites $x \in \Omega_s$ with NN two-site bonds $\langle x, y \rangle \in \Omega_b$. The coordination number of site $x \in \Omega_s$ within the cluster Ω will be denoted by q_x. According to the previous analysis, in the inverse format, the cluster Ω can be considered separately from the system with the given internal densities $\{\rho_x^*\}$ if we take into account the modification $z_x \to \tilde{z}_x$ when the coordination number of point x has been changed upon the deletion of the cluster Ω. It follows that the multisite probability of empty sites $\langle \prod_{x \in \Omega_s} \bar{\sigma}_x \rangle^*$ is then equal to $1/Z(\Omega)$ with $Z(\Omega)$ the partition function of the cluster Ω. In order to calculate $Z(\Omega)$, we will reduce the cluster size via successive deletion of its boundary points $x \in \partial\Omega_s$ with cluster coordination number $q_x = 1$. The two-site inverse problem for site $x \in \partial\Omega_s$ results in $\tilde{z}_x = \rho_x^*/(1-\rho_x^*-\rho_{x+1}^*)$, where site $x+1$ is the only NN of x in Ω. Elimination of point $x \in \partial\Omega_s$ picks up the multiplicative contribution $(1+\tilde{z}_x) = (1-\rho_{x+1}^*)/(1-\rho_x^*-\rho_{x+1}^*)$ to $Z(\Omega)$ as well as multiplying z_{x+1} (resp. $\tilde{z}_{x+1}$) by the factor $(1-\rho_x^*-\rho_{x+1}^*)/(1-\rho_{x+1}^*)$, keeping in this way the correct form of the inverse profile equation for site $x+1$ upon the deletion of site x. Performing this elimination procedure for every boundary site at every elimination level down to zero number of cluster points, we collect and multiply all factors generated and arrive at

$$Z(\Omega) = \prod_{x \in \Omega_s} (1 - \rho_x^*)^{q_x - 1} \Big/ \prod_{\langle x, y \rangle \in \Omega_b} (1 - \rho_x^* - \rho_y^*)$$

Consequently,

$$\left\langle \prod_{x \in \Omega_s} \bar{\sigma}_x \right\rangle^* = \frac{\prod_{\langle x, y \rangle \in \Omega_b} \langle \bar{\sigma}_x \bar{\sigma}_y \rangle^*}{\prod_{x \in \Omega_s} (\langle \bar{\sigma}_x \rangle^*)^{q_x - 1}} = \frac{\prod_{\langle x, y \rangle \in \Omega_b} (1 - \rho_x^* - \rho_y^*)}{\prod_{x \in \Omega_s} (1 - \rho_x^*)^{q_x - 1}} \tag{8}$$

Using the inverse relation (7) and assuming $\rho_x = \rho_x^*$, it is easy to verify that this form of equilibrium correlations annuls the rhs of all equations (6).

3.2. Nonequilibrium Correlations

The exact local formula (8) for multisite correlations of empty sites in the *inhomogeneous* equilibrium regime is appealing: the probability of an empty cluster is factorized into the NN two-site probabilities of empty sites. The denominator compensates the "superfluous" $(q_x - 1)$-times presence of each site x in NN pairs. Under nonequilibrium conditions, the structure of higher-order correlations (of empty sites) is much more complicated: every cluster shape represents a new topological element which follows its own time evolution. On the other hand, the NN structure of equilibrium correlations rigidly restricts, and simultaneously suggests, the possible choices of realistic forms of nonequilibrium correlations in the inhomogeneous regime.

Let us treat the model at the lth approximation level as defined at the beginning of this section, i.e., consider the chain of equations (6) for all topologically nonequivalent clusters of size $\leqslant l$. For every higher-order probability $\langle \prod_{x \in \Omega_s} \bar{\sigma}_x \rangle_t$ of an empty cluster Ω with $|\Omega_s| > l$ occurring in the chain of equations we postulate the following hierarchical decoupling procedure. First, we find all possible topological realizations of clusters of size l inside Ω,

$$\{\Omega^{(i)}(l) : |\Omega_s^{(i)}(l)| = l, \{\Omega_s^{(i)}(l), \Omega_b^{(i)}(l)\} \subset \Omega\}$$

