

The dynamics of the Blume-Emery-Griffiths model

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Abstract

The Fock-space method is presented to analyze the dynamics of the Blume-Emery-Griffiths (BEG) model including both spin-flip and spin-exchange processes with weighted transition rates. In this connection, the master equation on a lattice is formulated in a Quantum-Hamiltonian technique with second quantized operators. Introducing raising and lowering Para-Fermi operators for spin $S = 1$ the master equation is established for a three-state model where two states represent two different kinds of particles and the remaining state corresponds to an empty state. The coupled dynamical equations for the particle density and the local relative composition are derived including fluctuation corrections in lowest order of a gradient expansion. Although the underlying dynamics are subjected to the exclusion principle the resulting equations of motion may be classified according to the scheme due to Halperin and Hohenberg where the field-dependent kinetic coefficients are given explicitly. The homogeneous stationary solutions of these dynamical equations correspond to the mean-field approximation of the BEG Hamiltonian. For a special case, the diluted kinetic Ising model, phase separation is observed below a characteristic temperature. Furthermore, the crossover between thermal and non-thermal driven processes is discussed.

1 Introduction

Recently, much attention has been devoted to the understanding of the kinetics of non-equilibrium phenomena. Various discrete kinetic models and continuous equations for such processes have been investigated analytically and numerically. Applications are discussed in relation to many problems, such as crystal

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growth, vapor deposition, bacterial colony growth, fire front motion, flux line in superconductors, directed polymers, chemical reactions, diffusion processes and glasses [1–8].

The main goal of the present paper is to apply a method which enables us to derive the underlying dynamical equations in a closed form based on microscopic assumptions. To reach this aim we start from the master equation for classical many-body systems [9–11]. This basic equation is defined on a lattice where each configuration is determined by the occupation of the lattice cells. Usually, every cell of size l can be occupied by a restricted or unrestricted number of particles or by only one specimen from a set of different kinds of particle (Within this paper the particle sorts are limited to three.). Therefore, a technique is needed to include such an exclusive Pauli-like principle. A very effective method in analyzing a master equation is the Fock-space formalism firstly introduced by Doi [12, 13], reformulated by Grassberger and Scheunert [14] and elaborated by Peliti [15] and Sandow et al. [16]. Originally, the approach [12–16] had been formulated in terms of Bose operators, later the method had been extended to a fermionic description [17–20] (for a comprehensive review see e.g. [21, 22]). Here, we want to present a further extension to a three-state model as an example for a multi-state system using Para-Fermi statistics [23, 24].

Moreover, between or inside of the cells some elementary processes take place originated on the scale of the cell size. Examples are flip or exchange processes. Both mechanisms will be incorporated in our model. To study the influence of temperature on the system the transition rates are weighted by the Hamiltonian of the Blume–Emery–Griffiths (BEG) model [25] according to the principle of detailed balance.

The applied BEG model is a special spin-1 model with bilinear and biquadratic nearest-neighbor pair interactions. It could be used to describe such phenomena as phase separation and superfluid ordering in ^3He - ^4He mixtures, condensation and solidification of binary fluids and phase separation as well as ferromagnetism in binary alloys [26–28]. Omitting the biquadratic exchange one obtains the Blume-Capel model [29, 30]. The model has been examined in different ways. Most of the earlier studies used the mean-field approximation to determine the equilibrium properties [25–28, 31]. The more recent ones applied renormalization group [32] or Monte-Carlo simulations [33, 34]. The investigations of the non-equilibrium properties are relatively few apart from the path-probability method [35] or the kinetic Glauber model [36].

Advantageous, the Fock-space method for the master equation enables us to produce the evolution equations of the observables (in the present case the density and the relative composition) in a closed form using the algebraic properties of the applied operators. In the present paper, the dynamics of the BEG model is mapped on the kinetics of a three-state system (Spin-1 model with $S = 0, \pm 1$). Whereas in Fermi-like systems only *one* relevant observable exists (usually the density *or* the relative composition) this model possesses *two* relevant observables, the density *and* the relative composition corresponding to two types of

ordering. Our special interest consists of the dynamical coupling between both.

Notice, that this paper is more devoted to demonstrate a new approach for the treatment of the dynamics of a three-state model than to analyze special systems (like those mentioned above) which will be done in forthcoming papers.

This paper is organized in the following manner: Section 2 summarizes the Fock-space representation of the master equation. In section 3 the Para-Fermi statistics is discussed and used to describe a general three-state system (with an empty state as the third component) by exploiting the algebraic properties of introduced operators. The relation between the evolution operator and the dynamics of the model is explained in section 4. In section 5 the dynamical equations are derived in detail using a mean-field approximation including fluctuation corrections in lowest order. The resulting coupled equations of evolution for the density and relative composition are discussed in general. A comparison with the classification due to Hohenberg and Halperin scheme [37] is carried out. Finally, dynamical equations and correlation functions are studied in some special cases (Section 6).

2 Fock-Space Representation

The system of interest is divided in small cells of size l . Then the state of the total system is characterized by a set of occupation numbers $\vec{n}=\{n_i\}$ where n_i denotes the occupation number of lattice site i . In our model, n_i should be restricted to the values 0, 1 and 2. If the probability for a certain configuration \vec{n} at time t is abbreviated by $P(\vec{n}, t)$ the one-step master equation may be written in the form

$$\partial_t P(\vec{n}, t) = L' P(\vec{n}, t). \quad (1)$$

The linear operator L' is specified by the dynamics of the system. According to Doi [12, 13] the probability $P(\vec{n}, t)$ can be related to the state vector $|\Pi(t)\rangle$ in a Fock space with the base vectors $|\vec{n}\rangle$. In addition, L' can be assigned to the time evolution operator \hat{L} resulting in the equivalent Fock-space master equation

$$\partial_t |\Pi(t)\rangle = \hat{L} |\Pi(t)\rangle \quad (2)$$

by means of (1). Because the base vectors can be composed from the vacuum state by creation and annihilation operators \hat{L} may be expressed in terms of second quantized operators. Apart from the structure of \hat{L} their algebraic properties (commutation relationships) determine the dynamics. The expansion

$$|\Pi(t)\rangle = \sum_{\{n_i\}} P(\vec{n}, t) |\vec{n}\rangle \quad (3)$$

assigns $|\Pi(t)\rangle$ with the base vectors $|\vec{n}\rangle$ by means of the probabilities $P(\vec{n}, t)$ and establishes a connection between the formalism of the quantum mechanics

and the approach based on the master equation. Supposing an arbitrary physical quantity \hat{G} can be decomposed in its diagonal form,

$$\hat{G} = \sum_{\{\mathbf{n}_i\}} \hat{G}(\vec{n}) |\vec{n}\rangle \langle \vec{n}|, \quad (4)$$

its expectation value is given by

$$\langle \hat{G}(t) \rangle = \sum_{\{\mathbf{n}_i\}} P(\vec{n}, t) G(\vec{n}) = \langle r | \hat{G} | \Pi(t) \rangle. \quad (5)$$

Notice, that in contrast to the quantum mechanics the average is only linear in the state vector. The bra-vector, $\langle r |$, is the reference state related to the base vectors by $\langle r | = \sum \langle \vec{n} |$. To allow $P(\vec{n}, t) \neq 0$ for every \vec{n} the reference state must include all possible base vectors. It will be specified in the following section. As a consequence, the reference vector fulfils the normalization condition $\langle r | \Pi(t) \rangle = 1$ which manifests the conservation of the probabilities. The time evolution of the operator \hat{G} can be written

$$\partial_t \langle \hat{G}(t) \rangle = \langle r | \hat{G} \hat{L} | \Pi(t) \rangle = \langle r | [\hat{G}, \hat{L}]_- | \Pi(t) \rangle \quad (6)$$

by deriving (5) and inserting into (2). In this connection, $\langle r | \hat{L} = 0$ was applied resulting from the conservation of the total probability. Up to now this procedure for the time evolution operator is general valid and independent from the used type of operators. Hence, the next task is to specify the operators and adapt them to the model.