with the corresponding contribution $\prod_i \langle \prod_{x \in \Omega_s^{(i)}(l)} \bar{\sigma}_x \rangle_t$. The factorization of $\langle \prod_{x \in \Omega_s} \bar{\sigma}_x \rangle_t$ through all l-site correlations evidently covers all $(l-1)$-site clusters $\{\Omega^{(i)}(l-1)\}$ with the possible multiple (and, consequently, "superfluous") presence of some of them in more than one l-site correlation. Therefore, on the second hierarchical level we divide $\prod_i \langle \prod_{x \in \Omega_s^{(i)}(l)} \bar{\sigma}_x \rangle_t$ by $\prod_i' \langle \prod_{x \in \Omega_s^{(i)}(l-1)} \bar{\sigma}_x \rangle_t^{n_i}$, where the prime denotes the product over all superfluous correlations of size $l-1$ and n_i is the superfluous multiplicity. We proceed in this way up to $l=1$, dividing or multiplying, as required, the correlation formula at every hierarchical level l' by superfluous correlations arising at *all* previous levels $>l'$. For the original multisite correlation, this natural decoupling scheme ensures by its construction the exact decoupling property (8) at equilibrium.

As an example, we treat the cluster

$$\Omega = \{\Omega_s = \{1, 2, 3, 4, 5\}; \Omega_b = \{\langle 1, 2\rangle, \langle 2, 3\rangle, \langle 3, 4\rangle, \langle 3, 5\rangle\}\} \quad (9)$$

represented graphically in Fig. 1, at the approximation level $l=4$. The correlation function $\langle \bar{\sigma}_1 \bar{\sigma}_2 \bar{\sigma}_3 \bar{\sigma}_4 \bar{\sigma}_5 \rangle_t$ decouples at the first level to three four-site correlations with the corresponding contribution

$$\langle \bar{\sigma}_1 \bar{\sigma}_2 \bar{\sigma}_3 \bar{\sigma}_4 \rangle_t \, \langle \bar{\sigma}_1 \bar{\sigma}_2 \bar{\sigma}_3 \bar{\sigma}_5 \rangle_t \, \langle \bar{\sigma}_2 \bar{\sigma}_3 \bar{\sigma}_4 \bar{\sigma}_5 \rangle_t$$

Each of the three realizations of three-site clusters in Ω, namely $\Omega^{(1)}(3) = \{\{1, 2, 3\}; \{\langle 1, 2\rangle, \langle 2, 3\rangle\}\}$, $\Omega^{(2)}(3) = \{\{2, 3, 4\}; \{\langle 2, 3\rangle, \langle 3, 4\rangle\}\}$, and $\Omega^{(3)}(3) = \{\{2, 3, 5\}; \{\langle 2, 3\rangle, \langle 3, 5\rangle\}\}$, appears in two four-site correlations, while $\Omega^{(4)}(3) = \{\{3, 4, 5\}; \{\langle 3, 4\rangle, \langle 3, 5\rangle\}\}$ has no superfluous presence in four-site correlations, so that we divide the product of three four-site correlations by

$$\langle \bar{\sigma}_1 \bar{\sigma}_2 \bar{\sigma}_3 \rangle_t \, \langle \bar{\sigma}_2 \bar{\sigma}_3 \bar{\sigma}_4 \rangle_t \, \langle \bar{\sigma}_2 \bar{\sigma}_3 \bar{\sigma}_5 \rangle_t$$

As concerns two-site clusters, three of them, $\Omega^{(1)}(2) = \{\{1, 2\}; \{\langle 1, 2\rangle\}\}$, $\Omega^{(2)}(2) = \{\{3, 4\}; \{\langle 3, 4\rangle\}\}$, and $\Omega^{(3)}(2) = \{\{3, 5\}; \{\langle 3, 5\rangle\}\}$, have the correct multiplicity—they appear twice in four-site correlations and one time in three-site correlations. The last one, $\Omega^{(4)}(2) = \{\{2, 3\}; \{\langle 2, 3\rangle\}\}$, is contained in three four-site as well as three-site correlations and therefore

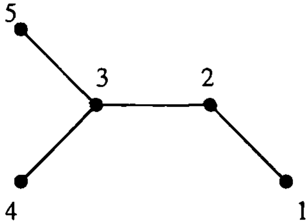

Fig. 1. A cluster on the Bethe lattice.

we multiply our previous expression by $\langle\bar{\sigma}_2\bar{\sigma}_3\rangle_t$. Finally, the probabilities of empty single sites give the trivial contribution 1 and we get

$$\left\langle\prod_{x\in\Omega_s}\bar{\sigma}_x\right\rangle_t=\frac{\langle\bar{\sigma}_1\bar{\sigma}_2\bar{\sigma}_3\bar{\sigma}_4\rangle_t\,\langle\bar{\sigma}_1\bar{\sigma}_2\bar{\sigma}_3\bar{\sigma}_5\rangle_t\,\langle\bar{\sigma}_2\bar{\sigma}_3\bar{\sigma}_4\bar{\sigma}_5\rangle_t\,\langle\bar{\sigma}_2\bar{\sigma}_3\rangle_t}{\langle\bar{\sigma}_1\bar{\sigma}_2\bar{\sigma}_3\rangle_t\,\langle\bar{\sigma}_2\bar{\sigma}_3\bar{\sigma}_4\rangle_t\,\langle\bar{\sigma}_2\bar{\sigma}_3\bar{\sigma}_5\rangle_t}\tag{9'}$$

4. LOWEST $l=2$ ORDER OF THE DECOUPLING SCHEME

Let us investigate the lowest, $l=2$, order of the proposed hierarchical decoupling and consider only the first two differential equations of the set (6) where the probability of an empty $(q+1)$-site cluster with the central x-vertex is factorized into the NN two-site probabilities of empty sites:

$$\left\langle\bar{\sigma}_x\prod_{a=1}^{q}\bar{\sigma}_{x+a}\right\rangle_t=\frac{\prod_{a=1}^{q}\langle\bar{\sigma}_x\bar{\sigma}_{x+a}\rangle_t}{\langle\bar{\sigma}_x\rangle_t^{q-1}}\tag{10}$$

Here, the denominator arises due to the q-times presence of site x in NN pairs. The proposed form of nonequilibrium correlations in the lowest order is thus identical to that of equilibrium correlations (8). Equations (6a) and (6b) read

$$\dot{\rho}_x=z_x\frac{\prod_{a=1}^{q}(1-\rho_x-\rho_{x+a})}{(1-\rho_x)^{q-1}}-\rho_x\tag{11}$$

With regard to the form of the inverse profile (7), the asymptotic equilibrium solution of (11), $\{\rho_x^*\}$, is indeed exact.

We now apply our inhomogeneous version of Glauber dynamics to the process of crystallization of the lattice gas in a constant external potential $z_x=z$, associated with the symmetry breaking between the adjacent sublattices 1 and 2, one of them having a higher density of particles. The motivation comes from the fact[14] that at equilibrium the pair of inverse profile relations

$$z=\frac{\rho_1^*(1-\rho_1^*)^{q-1}}{(1-\rho_1^*-\rho_2^*)^q},\qquad z=\frac{\rho_2^*(1-\rho_2^*)^{q-1}}{(1-\rho_1^*-\rho_2^*)^q}\tag{12}$$

produces (for $q>2$) as the only stable solutions those with different sublattice densities $\rho_1^*\neq\rho_2^*$, as soon as the activity z is higher than the critical activity z_c given by

$$z_c=\frac{(q-1)^{q-1}}{(q-2)^q},\qquad \rho_c^*=\frac{1}{q}\tag{13}$$

It is clear that if we let the system evolve from a fluid phase $\rho_x = \rho$ under imposed $z > z_c$, it tends toward its equilibrium crystal phase through a density sublattice bifurcation either at initial or some specific nonzero time.

We will study the pair of evolution equations implied by (11) with constant activity z, but with the possibility of the sublattice density alternation:

$$\dot{\rho}_1 = z\frac{(1-\rho_1-\rho_2)^q}{(1-\rho_1)^{q-1}} - \rho_1 \tag{14a}$$

$$\dot{\rho}_2 = z\frac{(1-\rho_1-\rho_2)^q}{(1-\rho_2)^{q-1}} - \rho_2 \tag{14b}$$

It is clear that these equations always provide a symmetric solution $\rho_1 = \rho_2 = \rho$ with equivalent sublattice densities. Let us examine the stability of such symmetric solutions. Putting into (14a) and (14b) $\rho_1 = \rho + \delta\rho_1$, $\rho_2 = \rho + \delta\rho_2$ with $\delta\rho_1$, $\delta\rho_2 \ll 1$ and ρ defined by

$$\dot{\rho} = z\frac{(1-2\rho)^q}{(1-\rho)^{q-1}} - \rho$$

we obtain, in the first order of $\delta\rho_1$, $\delta\rho_2$ and after diagonalization,

$$\begin{pmatrix} \dot{\delta}(\rho_1+\rho_2) \\ \dot{\delta}(\rho_1-\rho_2) \end{pmatrix} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \begin{pmatrix} \delta(\rho_1+\rho_2) \\ \delta(\rho_1-\rho_2) \end{pmatrix} \tag{15a}$$