3 Three-state Model

To avoid a double occupation and to describe elusive behavior at a certain lattice site the evolution operator \hat{L} in Eq.(2) may be expressed in terms of Pauli operators commuting at different sites and anticommuting at the same site. Recently, this approach has been extended to include a p -fold occupation [4,6,7]. It had been demonstrated that the afore mentioned situation can be concisely formulated in terms of local raising and lowering operators \tilde{a}_i^\dagger and \tilde{a}_i which are characterized by the double-commutator relation [23,24,38]

$$[\tilde{a}_i, [\tilde{a}_j^\dagger, \tilde{a}_k]_-]_- = 2\delta_{ij}\delta_{ik}\tilde{a}_k. \quad (7)$$

Notice, that the operators for different lattice sites commute in contrast the ordinary commutation rules for Para-Fermi statistics. To prove the double commutation relation it is convenient to expand the raising and lowering operators in terms of conventional Fermi operators b_i ,

$$\tilde{a}_i = \sum_{m=1}^p b_i(m), \quad (8)$$

where p denotes the maximal degree of the occupation and

$$[b_i(m), b_i^\dagger(n)]_+ = \delta_{m,n}. \quad (9)$$

Applying \tilde{a}_i and \tilde{a}_j^\dagger to a state yields

$$\tilde{a}_i^\dagger |n_i\rangle = \sqrt{(n_i + 1)(p - n_i)} |n_i + 1\rangle \quad (10)$$

$$\tilde{a}_i |n_i\rangle = \sqrt{n_i(p + 1 - n_i)} |n_i - 1\rangle. \quad (11)$$

In the subsequent sections we want to restrict ourselves to a three-state model. Hence, the possible base vectors are denoted by $|0\rangle$, $|1\rangle$ and $|2\rangle$ indicating in general empty, single and double occupied sites. However, they can be interpreted as well in some other fashions (compare [4, 7])

State	Ising model	Two-component model	Chemical reactions
$ 2\rangle$	Spin up	Substance A	Substance A
$ 1\rangle$	Empty size	Vacancy Θ	Substance B
$ 0\rangle$	Spin down	Substance B	Substance C

(12)

In the following sections the interpretation as a two-component system will be preferred. According to the rules (10) and (11) the action of the annihilation and creation operators onto the base states is given by (all for the same lattice index)

$$\tilde{a} |n\rangle = \sqrt{2}(1 - \delta_{n,0}) |n - 1\rangle \text{ and } \tilde{a}^\dagger |n\rangle = \sqrt{2}(1 - \delta_{n,2}) |n + 1\rangle \quad (13)$$

and $n = 0, 1, 2$. Hence, for simplifying all following equations one may choose $a_i^\dagger = \frac{\tilde{a}_i^\dagger}{\sqrt{2}}$ and $a_i = \frac{\tilde{a}_i}{\sqrt{2}}$, respectively. Using these operators the reference state vector $|r\rangle$ can be created by

$$|r\rangle = [1 + a^\dagger + (a^\dagger)^2] |0\rangle. \quad (14)$$

It is reasonable to define three projectors, \hat{A} , $\hat{\theta}$ and \hat{B} , where

$$\hat{A} |n\rangle = \delta_{n,2} |n\rangle, \hat{\theta} |n\rangle = \delta_{n,1} |n\rangle \text{ and } \hat{B} |n\rangle = \delta_{n,0} |n\rangle. \quad (15)$$

The projectors may be represented in elementary raising and lowering operators

$$\hat{B} = a a^\dagger a^\dagger = 1 - a^\dagger a, \hat{A} = a^\dagger a^\dagger a a = 1 - a a^\dagger. \quad (16)$$

bearing in mind $\hat{\theta} = 1 - \hat{A} - \hat{B}$. In this connection, the expression $\hat{N} = (1 - \hat{B}) + \hat{A}$ plays the role of the number operator with its eigenvalue relation $\hat{N} |n\rangle = n |n\rangle$. Naturally, the operators reveal the typical properties of projectors

$$\alpha\beta = \delta(\alpha, \beta) \alpha \text{ where } \alpha, \beta \in \{\hat{A}, \hat{\theta}, \hat{B}\} \quad (17)$$

and $\delta(\alpha, \beta) = 1$ only if both operators are identical else $\delta(\alpha, \beta) = 0$. Summarizing, these projectors map the states into the corresponding subspaces. To simplify the further calculations one can exploit the following relations

$$\begin{aligned} \hat{B}a^\dagger &= \hat{A}a = 0, & a(1 - \hat{B}) &= a, \\ \hat{A}a^\dagger &= a^\dagger(1 - \hat{B}), & (1 - \hat{B})a &= a\hat{A}, \\ (1 - \hat{A})a^\dagger &= a^\dagger\hat{B}, & Ba &= a(1 - \hat{A}). \end{aligned} \quad (18)$$

The usage of the expansion for the reference vector (14) and of the decompositions of the projectors (16) enables us to derive additional equivalence relations

$$\begin{aligned} \langle r | a^\dagger &= \langle r | (1 - \hat{A}), & \langle r | a &= \langle r | (1 - \hat{B}), \\ \langle r | a^\dagger a &= \langle r | (1 - \hat{B}), & \langle r | aa^\dagger &= \langle r | (1 - \hat{A}), \\ \langle r | aa &= \langle r | \hat{A}, & \langle r | a^\dagger a^\dagger &= \langle r | \hat{B}. \end{aligned} \quad (19)$$

Finally, we present some helpful commutation relation

$$\begin{aligned} [a^\dagger, \hat{A}] &= -a^\dagger(1 - \hat{B}), & [a^\dagger, \hat{B}] &= a^\dagger\hat{B}, \\ [a, \hat{B}] &= -a(1 - \hat{A}), & [a, \hat{A}] &= a\hat{A}. \end{aligned} \quad (20)$$

4 Model and Evolution Operator

Two elementary processes are incorporated in our model, the Glauber or flip dynamics and the Kawasaki or exchange dynamics.

Firstly, the Glauber dynamics [39] is characterized by a local flip processes from one state to another, and comprehends spin flip, chemical reactions or creation and annihilation of particles (compare to (12)). Within this paper it is regarded only as an one-site effect but extensions should be easily made. The related order parameter is *non-conserved* and corresponds to the *model A* due to [37]. In this sense, we study three one-site transitions at cell i indicated in our notation by

$$A_i \rightleftharpoons B_i, \quad A_i \rightleftharpoons \Theta_i, \quad B_i \rightleftharpoons \Theta_i.$$

The assigned kinetics coefficients (reaction rates) giving a measure for the velocities of the processes are λ_{AB} , $\lambda_{A\theta}$, $\lambda_{B\theta}$ and λ_{BA} , $\lambda_{\theta A}$, $\lambda_{\theta B}$, respectively.