$$\lambda_+ = -1 + z(q-1)\left(\frac{1-2\rho}{1-\rho}\right)^q - 2zq\left(\frac{1-2\rho}{1-\rho}\right)^{q-1} \tag{15b}$$

$$\lambda_- = -1 + z(q-1)\left(\frac{1-2\rho}{1-\rho}\right)^q \tag{15c}$$

The eigenvalue λ_+ is always negative and so it can never be the source of instability in time. On the other hand, λ_- may be positive and can cause an instability on the line $\rho_1 = \rho_2$. Let us denote by $\rho_T(z)$ the density threshold of the instability. It clearly satisfies the equation

$$z(q-1)\left(\frac{1-2\rho_T}{1-\rho_T}\right)^q = 1 \tag{16}$$

and the symmetric solution is stable for all $\rho > \rho_T$.

In dependence on the strength of the chemical potential, we distinguish three different nonequilibrium regimes of the system.

(i) $0 \leqslant z \leqslant 1/(q-1)$: $\lambda_- < 0$ in this region of activity values, and so the system evolves smoothly to the asymptotic ρ^* for an arbitrary value of initial ρ.

(ii) $1/(q-1) \leqslant z \leqslant z_c$: The equilibrium density ρ^* is still homogeneous. But, while from the side of high densities, $\rho > \rho^*$, the system exhibits behavior similar to the one in the previous case, a density bifurcation arises at the initial time for $0 \leqslant \rho \leqslant \rho_T$. The difference between sublattice occupations vanishes as $\rho_1, \rho_2 \rightarrow \rho^*$. For $z = z_c$ we have $\rho_T = \rho_c^*$.

(iii) $z > z_c$: The equilibrium sublattice occupations, defined through (12), are nonsymmetric, $\rho_1^* \neq \rho_2^*$. For small ρ, the density bifurcation takes place at initial time and the sublattice densities "move" toward one of the two nonsymmetric fixed points. For high ρ, the sublattice densities coincide up to the time when $\rho = \rho_T$ ($> 1/q$). Then they bifurcate and move toward one of the fixed points (ρ_1^*, ρ_2^*). These are the stable fixed points, which

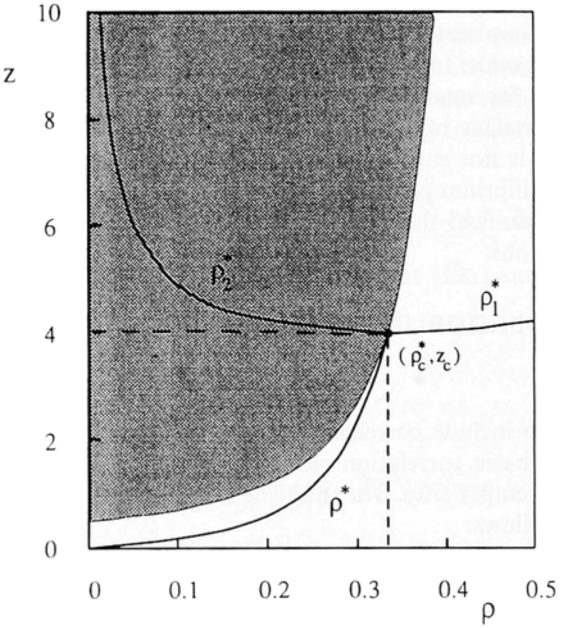

Fig. 2. The nonequilibrium phase diagram of a hard-core lattice gas of density ρ and activity z on the Bethe lattice of coordination 3 constructed at decoupling level $l = 2$: lines ρ^* and ρ_1^*, ρ_2^* represent stable equilibrium homogeneous and inhomogeneous (18) solutions, respectively; for further explanation see the text.

can be seen by considering in (14a) and (14b) small deviations $\delta\rho_1$, $\delta\rho_2$ from (ρ_1^*, ρ_2^*), given by (12). The algebra yields

$$\begin{pmatrix} \dot{\delta\rho}_1 \\ \dot{\delta\rho}_2 \end{pmatrix} = \begin{pmatrix} -\dfrac{1-\rho_1^*-\rho_2^*+q\rho_1^*\rho_2^*}{1-\rho_1^*} & -q\rho_1^* \\ -q\rho_2^* & -\dfrac{1-\rho_1^*-\rho_2^*+q\rho_1^*\rho_2^*}{1-\rho_2^*} \end{pmatrix} \begin{pmatrix} \delta\rho_1 \\ \delta\rho_2 \end{pmatrix} \tag{17}$$

For, e.g., $q=3$ with $z_c=4$, explicit forms of ρ_1^*, ρ_2^* are available,

$$\rho_1^* = \frac{(z-2)+[z(z-4)]^{1/2}}{2(z-1)}, \qquad \rho_2^* = \frac{(z-2)-[z(z-4)]^{1/2}}{2(z-1)} \tag{18}$$

and always provide, for $z > z_c$, two negative eigenvalues for the 2×2 matrix in relation (17).