Secondly, the Kawasaki dynamics [40] is necessary a spatial process where a spin- or particle exchange takes place between two sites. Unlike the first case the assigned order parameter is *conserved* corresponding to *model B* in the classification scheme. In this connection, we want to restrict our consideration to nearest-neighbors exchange processes denoted by

$$A_i B_j \rightleftharpoons A_j B_i, \quad A_i \Theta_j \rightleftharpoons A_j \Theta_i, \quad B_i \Theta_j \rightleftharpoons B_j \Theta_i$$

and assigned to the kinetics coefficients (exchange rates) k_{AB} , $k_{A\theta}$, $k_{B\theta}$.

Further, we express \hat{L} by means of the Fock-space method. As mentioned in the section above, the total probability are conserved if $\langle r | \hat{L} = 0$. It is advantageous for the calculation to split the time evolution operator for every single dynamics in two parts

$$\hat{L} = \hat{L}_r \hat{L}_c. \quad (21)$$

If \hat{L}_r fulfils the conservation then \hat{L} does it as well. Hence, \hat{L}_c is free to include further dynamics and restrictions to the states. A detailed computation shows that

$$\hat{L}_r = a_i^\dagger + a_i^2 - 1 \quad (22)$$

for one-site process (flip) and

$$\hat{L}_r = a_r^\dagger + a_r^2 - a_s^\dagger - a_s^2 \quad (23)$$

for a two-site process (exchange). If one specifies \hat{L}_c appropriated to the dynamics the following time-evolution operator emerges

$$\begin{aligned} \hat{L} &= L_{SF} + L_{SE} \\ L_{SF} &= + \sum_i (a_i^\dagger - 1) a_i^\dagger a_i [\lambda_{\theta A} a_i \parallel a_i^\dagger \parallel - \lambda_{A\theta} \parallel a_i \parallel] \\ &\quad + \sum_i (a_i - 1) a_i a_i^\dagger [\lambda_{\theta B} a_i^\dagger \parallel a_i \parallel - \lambda_{B\theta} \parallel a_i^\dagger \parallel] \\ &\quad + \sum_i \lambda_{BA} (1 - a_i a_i) [\parallel a_i^\dagger a_i^\dagger \parallel] + \sum_i \lambda_{AB} (1 - a_i^\dagger a_i^\dagger) [\parallel a_i a_i \parallel] \\ L_{SE} &= + \sum_{\langle rs \rangle} k_{A\theta} (a_r^\dagger a_s - 1) a_r^\dagger a_r a_r a_s^\dagger a_s^\dagger a_s \parallel a_r^\dagger a_s \parallel + \text{terms } (r \leftrightarrow s) \\ &\quad + \sum_{\langle rs \rangle} k_{B\theta} (a_r a_s^\dagger - 1) a_r a_r^\dagger a_r^\dagger a_s a_s a_s^\dagger \parallel a_r a_s^\dagger \parallel + \text{terms } (r \leftrightarrow s) \\ &\quad + \sum_{\langle rs \rangle} k_{AB} (1 - a_r a_r a_s^\dagger a_s^\dagger) \parallel a_r^\dagger a_r^\dagger a_s a_s \parallel + \text{terms } (r \leftrightarrow s) \end{aligned} \quad (24)$$

with the notation

$$\parallel O \parallel = \exp \left[\frac{-\beta H}{2} \right] O \exp \left[\frac{\beta H}{2} \right]. \quad (25)$$

This term is introduced in accordance with the principle of detailed balance applied in the Fock-space formalism [41]. It can be interpreted as a generalized kinetic coefficient thermal weighted by $\exp(-\frac{1}{2}\beta\Delta H)$ where the energy difference ΔH represents the energy gain or loss due to the elementary step. $\langle rs \rangle$ symbolizes the sum of the nearest-neighbor pairs with indices r, s . As H we chose the Hamiltonian of the Blume-Emery-Griffiths model [25] leading to the correct thermodynamical equilibrium. Neglecting the crystal field term the Hamiltonian can be written [26, 31]

$$H = h \sum_p s_p + J_0 \sum_{\langle pq \rangle} s_p s_q + J_1 \sum_{\langle pq \rangle} (s_p^2 s_q + s_p s_q^2) + J_2 \sum_{\langle pq \rangle} s_p^2 s_q^2. \quad (26)$$

Using the equivalence

$$s_p = \hat{A}_p - \hat{B}_p \quad \text{and} \quad s_p^2 = \hat{A}_p + \hat{B}_p \quad (27)$$

and introducing new energies

$$J_{AA} = J_0 + 2J_1 + J_2, \quad J_{BB} = J_0 - 2J_1 + J_2, \quad J_{AB} = J_2 - J_0 \quad (28)$$

the Hamiltonian may be reformulated for binary mixtures in a bath of vacancies

$$H = h \sum_p (\hat{A}_p - \hat{B}_p) + J_{AA} \sum_{\langle pq \rangle} \hat{A}_p \hat{A}_q + 2J_{AB} \sum_{\langle pq \rangle} \hat{A}_p \hat{B}_q + J_{BB} \sum_{\langle pq \rangle} \hat{B}_p \hat{B}_q. \quad (29)$$

In our notation negative energy J means attraction and positive values indicates repulsion between the particles. h stands for the external field.

Subject to the Hamiltonian, the evolution equations (6) and the relations derived in the previous section one obtains the temporal development of the expectation value for the operator \hat{A} at site k

$$\begin{aligned} \partial_t \langle \hat{A}_k \rangle &= +\lambda_{\theta A} \langle \theta_k M_k \exp(-\frac{1}{2}\beta h) \rangle - \lambda_{A\theta} \langle \hat{A}_k N_k \exp(\frac{1}{2}\beta h) \rangle \\ &+ \lambda_{BA} \langle \hat{B}_k M_k O_k \exp(-\beta h) \rangle - \lambda_{AB} \langle \hat{A}_k N_k P_k \exp(\beta h) \rangle \\ &+ \gamma_{A\theta} \left[\langle \theta_k M_k \Delta_k (\hat{A}_k N_k) \rangle - \langle \hat{A}_k N_k \Delta_k (\theta_k M_k) \rangle \right] \\ &+ \gamma_{AB} \left[\langle \hat{B}_k M_k O_k \Delta_k (\hat{A}_k N_k P_k) \rangle - \langle \hat{A}_k N_k P_k \Delta_k (\hat{B}_k M_k O_k) \rangle \right] \end{aligned} \quad (30)$$

and analogue for the operator \hat{B} at site k

$$\begin{aligned} \partial_t \langle \hat{B}_k \rangle &= +\lambda_{\theta B} \langle \theta_k P_k \exp(\frac{1}{2}\beta h) \rangle - \lambda_{B\theta} \langle \hat{B}_k O_k \exp(-\frac{1}{2}\beta h) \rangle \\ &+ \lambda_{AB} \langle \hat{A}_k N_k P_k \exp(\beta h) \rangle - \lambda_{BA} \langle \hat{B}_k M_k O_k \exp(-\beta h) \rangle \\ &+ \gamma_{B\theta} \left[\langle \theta_k P_k \Delta_k (\hat{B}_k N_k) \rangle - \langle \hat{B}_k O_k \Delta_k (\theta_k M_k) \rangle \right] \\ &+ \gamma_{AB} \left[\langle \hat{A}_k N_k P_k \Delta_k (\hat{B}_k M_k O_k) \rangle - \gamma_{BA} \langle \hat{B}_k M_k O_k \Delta_k (\hat{A}_k N_k P_k) \rangle \right] \end{aligned} \quad (31)$$