For coordination number $q=3$, the instability region in the (ρ, z) plane is represented by shading in Fig. 2. We see that the factorization of the cluster correlations via the two-site probabilities of empty sites, although ensuring the tendency of the system with inhomogeneous densities to the correct equilibrium state, is too simple to predict adequately the true nonequilibrium behavior. In particular, the appearance of the instability on the line $\rho_1=\rho_2=\rho$ for small ρ *before* the activity acquires its critical value is evidently an artefact of the decoupling. The failure of the lowest-order approximation is not surprising: it neglects the important role of fluctuations in nonequilibrium phase transitions and thus represents a kind of nonequilibrium mean-field theory respecting, however, the exclusion character of NN interactions.

5. HIGHER DECOUPLING DEGREES

5.1. $l=3$

In order to include correlations in the instability picture, we increase the number of basic correlation elements by considering as well three-site probabilities of empty sites. The multisite correlations in (6a)–(6c) are then decoupled as follows:

$$\left\langle \bar{\sigma}_x \prod_{a=1}^{q} \bar{\sigma}_{x+a} \right\rangle_t = \frac{\prod_{a=1}^{q} \prod_{b=1,b>a}^{q} \langle \bar{\sigma}_x \bar{\sigma}_{x+a} \bar{\sigma}_{x+b} \rangle_t}{\prod_{a=1}^{q} \langle \bar{\sigma}_x \bar{\sigma}_{x+a} \rangle_t^{q-2}} \times \langle \bar{\sigma}_x \rangle_t^{(q-1)(q-2)/2} \tag{19a}$$

where the denominator reflects the $(q-1)$-times appearance of each NN bond in the product of three-site correlations, and the last term compensates for the "superfluous" presence of the central xth site in three- and two-site correlations;

$$\left\langle \bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\prod_{c}\bar{\sigma}_{(x+a)+c}\right\rangle_t = \frac{\langle \bar{\sigma}_{x+b}\bar{\sigma}_{x}\bar{\sigma}_{x+a}\rangle_t}{\langle \bar{\sigma}_{x}\bar{\sigma}_{x+a}\rangle_t} \times \left\langle \bar{\sigma}_{x+a}\prod_{c}\bar{\sigma}_{(x+a)+c}\right\rangle_t \tag{19b}$$

Inserting these decouplings into (6a)–(6c), we obtain a closed system of equations to be solved for site densities and three site probabilities of empty sites. At $t \to \infty$ the system reaches the correct equilibrium state characterized by the inverse profile (9) for the applied potential and the exact form of three-site correlations

$$\langle \bar{\sigma}_{x}\bar{\sigma}_{x+a}\bar{\sigma}_{x+b}\rangle_{t\to\infty} = \frac{(1-\rho_x^*-\rho_{x+a}^*)(1-\rho_x^*-\rho_{x+b}^*)}{(1-\rho_x^*)} \tag{20}$$

In order to describe the process of crytallization, we will now concentrate on the case of constant activity z while allowing inhomogeneity in particle densities on adjacent sublattices 1 and 2. The probabilities of a connected cluster of three empty sites with the central site on sublattice 1 or 2 will be denoted by $g_1^{(3)}$ and $g_2^{(3)}$, respectively. According to their definition, they are limited by

$$\max\{0, 1-\rho_\alpha-2\rho_\beta\} \leqslant g_\alpha^{(3)} \leqslant \min\{1, 2-\rho_\alpha-2\rho_\beta\} \tag{21}$$

where $(\alpha, \beta) = (1, 2)$ or $(2, 1)$. Taking into account (19a) and (19b), we find that Eqs. (6a) and (6c) yield

$$\dot{\rho}_1 = zf_1 - \rho_1 \tag{22a}$$

$$\dot{\rho}_2 = zf_2 - \rho_2 \tag{22b}$$

$$\dot{g}_1^{(3)} = -zf_1 - 2z\left(\frac{g_1^{(3)}f_2}{1-\rho_1-\rho_2}\right) - 2g_1^{(3)} + 2 - \rho_1 - 2\rho_2 \tag{22c}$$

$$\dot{g}_2^{(3)} = -zf_1 - 2z\left(\frac{g_2^{(3)}f_1}{1-\rho_1-\rho_2}\right) - 2g_2^{(3)} + 2 - \rho_2 - 2\rho_1 \tag{22d}$$

with f_α $(\alpha = 1, 2)$ defined by

$$f_\alpha = \frac{(g_\alpha^{(3)})^{q(q-1)/2}}{(1-\rho_1-\rho_2)^{q(q-2)}}(1-\rho_\alpha)^{(q-1)(q-2)/2} \tag{22e}$$

The investigation of the stability of the set of differential equations (22a)–(22e) with respect to the symmetric solutions $\rho_1 = \rho_2 = \rho$, $g_1^{(3)} = g_2^{(3)} = g^{(3)}$ can be performed in the whole space of $\{\rho, g^{(3)}\}$ values allowed by formula (21). For simplicity, we will restrict ourselves to physical situations in which the initial state of the system corresponds to a stable $(\rho \leqslant \rho_c^*)$ or unstable $(\rho > \rho_c^*)$ homogeneous equilibrium state with "equilibriumlike" constrained multisite correlations of type (8). The corresponding activity is modified at initial time $t = 0$ to the prescribed value z and our task is to answer whether or not there is a tendency at $t = 0$ for a sublattice density bifurcation. Putting $\rho_1 = \rho + \delta\rho_1$, $\rho_2 = \rho + \delta\rho_2$, $g_1^{(3)} = g^{(3)} + \delta g_1^{(3)}$, $g_2^{(3)} = g^{(3)} + \delta g_2^{(3)}$ with $g^{(3)} = (1-2\rho)^2/(1-\rho)$ into (22a)–(22e) and expanding all terms up to the first order in $\delta\rho_1$, $\delta\rho_2$, $\delta g_1^{(3)}$, $\delta g_2^{(3)}$, we find

$$\begin{pmatrix} \dot{\delta\rho}_1 \\ \dot{\delta\rho}_2 \\ \dot{\delta g}_1^{(3)} \\ \dot{\delta g}_2^{(3)} \end{pmatrix} = \begin{pmatrix} \begin{pmatrix} a_{11} & b_{11} \\ b_{11} & a_{11} \end{pmatrix} & \begin{pmatrix} a_{12} & b_{12} \\ b_{12} & a_{12} \end{pmatrix} \\ \begin{pmatrix} a_{21} & b_{21} \\ b_{21} & a_{21} \end{pmatrix} & \begin{pmatrix} a_{22} & b_{22} \\ b_{22} & a_{22} \end{pmatrix} \end{pmatrix} \begin{pmatrix} \delta\rho_1 \\ \delta\rho_2 \\ \delta g_1^{(3)} \\ \delta g_2^{(3)} \end{pmatrix} \tag{23}$$

where the matrix elements are functions of (ρ, z). Since the transformation matrix in (23) has the block-cyclic form, all its eigenvalues are available in analytic form. Three of them are negative in the whole region of the allowed values of (ρ, z), while the fourth one is positive provided that

$$(a_{11} - b_{11})(a_{22} - b_{22}) - (a_{12} - b_{12})(a_{21} - b_{21}) < 0 \tag{24}$$

This inequality can be achieved only when the real activity z lies in the interval $(z_{\text{min}}, z_{\text{max}})$ with z_{min} and z_{max} defined by

$$z_{\text{min}} = \frac{(1-\rho)^{q-1}}{2(q-1)(1-2\rho)^q} \left[2 + (q-3)\rho - \sqrt{D}\right] \tag{25a}$$

$$z_{\text{max}} = \frac{(1-\rho)^{q-1}}{2(q-1)(1-2\rho)^q} \left[2 + (q-3)\rho + \sqrt{D}\right] \tag{25b}$$

$$D = \left[\rho^2(q^3 - 8q^2 + 5q - 2) + 4\rho q(q+1) - 4q\right]/(q-2) \tag{25c}$$

The direction in which the instability takes place is the expected sublattice-symmetry breaking combination

$$c_1(\rho, z)(\rho_1 - \rho_2) + c_3(\rho, z)(g_1^{(3)} - g_2^{(3)}) \tag{26}$$

For coordination number $q = 3$, the instability region in the (ρ, z) plane is indicated by shading in Fig. 3. Now, the scenario turns out to be consistent. Increasing activity z from 0 up to z_c $(=4)$, one observes no