Here, we used the abbreviations

$$\begin{aligned} N_k &= \exp(\beta J_{AA} \sum_{j(k) \neq r} \hat{A}_j + \beta J_{AB} \sum_{j(k) \neq r} \hat{B}_j), \\ O_k &= \exp(\beta J_{AB} \sum_{j(k) \neq r} \hat{A}_j + \beta J_{BB} \sum_{j(k) \neq r} \hat{B}_j), \\ M_k &= N_k^{-1} \quad \text{and} \quad P_k = O_k^{-1}. \end{aligned} \quad (32)$$

It should be noticed that $\sum_{j(k)} \langle O_j - O_k \rangle$ corresponds to the discrete form of the Laplacian Δ_k acting on O at the site k . The notation $j(k)$ represents the

summation of all sites j adjacent to the site k . In case of exchange processes $j(k) \neq r$ means that the summation excludes the site r which is the position of the corresponding exchanged particle. $\gamma_{\alpha\beta}$ is a further abbreviation being equal to $2k_{\alpha\beta}l^2$ where l is the lattice unit and $\alpha, \beta \in \{A, B, \Theta\}$.

5 Equations of Evolution

5.1 Classification Scheme

In this section we will incorporate the dynamical equations to the classification scheme proposed by Hohenberg and Halperin [37]. As discussed in the previous section two different kinds of dynamics are considered corresponding to model A and B. If F is the free energy and φ_α the order parameter of interest one may relate them assuming a non-conserved behavior by the deterministic equation for *model A*

$$\partial_t \varphi_\alpha = -\Gamma_{\alpha\beta} \frac{\delta F}{\delta \varphi_\beta}. \quad (33)$$

However, if one analyses a conserved dynamics of φ_α corresponding to *model B* the relationship between both is given by the Cahn-Hilliard equation [43],

$$\partial_t \varphi_\alpha = \nabla \Gamma'_{\alpha\beta} \nabla \frac{\delta F}{\delta \varphi_\beta} \quad (34)$$

where $\Gamma_{\alpha\beta}$ and $\Gamma'_{\alpha\beta}$ are kinetic coefficients. As show below, the here introduced procedure leads to dynamical equations which can be classified according to (33,34) with general kinetic coefficients depending on the order parameters.

5.2 Equilibrium Properties

In the present model two relevant observables describe the behavior of the system, the relative composition, or in terms of BEG model the magnetization density, m and the particle density n . It should be stressed that m is the critical observable the dynamics of which consists of a conserved and a non-conserved part. The reason is that the flip processes change the total relative composition while exchange steps hold the total relative composition fixed. The other observable, n , reveals a strictly conserved behavior because we do not want to allow creation and annihilation processes of A and B particles. In order to derive an evolution equation by means of the free energy one may apply the Bragg-Williams formalism [26]. We start with the free energy (z is the number of nearest-neighbored sites.)

$$\begin{aligned} \beta F = & (1-n) \ln(1-n) + \frac{(n-m)}{2} \ln \frac{(n-m)}{2} \\ & + \frac{(n+m)}{2} \ln \frac{(n+m)}{2} + \beta z (J_0 m^2 + 2J_1 m n + J_2 n^2) \end{aligned} \quad (35)$$

where the particle density and the relative composition density are given by

$$m = n_A - n_B \quad (36)$$

$$n = n_A + n_B \quad (37)$$

if n_α is the density of substance α . The free energy (35) results as a special case from the general form

$$\beta F = \sum_{\alpha} n_{\alpha} \ln n_{\alpha} + \beta z \sum_{\alpha < \gamma} J_{\alpha\gamma} n_{\alpha} n_{\gamma}. \quad (38)$$

The first term represents the entropic contribution to the free energy whereas the second part yields the internal energy of the systems if $J_{\alpha\gamma}$ is the interaction energy between the substance α and γ . Specifying the densities to n_A , n_B and $1 - n = 1 - n_A - n_B$ it follows immediately the free energy (35). Minimizing this expression with respect to m and n leads to the equilibrium solution

$$\bar{m} = \frac{-2 \exp(-J_Q) \sinh(J_L)}{1 + 2 \exp(-J_Q) \cosh(J_L)}, \quad (39)$$

$$\bar{n} = \frac{2 \exp(-J_Q) \cosh(J_L)}{1 + 2 \exp(-J_Q) \cosh(J_L)} \quad (40)$$

with the arguments

$$J_L = \beta(h + 2zJ_0\bar{m} + 2zJ_1\bar{n}) \text{ and} \quad (41)$$

$$J_Q = 2z\beta(J_1\bar{m} + J_2\bar{n}). \quad (42)$$

The mean-field approximation of the Hamiltonian leads to the identical result if one identifies $\bar{m} = \langle s \rangle$ and $\bar{n} = \langle s^2 \rangle$ (see appendix A). The equilibrium solution (39) and (40) yields a simple equality between \bar{m} and \bar{n}

$$\bar{m} = \bar{n} \tanh[-\beta h - 2\beta z (J_0\bar{m} + J_1\bar{n})]. \quad (43)$$

This equation gives us an explicit dependency of \bar{m} on \bar{n} if $J_0 = 0$. Additionally, the equilibrium value of the free energy, F_E , can be computed to

$$\beta F_E = \ln(1 - \bar{n}) - \beta z (J_0\bar{m}^2 + J_1\bar{m}\bar{n} + J_2\bar{n}^2). \quad (44)$$

5.3 Dynamical Equations

The next step is to adapt the dynamical equations (30,31) to the classification scheme and to the free energy (35). Remaining in the particle picture (two-component system with vacancies) it is reasonable to neglect the particle exchange $AB \rightleftharpoons BA$ ($\gamma_{AB} = 0$) due to high energy barriers. As well as the creation and the annihilation of particles should be prohibited in our system ($\lambda_{A\theta} = \lambda_{B\theta} = \lambda_{\theta A} = \lambda_{\theta B} = 0$). Thus, only exchange via vacancies with the

kinetic transport coefficient $\gamma_{A\theta} = 2k_{A\theta}l^2$ and $\gamma_{B\theta} = 2k_{B\theta}l^2$ remains possible. In addition to the exchange dynamics we examine the flip dynamics $B \rightleftharpoons A$ with $\lambda_{AB} = \lambda_{BA}$ (symmetry of the model). Inserting these restrictions in (30,31) two coupled differential equations for $\langle \hat{A} \rangle$ and $\langle \hat{B} \rangle$ are obtained including the lowest order fluctuation corrections. Taking the continuous limit, $\langle \hat{A}_k \rangle \rightarrow n_A(\vec{x}, t)$ and $\langle \hat{B}_k \rangle \rightarrow n_B(\vec{x}, t)$, leads to evolution equations

$$\begin{aligned} \partial_t n_A &= +\lambda_{AB} [n_B \langle MO \rangle \exp(-\beta h) - n_A \langle NP \rangle \exp(\beta h)] \\ &\quad +\gamma_{A\theta} \nabla [(1 - n_A - n_B) n_A (\langle M \nabla N \rangle - \langle N \nabla M \rangle)] \\ &\quad +\gamma_{A\theta} \nabla [(1 - n_B) \nabla n_A + n_A \nabla n_B], \end{aligned} \quad (45)$$

$$\begin{aligned} \partial_t n_B &= +\lambda_{AB} [n_A \langle NP \rangle \exp(\beta h) - n_B \langle MO \rangle \exp(-\beta h)] \\ &\quad +\gamma_{B\theta} \nabla [(1 - n_A - n_B) n_B (\langle P \nabla O \rangle - \langle O \nabla P \rangle)] \\ &\quad +\gamma_{B\theta} \nabla [(1 - n_A) \nabla n_B + n_B \nabla n_A]. \end{aligned} \quad (46)$$

Such a decoupling is comparable with the coarse-graining procedure in equilibrium theory. This equation are valid for long spatial structures $\gg l$ and long time scales.

Now we want to neglect gradient terms of higher order in Eqs.(45,46) and approximate

$$\nabla \langle N \rangle \simeq (\beta J_{AA}(z \nabla n_A) + \beta J_{AB}(z \nabla n_B)) \langle N \rangle$$

and all other exponential terms of (32) in the same manner.

Further, to simplify the equations we restrict ourselves to the symmetric case of the diffusion coefficients

$$\gamma_0 = \gamma_{A\theta} = \gamma_{B\theta}.$$

Finally, it results a system of two coupled kinetic equations

$$\begin{aligned} \partial_t n &= -\gamma_0 \nabla j_n \\ &= +\gamma_0 \Delta n + \gamma_0 \nabla 2\beta z(1 - n) (J_2 n \nabla n + J_1 n \nabla m + J_1 m \nabla n + J_0 m \nabla m), \end{aligned} \quad (47)$$

$$\begin{aligned} \partial_t m &= -\gamma_0 \nabla j_m \\ &\quad +2\lambda_{AB}(n \sinh(-\beta h - 2\beta(zJ_0 m + l^2 J_0 \Delta m + zJ_1 n + l^2 J_1 \Delta n))) \\ &\quad -m \cosh(-\beta h - 2\beta(zJ_0 m + l^2 J_0 \Delta m + zJ_1 n + l^2 J_1 \Delta n)) \\ &= +\gamma_0 \Delta m + \gamma_0 \nabla (m \nabla n - n \nabla m) \\ &\quad +\gamma_0 \nabla 2\beta z(1 - n) (J_1 n \nabla n + J_0 n \nabla m + J_2 m \nabla n + J_1 m \nabla m) \\ &\quad +2\lambda_{AB}(n \sinh(-\beta h - 2\beta(zJ_0 m + l^2 J_0 \Delta m + zJ_1 n + l^2 J_1 \Delta n))) \\ &\quad -m \cosh(-\beta h - 2\beta(zJ_0 m + l^2 J_0 \Delta m + zJ_1 n + l^2 J_1 \Delta n)). \end{aligned} \quad (48)$$

If any spontaneous reaction or flip is prohibited ($\lambda_{AB} = 0$) both equations can be written as gradients of currents, i.e. both density and relative composition are

conserved quantities, representing continuity equations. Notice, that a non-zero coefficient λ_{AB} instantaneously leads to a violation of the conserved dynamics. Initially, we explore the case of vanishing mutual interaction or equivalently of infinite temperature ($\beta = 0$). The evolution of the density (47) goes over to the ordinary diffusion equation. But Eq.(48) yields a form already-known from the study of exclusion processes [17, 44]

$$\partial_t m = \gamma_0 \Delta m + \gamma_0 \nabla(m \nabla n - n \nabla m) \quad (49)$$

if one neglects the flip dynamics ($\lambda_{AB} = 0$). The second term represents a restricted diffusion originating from the dynamical coupling to the particle density n . The equation remains invariant under the transformation $m \rightarrow -m$ reflecting the missing preference of one kind of particles. However, in contrast to the typical transport processes, there is no symmetry under the transformation $n \rightarrow (1 - n)$ expressing the equivalence between the description of vacancies and particles. Rewriting this very last equation by replacing $v = 1 - n$ yields

$$\partial_t m = \gamma_0 \nabla(v \nabla m - m \nabla v). \quad (50)$$

There is a gain of the relative decomposition if an A particle diffuses to the area of interest (a loss if a B particle diffuse) and therefore displaces a vacancy (first term). However, the second term is the loss (gain) term indicating the opposite process. Taking the evolution for the vacancies

$$\partial_t v = \gamma_0 \Delta v \quad (51)$$

into account reveals that it exist a separation of the time scales within the system [44]. The vacancy density relaxes fast with the diffusion coefficient γ_0 to its equilibrium value $\bar{v} = \frac{N_0 - N}{N_0}$ (N_0 denotes the total number of lattice sites and N is the number of all particles.). Notice, due to the total conservation of the density this value only depends on the initial condition and is in general different from $1 - \bar{n}$. In contrast, the diffusion coefficient for the decomposition is mere $\gamma_0 v \simeq \gamma_0 O(N_0^{-1})$. Further, for late time regime the vacancies are uniformly distributed and v reduce to \bar{v} . Thus the equation of evolution for the relative composition transforms to the ordinary diffusion equation

$$\partial_t m = \gamma_0 \bar{v} \Delta m. \quad (52)$$

indicating that the relaxation of the decomposition slows down if the vacancy concentration decreases. Obviously, the occurrence of vacancies is needed to equilibrate the relative decomposition because the direct exchange between A and B particles is suppressed in our model.

On the other hand, the consideration of pure flip processes results in

$$\partial_t n = 0 = \partial_t(\bar{n}). \quad (53)$$

$$\begin{aligned} \partial_t m &= +2\lambda_{AB}(\bar{n} \sinh(-\beta h - 2\beta(zJ_0 m - l^2 J_0 \Delta m - zJ_1 \bar{n}))) \\ &\quad - m \cosh(-\beta h - 2\beta(zJ_0 m - l^2 J_0 \Delta m - zJ_1 \bar{n})). \end{aligned} \quad (54)$$

Obviously, the density becomes a constant \bar{n} and therefore the only varying quantity is the relative composition m . If one examines the second equation in a homogeneous equilibrium state $m = \bar{m}$ one obtains

$$\bar{m} = \bar{n} \tanh(-\beta h - 2\beta z (J_0 \bar{m} - J_1 \bar{n})) \quad (55)$$

the same result as in (43). Hence, the homogeneous equilibrium solution of our equations of motion is completely equivalent to that one resulting from the Hamiltonian (26) or from the free energy (35).

5.4 The Classification of the dynamical equations

Following the classification scheme proposed by Hohenberg and Halperin [37] one may rewrite equations (47,48) in a compact form relating to the transport processes only

$$\partial_t n = \gamma_0 \nabla \beta (1-n) n \nabla \frac{\delta F}{\delta n} + \gamma_0 \nabla \beta (1-n) m \nabla \frac{\delta F}{\delta m}, \quad (56)$$

$$\partial_t m = \gamma_0 \nabla \beta (1-n) m \nabla \frac{\delta F}{\delta n} + \gamma_0 \nabla \beta (1-n) n \nabla \frac{\delta F}{\delta m}. \quad (57)$$

This set of equations represents a generalized form of the known Cahn-Hilliard equation [43]. Obviously, these equations reveal the Onsager symmetry and remain invariant under transformation $m \rightarrow -m$. The temporal evolution of the particle density n is only dependent on the gradient terms as expected (globally conserved quantity).