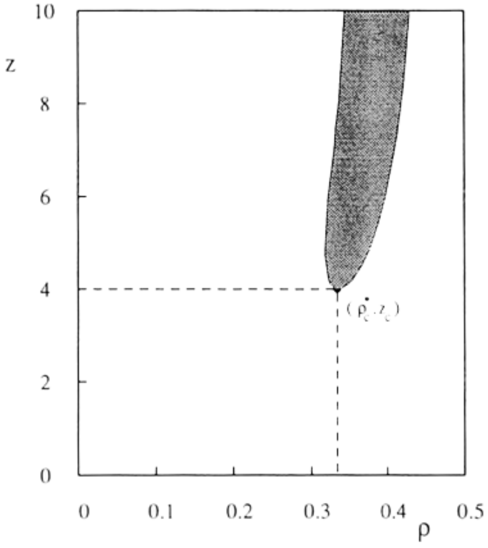

Fig. 3. As in Fig 2, at decoupling level $l = 3$.

instability on the hypersurface $\rho_1 = \rho_2$, $g_1^{(3)} = g_2^{(3)}$. As soon as $z = z_c$, the instability arises at the exact critical density $\rho_c^* = \frac{1}{3}$. Increasing z further, we find that the nonsymmetric fixed points play the dominant role and, simultaneously, there exists an instability interval in ρ depending on the strength of the external potential.

5.2. $l = 4$

There exist two different topological realizations of four-site clusters on the Bethe lattice with $q \geqslant 3$: the first consists of one central site at sublattice 1 (correlation notation $g_1^{(4)}$) or 2 ($g_2^{(4)}$) and its arbitrary three NN's on sublattices 2 and 1, respectively; the other is the sublattice-independent sequence, within the cluster, of one- and two-coordinated vertices ($g_{12}^{(4)}$). Proceeding in the previously outlined way, we obtain for $q = 3$, after some algebra, the following set of evolution equations:

$$\dot\rho_1 = zg_1^{(4)} - \rho_1 \tag{27a}$$

$$\dot\rho_2 = zg_2^{(4)} - \rho_2 \tag{27b}$$

$$\begin{aligned}\dot g_1^{(3)} = {} & -zg_1^{(4)} - 2z\frac{g_2^{(4)}(g_{12}^{(4)})^2}{g_1^{(3)}(g_2^{(3)})^2}(1-\rho_1-\rho_2) \\ & -2g_1^{(3)} + 2 - \rho_1 - 2\rho_2 \end{aligned} \tag{27c}$$

$$\begin{aligned}\dot{g}_2^{(3)} = {} & -zg_2^{(4)} - 2z\frac{g_1^{(4)}(g_{12}^{(4)})^2}{(g_1^{(3)})^2 g_2^{(3)}}(1-\rho_1-\rho_2) \\ & -2g_2^{(3)} + 2 - \rho_2 - 2\rho_1 \end{aligned} \tag{27d}$$

$$\begin{aligned}\dot{g}_1^{(4)} = {} & -zg_1^{(4)} - 3z\frac{g_1^{(4)}g_2^{(4)}(g_{12}^{(4)})^4}{(g_1^{(3)})^4 (g_2^{(3)})^4}(1-\rho_1-\rho_2)^3 \\ & -3g_1^{(4)} + 3g_1^{(3)} + \rho_1 \end{aligned} \tag{27e}$$

$$\begin{aligned}\dot{g}_2^{(4)} = {} & -zg_2^{(4)} - 3z\frac{g_1^{(4)}g_2^{(4)}(g_{12}^{(4)})^4}{(g_1^{(3)})^4 (g_2^{(3)})^4}(1-\rho_1-\rho_2)^3 \\ & -3g_2^{(4)} + 3g_2^{(3)} + \rho_2 \end{aligned} \tag{27f}$$

$$\begin{aligned}\dot{g}_{12}^{(4)} = {} & -z\frac{(g_{12}^{(4)})^2(1-\rho_1-\rho_2)}{g_1^{(3)}g_2^{(3)}}\left[\frac{g_1^{(4)}}{g_1^{(3)}} + \frac{g_2^{(4)}}{g_2^{(3)}}\right] \\ & -z\frac{(g_{12}^{(4)})^3(1-\rho_1-\rho_2)}{(g_1^{(3)})^2(g_2^{(3)})^2}[g_1^{(4)} + g_2^{(4)}] \\ & -2g_{12}^{(4)} + 2(1-\rho_1-\rho_2) \end{aligned} \tag{27g}$$