Moreover, if one regards a non-linear diffusion by means of the first and second Fick's Laws (compare with [42]) one may express the temporal development of an arbitrary density ρ

$$\partial_t \rho = \nabla D(\rho) \nabla \rho = \nabla \sigma(\rho) \nabla \frac{\delta F}{\delta \rho} \quad (58)$$

where diffusion constant is denoted by $D(\rho)$ and the Onsager mobility is given by $\sigma(\rho)$. Hence, the Onsager mobilities are given by the pre-factors in front of the gradient terms in Eqs.(56,57). We can read off

$$\sigma_{n,m} = \beta(1-n)m = \sigma_{m,n}, \quad \sigma_{n,n} = \beta(1-n)n = \sigma_{m,m}. \quad (59)$$

Generally, all mobilities depend on $(1-n)$. Obviously, the diffusion does not take place in case of $n = 1$ because of missing empty sites being necessary for the particle transport. The diagonal terms $\sigma_{n,n}$ and $\sigma_{m,m}$ remain invariant under the transformation $n \rightarrow (1-n)$ reflecting the particle–vacancy symmetry. The non-diagonal terms $\sigma_{n,m}$ and $\sigma_{m,n}$ do not reveal such a symmetry.

If one wants to include the flip dynamics as well one must add the term

$$-2\lambda_{AB} n \frac{\delta F}{\delta m}$$

which is valid only for small relative composition density m and small particle density n (compare appendix B). Hence, in contrast to n , the equation of motion for m contains conserved terms and a non-conserved term $\propto \frac{\delta F}{\delta m}$.

As shown, this approach enables us to derive the Onsager coefficients directly from the master equation basing on a microscopic dynamics. Therefore, further assumptions are not necessary to determine them.

To gain more insight the model is studied for three separate cases within the next section: firstly, a *diluted kinetic Ising* model ($J_1 = J_2 = 0$), secondly, an *asymmetric model* ($J_0 = J_2 = 0$) and finally a *condensation model* ($J_0 = J_1 = 0$).

6 Specialized Models

6.1 Diluted Kinetic Ising Model

Firstly, let us start exploring the diluted kinetic Ising model differing from the ordinary kinetic Ising model by the inclusion of vacancies. This special model results if one sets $J_2 = J_1 = 0$ or equivalently $J_{AA} = J_{BB} = -J_{AB} = J_0$. Then the system can be interpreted as a lattice gas in which the particles of the same kind interact attractively or repulsively with each other and those of the different kind interact in the opposite manner. Adapting the evolution equations (47) and (48) to this special conditions yields

$$\begin{aligned}
\partial_t n &= -\gamma_0 \nabla j_{n,0} \\
&= +\gamma_0 \Delta n + \gamma_0 \nabla 2\beta z J_0 (1-n) m \nabla m, \\
\partial_t m &= -\gamma_0 \nabla j_{m,0} \\
&\quad + 2\lambda_{AB} (n \sinh(-\beta h - 2\beta z J_0 m - 2l^2 \beta J_0 \Delta m) \\
&\quad - m \cosh(-\beta h - 2\beta z J_0 m - 2l^2 \beta J_0 \Delta m)) \\
&= +\gamma_0 \Delta m + \gamma_0 \nabla (2\beta z J_0 (1-n) n \nabla m + m \nabla n - n \nabla m) \\
&\quad + 2\lambda_{AB} (n \sinh(-\beta h - 2\beta z J_0 m - 2l^2 \beta J_0 \Delta m) \\
&\quad - m \cosh(-\beta h - 2\beta z J_0 m - 2l^2 \beta J_0 \Delta m))
\end{aligned} \tag{60}$$

Further, one may particularize the density-relative-composition relation (43) leading to

$$\bar{m} = \bar{n} \tanh(-2\beta z J_0 \bar{m}) \cong \bar{n} \bar{m} (-2\beta z J_0) \left(1 - \frac{1}{3} \bar{m}^2 (-2\beta z J_0)^2 \right). \tag{62}$$

This allow us to define a density depended critical temperature

$$T_c = -2\bar{n} z J_0 = \bar{n} T_c^{Ising} \tag{63}$$

according with [45] and Monte Carlo simulations [46]. Notice, T_c^{Ising} is the mean-field critical temperature of the ordinary Ising model. Therefore, the

critical temperature decreases if the density decreases as well. Because of the missing constraints by the energetic interaction of the neighbor particles the system is prevented to establish an order above T_c . The more vacancies exist inside the system the more the effect gains strength. Obviously, above T_c it exists only one equilibrium solution $\bar{m}=0$, whereas below there are three solutions

$$\bar{m} = 0 \quad (64)$$

$$\bar{m}^2 \simeq 3\bar{n}^2 \left(\frac{T}{T_c}\right)^2 \left(1 - \frac{T}{T_c}\right). \quad (65)$$

One may examine the stability of the solutions by linearizing the equations with $n(t, x) = \bar{n} + \delta n(t, x)$ and $m(t, x) = \bar{m} + \delta m(t, x)$ leading to

$$\partial_t \begin{pmatrix} \delta n(t, x) \\ \delta m(t, x) \end{pmatrix} = M_0 \begin{pmatrix} \delta n(t, x) \\ \delta m(t, x) \end{pmatrix}. \quad (66)$$

Applying the Fourier transformation one obtains the eigenvalues of the matrix M_0

$$\begin{aligned} \kappa_{1/2} &= R_1 \pm \sqrt{R_1^2 + R_2} \text{ with} \\ R_1 &= +\frac{1}{2}\gamma_0(2 - \bar{n})q^2 + \frac{1}{2}\gamma_0\hat{J}_0\bar{n}(1 - \bar{n})q^2 \\ &\quad - \lambda_{AB}\frac{l^2}{z} \left[\hat{J}_0\bar{n} \cosh(-\hat{J}_0\bar{m}) - \hat{J}_0\bar{m} \sinh(-\hat{J}_0\bar{m}) \right] q^2 \\ &\quad + \lambda_{AB} \left[(1 + \hat{J}_0\bar{n}) \cosh(-\hat{J}_0\bar{m}) - \hat{J}_0\bar{m} \sinh(-\hat{J}_0\bar{m}) \right] \\ R_2 &= +\gamma_0\hat{J}_0\bar{m}(1 - \bar{n})q^2 \left[\gamma_0\bar{m}q^2 - 2\lambda_{AB} \sinh(-\hat{J}_0\bar{m}) \right] \\ &\quad - \gamma_0^2(1 - \bar{n})(1 + \hat{J}_0\bar{n})q^4 \\ &\quad + 2\gamma_0\lambda_{AB}\frac{l^2}{z} \left[\hat{J}_0\bar{n} \cosh(-\hat{J}_0\bar{m}) - \hat{J}_0\bar{m} \sinh(-\hat{J}_0\bar{m}) \right] q^4 \\ &\quad - 2\gamma_0\lambda_{AB} \left[(1 + \hat{J}_0\bar{n}) \cosh(-\hat{J}_0\bar{m}) - \hat{J}_0\bar{m} \sinh(-\hat{J}_0\bar{m}) \right] q^2. \quad (67) \end{aligned}$$

using the abbreviation $\hat{J}_0 = 2\beta z J_0$. As expected both eigenvalues $\kappa_{1/2}$ are negative above T_c for dominating exchange processes, whereas below T_c there are three different branches of \bar{m} . Eigenvalues assigned to branches with non-zero \bar{m} are both negative (i.e. stable), but one of the eigenvalues related to $\bar{m} = 0$ branch becomes positive, the other one remains negative. Focussing only on the flip dynamics at $q = 0$ one finds $\kappa_1 = 0$ and

$$\kappa_2 = -2\lambda_{AB} \left[(1 + \hat{J}_0\bar{n}) \cosh(-\hat{J}_0\bar{m}) - \hat{J}_0\bar{m} \sinh(-\hat{J}_0\bar{m}) \right]. \quad (68)$$

Exploiting this for zero \bar{m} the second eigenvalue, $\kappa_2 = -2\lambda_{AB} \left(1 - \frac{T_c}{T}\right)$, becomes negative above and positive below the critical temperature T_c . However, for non-zero \bar{m} below T_c , one obtains $\kappa_2 < 0$.

Moreover, the consideration of the correlation functions supports the achieved results. Inspecting the correlation functions $G_{n,n}(t) = \langle \delta n(t) \delta n(0) \rangle$, $G_{n,m}(t) = \langle \delta n(t) \delta m(0) \rangle$ and $G_{m,m}(t) = \langle \delta m(t) \delta m(0) \rangle$ leads after Fourier transformation to the equation system

$$\partial_t \begin{pmatrix} G_{n,n}(t) \\ G_{n,m}(t) \\ G_{m,m}(t) \end{pmatrix} = \tilde{M}_0 \begin{pmatrix} G_{n,n}(t) \\ G_{n,m}(t) \\ G_{m,m}(t) \end{pmatrix} + \text{terms}(t=0)\delta(q=0). \quad (69)$$

Focusing on the eigenvalues of \tilde{M}_0 one may read off the correlation length ξ and the relaxation times τ from the critical eigenvalue because \tilde{M}_0 can be decomposed in terms of $\exp[-(\xi^{-2} + q^2)\frac{t}{\tau}]$. If one regards the case above the critical temperature T_c the squared correlation length separates into two parts, i.e.

$$\xi^2(T, \bar{n}) = \frac{l^2 T_c}{z T} \left(1 - \frac{T_c}{T}\right)^{-1} + \frac{\gamma_0}{2\lambda_{AB}}(1 - \bar{n}) = \xi^2(T, 1) + \xi^2(\infty, \bar{n}) \quad (70)$$

The first term represents the temperature dependence of the pure Ising system whereas the second term denotes the contribution of the dilution for infinite temperature. Not surprisingly, the critical exponents ν with $\xi = (T - T_c)^{-\nu}$ takes the classical value for mean-field solution 2 if $T \rightarrow T_c$. In case of structures much larger than ξ the correlations diminish with the same velocity independently from their sizes. But within structures smaller than the correlation length ξ larger correlations need more time to decay than smaller ones. The relaxation time is given by

$$\tau = \left[2\lambda_{AB} \frac{l^2 T_c}{z T} + \gamma_0(1 - \bar{n}) \left(1 - \frac{T_c}{T}\right) \right]^{-1} \quad (71)$$

which would diverge at the critical temperature if the interaction term was neglected. Studies of the correlation length and the relaxation time of the stable solution for temperature below T_c reveal qualitatively similar behavior, especially the critical exponent ν is identical.

6.2 Asymmetric Model

Considering the case $J_0 = J_2 = 0$ which is fulfilled for $J_{AA} = -J_{BB} = 2J_1$ and $J_{AB} = 0$ this special model can be imagined as a binary system in which the particles of one component interact attractively and the other ones repulsively. The evolution equations (47) and (48) in terms of the fields m and n may be particularized

$$\begin{aligned} \partial_t n &= -\gamma_0 \nabla j_{n,1} \\ &= +\gamma_0 \Delta n + \gamma_0 \nabla 2\beta z J_1 (1 - n) (n \nabla m + m \nabla n), \\ \partial_t m &= -\gamma_0 \nabla j_{m,1} \end{aligned} \quad (72)$$

$$\begin{aligned}
& +2\lambda_{AB}(n \sinh(-\beta h - 2\beta(zJ_1 n + l^2 J_1 \Delta n))) \\
& -m \cosh(-\beta h - 2\beta(zJ_1 n + l^2 J_1 \Delta n)) \\
= & +\gamma_0 \Delta m + \gamma_0 \nabla(m \nabla n - n \nabla m) + \gamma_0 \nabla 2\beta z J_1 (1-n)(n \nabla n + m \nabla m) \\
& +2\lambda_{AB}(n \sinh(-\beta h - 2\beta(zJ_1 n + l^2 J_1 \Delta n))) \\
& -m \cosh(-\beta h - 2\beta(zJ_1 n + l^2 J_1 \Delta n)). \tag{73}
\end{aligned}$$

The homogeneous stationary solution for vanishing external field h is given by

$$\bar{m} = \bar{n} \tanh(-2\beta z J_1 \bar{n}) \tag{74}$$

using the relation (43). The relative composition is positive, i.e. it is preferred to accumulate A particles, whenever J_1 is negative (attractive interaction between A particles). Linearizing the equations in the same manner as above and considering the exchange dynamics only one obtains the eigenvalues of the stability matrix

$$\begin{aligned}
\kappa_{1/2} = & -\gamma_0 \left[\left(1 - \frac{\bar{n}}{2}\right) + \hat{J}_1(1 - \bar{n})\bar{m} \right] q^2 \\
& \pm \sqrt{\left(\hat{J}_1(1 - \bar{n})\bar{n} + \frac{\bar{n}}{2} \right)^2 - \hat{J}_1(1 - \bar{n})\bar{n}(\bar{m} - \bar{n})q^2}
\end{aligned} \tag{75}$$

with $\hat{J}_1 = 2\beta z J_1$. Inspecting the result in detail reveals that $\kappa_{1/2}$ are both negative. On the other hand, examining the flip dynamics only ($q = 0$) leads to the eigenvalue $\kappa_1 = 0$ and to the non-zero

$$\kappa_2 = -2\lambda_{AB} \cosh(-\hat{J}_1 \bar{n}). \tag{76}$$

The second eigenvalue remains always negative, i.e. the system behaves stably in case of small fluctuations.

6.3 Condensation Model

Finally, a condensation model should be explored where $J_0 = J_1 = 0$ is fulfilled by choosing $J_{AA} = J_{BB} = J_{AB} = J_2$. One may imagine this special case as a system with two indistinguishable kinds of particles and vacancies. If one focuses only on the parameter n (the second parameter m is coupled with it by (43)) the mean-field approximation yields

$$\partial_t n = -\gamma_0 \nabla j_{n,2} = +\gamma_0 \Delta n + \gamma_0 \nabla 2\beta z J_2 (1-n)n \nabla n. \tag{77}$$

Rewriting this equation leads to

$$\partial_t n = +\kappa_0 \Delta n + \mu (\nabla n)^2. \tag{78}$$

The κ_0 and μ are not constant, but spatial and temporal dependent quantities with

$$\kappa_0 = \gamma_0 [1 + 2\beta z J_2 (1 - n)n] \text{ and} \quad (79)$$

$$\mu = 2\gamma_0 \beta z J_2 (1 - 2n). \quad (80)$$

κ_0 plays the role of an effective diffusion coefficient. For small J_2 or high temperature one retains the ordinary diffusion equation. However, for strong coupling the interaction between the particles becomes important. I.e. for strong negative $J_2 < 0$ with $|J_2| > 2/z\beta$ it exists an instability expressing the strong attraction between the particles. Obviously, the evolution equation (78) reflects the particle-vacancy symmetry. Linearizing (77) as above it results in

$$\partial_t (\delta n(t, x)) = \kappa (\delta n(t, x)) \quad (81)$$

with

$$\kappa = -\kappa_0 q^2 = -\gamma_0 [1 + 2\beta z J_2 (1 - \bar{n})\bar{n}] q^2. \quad (82)$$

Exploiting the homogeneous equilibrium solution (40) and paying attention to the choice of the energies it leads to an implicit equation for the particle density

$$\bar{n} = \frac{2 \exp(-2\beta z J_2 \bar{n})}{1 + 2 \exp(-2\beta z J_2 \bar{n})}. \quad (83)$$

Taking the equilibrium solution (83) into account the eigenvalue κ in (82) remains always negative near the equilibrium.