The results of numerical investigation of the stability properties of the system of differential equations (27a)–(27g) in the symmetric subspace $\rho_1 = \rho_2 = \rho$ with equilibrium-constrained correlations $g_1^{(3)} = g_2^{(3)} = (1-2\rho)^2/(1-\rho)$, $g_1^{(4)} = g_2^{(4)} = g_{12}^{(4)} = (1-2\rho)^3/(1-\rho)^2$, are represented graphically in Fig. 4. The "tongue" (I) originating at the critical point ($\rho_c^* = 1/3$, $z_c = 4$) corresponds to the instability along direction

$$c_1(\rho, z)(\rho_1 - \rho_2) + c_3(\rho, z)(g_1^{(3)} - g_2^{(3)}) + c_4(\rho, z)(g_1^{(4)} - g_2^{(4)}) \tag{28a}$$

leading to a sublattice density bifurcation. Note that in comparison with the $l = 3$ case the instability region is relatively large. The other instability region (II) originates at $\rho = 0$ very near to the critical activity $z_c = 4$ and corresponds to an instability along

$$\begin{aligned} & c_1(\rho, z)(\rho_1 + \rho_2) + c_3(\rho, z)(g_1^{(3)} + g_2^{(3)}) \\ & \quad + c_4(\rho, z)(g_1^{(4)} + g_2^{(4)}) + \bar{c}_4(\rho, z)\, g_{12}^{(4)} \end{aligned} \tag{28b}$$

This indicates an abrupt exponential time increase in density and correlations which is a natural consequence of the fact that the system is far from equilibrium. As shown in Fig. 4, the instability regions intersect one another, and the system with (ρ, z) parameters inside this intersection exhibits a simultaneous tendency to exponential time increase in densities and correlations as well as to a sublattice density bifurcation. The instability

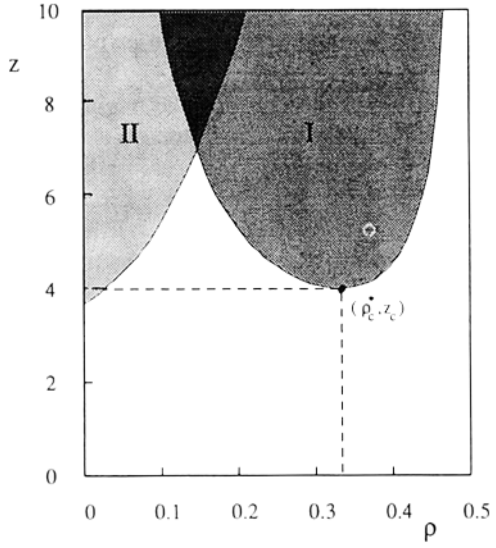

Fig. 4. As in Fig. 2, at decoupling level $l = 4$.

region (II) arising at the $l = 4$ approximation level might be intuitively associated with the first appearance of a cluster element containing both a vertex and its complete $q = 3$ coordination shell; we expect only small quantitative corrections in subsequent approximations.

6. CONCLUSION

The time evolution of a system of adsorbing and desorbing hard-core particles on a Bethe lattice in an inhomogeneous potential, governed by Glauber dynamics, is determined by the set of differential equations (6) for one-site densities and multisite probabilities of vacant connected clusters. At equilibrium, the articulation character of lattice points permits us to find not only the inverse profile relation (7) for applied potential, but also the exact density-dependent form of multisite correlations in the inhomogeneous regime (8), showing an interesting pairwise structure. This result motivated us in Section 3 to propose a natural hierarchical decoupling of nonequilibrium multisite correlations which automatically by its construction ensures the tendency of the system to true equilibrium with the exact form of the whole set of multisite correlations. This property is a necessary condition for obtaining consistently the nonequilibrium phase transition from a fluid to an inhomogeneous crystal phase under homogeneous external potential, accompanied by an instability leading to the bifurcation of sublattice densities. As soon as correlations are included in the instability mechanism (see Figs. 3 and 4), the results, although quantitatively dependent on the decoupling degree, are consistent in that instability in an equilibrated initial homogeneous state can arise only if the activity exceeds its critical value z_c (so that there exists an equilibrium crystal phase—the reason for a sublattice density bifurcation). The appearance of a new instability region for the system far from equilibrium (Fig. 4), associated with an exponential increase in densities and correlations in time, deserves attention. The numerical results indicate that there would be a correlation between the instabilities: both of them take place almost simultaneously when the activity acquires its critical value. This suggests a possible interplay "at distance" of different kinds of nonequilibrium instabilities.

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