7 Summary

Our main goal was to establish a method which allows a straight forward derivation of dynamical equations for a set of relevant observables. Applying this method leads to a coupled system of equations discussed in a mean-field approximation. Particularly, we have studied the relaxation times near the equilibrium corresponding to two elementary, Glauber and Kawasaki, processes in accordance with the *model A* and *model B*, respectively in the classification scheme due to Hohenberg and Halperin. The equilibrium solution of the BEG model is reflected in the homogeneous steady-state solution of our equations obtained by the mean-field approximation. Moreover, this solution agrees with the results derived from the Hamiltonian as well. Additionally, the relaxation time spectrum was examined in the long scale limit. There are modes which vanish for $q \rightarrow 0$ corresponding to the Goldstone modes while other modes tend to constant values describing a possible critical behavior. If those become zero a phase transition occurs, i.e. negative constant contributions indicate an unstable thermal system undergoing a kinetic phase separation. Further, we could reveal a connection between the free energy and the dynamical equations relating to the classification scheme of Hohenberg and Halperin. This leads to equations of type model B with well defined Onsager coefficients according with the introduced dynamics. These field-dependent coefficients reflect a more microscopic character due to their straight-forward derivation from the master equation.

The present method can be extended to a general description of coupled p -level (p -state) systems and so be used for the exploration of chemical reactions [4], a comprehensive analysis of the glass transition [7] or other related problems. In this connection, instead of the para-statistics one may use q -statistics as well [47, 48]. Furthermore, taking also higher correlation functions into account one obtains a hierarchy of equations which allows more insight in the local structure and its evolution of multi-state systems

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A MFA of the Hamiltonian

To carry out the mean-field approximation we use the Hamiltonian in (26) and apply the decomposition

$$s_i s_j = (s_i - \langle s \rangle)(s_j - \langle s \rangle) + s_i \langle s \rangle + s_j \langle s \rangle - \langle s \rangle^2, \quad (\text{A.1})$$

$$s_i^2 s_j = (s_i^2 - \langle s^2 \rangle)(s_j - \langle s \rangle) + s_i^2 \langle s \rangle + s_j \langle s^2 \rangle - \langle s^2 \rangle \langle s \rangle, \quad (\text{A.2})$$

$$s_i^2 s_j^2 = (s_i^2 - \langle s^2 \rangle)(s_j^2 - \langle s^2 \rangle) + s_i^2 \langle s^2 \rangle + s_j^2 \langle s^2 \rangle - \langle s^2 \rangle^2. \quad (\text{A.3})$$

Then we obtain the average values for the first and second moments

$$\langle s \rangle = \frac{-2 \exp(-J_Q) \sinh(J_L)}{1 + 2 \exp(-J_Q) \cosh(J_L)}, \quad (\text{A.4})$$

$$\langle s^2 \rangle = \frac{2 \exp(-J_Q) \cosh(J_L)}{1 + 2 \exp(-J_Q) \cosh(J_L)} \quad (\text{A.5})$$

if the fluctuations vanish. The reduced energies J_Q and J_L are given by

$$J_L = \beta(J + 2J_0 z \langle s \rangle + 2J_1 z \langle s^2 \rangle), \quad (\text{A.6})$$

$$J_Q = \beta(2J_1 z \langle s \rangle + 2J_2 z \langle s^2 \rangle) \quad (\text{A.7})$$

according with e.g. [26].

B Free energy

Starting with the Bragg-Williams free energy to derive the kinetic equations

$$\begin{aligned} \beta F = & [(1-n) \ln(1-n)] + \left[\frac{(n-m)}{2} \ln \frac{(n-m)}{2} + \frac{(n+m)}{2} \ln \frac{(n+m)}{2} \right] \\ & + [\beta z (J_0 m^2 + 2J_1 m n + J_2 n^2)] \end{aligned} \quad (\text{B.1})$$

which is split in three parts, every part for every square bracket term,

$$\beta F = F_1 + F_2 + F_3.$$

Firstly, we give the overall view of the equation of motion in terms of the variation of the free energy again

$$\partial_t n = \gamma_0 \nabla \beta (1-n) n \nabla \frac{\delta F}{\delta n} + \gamma_0 \nabla \beta (1-n) m \nabla \frac{\delta F}{\delta m} \quad (\text{B.2})$$

$$\partial_t m = \gamma_0 \nabla \beta (1-n) m \nabla \frac{\delta F}{\delta n} + \gamma_0 \nabla \beta (1-n) n \nabla \frac{\delta F}{\delta m} - 2\lambda_{AB} n \beta \frac{\delta F}{\delta m}. \quad (\text{B.3})$$

Now one may calculate the variation of each separated term and compare it with the equations of motion (47,48).

1. F_1 : Because this term is only dependent on n the only non-zero derivation of variation is given by

$$\nabla \frac{\delta F_1}{\delta n} = \frac{\nabla n}{(1-n)}. \quad (\text{B.4})$$

2. F_2 : Both derivations of the variations in respects to n and m are computed to

$$\nabla \frac{\delta F_2}{\delta n} = \frac{n\nabla n - m\nabla m}{n^2 - m^2} \quad \text{and} \quad (\text{B.5})$$

$$\nabla \frac{\delta F_2}{\delta m} = \frac{n\nabla m - m\nabla n}{n^2 - m^2} \quad (\text{B.6})$$

from which we may conclude

$$n\nabla \frac{\delta F_2}{\delta n} + m\nabla \frac{\delta F_2}{\delta m} = \nabla n \quad \text{and} \quad (\text{B.7})$$

$$m\nabla \frac{\delta F_2}{\delta n} + n\nabla \frac{\delta F_2}{\delta m} = \nabla m. \quad (\text{B.8})$$

Additionally, F_2 may be approximated for small m by

$$F_2 = n \ln \frac{n}{2} + \frac{m^2}{2n} \quad (\text{B.9})$$

resulting in the variation to

$$\frac{\delta F_2}{\delta m} = \frac{m}{n}. \quad (\text{B.10})$$

3. F_3 : The variation in respect to the relative composition for the last part of the free energy yields

$$\frac{\delta F_3}{\delta m} = 2\beta z(J_0 m + J_1 n).$$

Further, if one bears in mind the expansion for small values m and n ,

$$(n \sinh(-2\beta z J_w m) - m \cosh(-2\beta z J_w m)) \simeq -m - 2\beta z n(J_0 m + J_1 n), \quad (\text{B.11})$$

one approximately gets the original equations of motion (47) and (48).