A MEAN-FIELD METHOD FOR DRIVEN DIFFUSIVE SYSTEMS BASED ON MAXIMUM ENTROPY PRINCIPLE

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(ABSTRACT)

Here, we propose a method for generating a hierarchy of mean-field approximations to study the properties of the driven diffusive Ising model at nonequilibrium steady state. In addition, the present study offers a demonstration of the practical application of the information theoretic methods to a simple interacting nonequilibrium system. The application of maximum entropy principle to the system, which is in contact with a heat reservoir, leads to a minimization principle for the generalized Helmholtz free energy. At every level of approximation the latter is expressed in terms of the corresponding mean-field variables. These play the role of variational parameters. The rate equations for the mean-field variables, which incorporate the dynamics of the system, serve as constraints to the minimization procedure.

The method is applicable to high temperatures as well to the low temperature phase coexistence regime and also has the potential for dealing with first-order phase transitions. At low temperatures the free energy is nonconvex and we use a Maxwell costruction to find the relevant information for the system.

To test the method we carry out numerical calculations at the pair level of approximation for the 2-dimensional driven diffusive Ising model on a square lattice with attractive interactions. The results reproduce quite well all the basic properties of the system as reported from Monte Carlo simulations.

DEDICATION

To my parents

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CHAPTER I

INTRODUCTION

Most physical systems, involving many degrees of freedom, are not in equilibrium. Yet the development of the nonequilibrium statistical mechanics lags far behind its equilibrium counterpart. Therefore, the study of nonequilibrium phenomena is of fundamental interest. As a rule, nonequilibrium states are more diverse and complex than the equilibrium ones. One of the simplest nonequilibrium situations occurs when a system is maintained in a *steady state* by applying some external forces. Even in this case our understanding is quite incomplete compared to the equilibrium situation. Special interest is focused on a class of phenomena so similar to the equilibrium ones, that they are referred to as nonequilibrium (or kinetic) phase transitions. Sometimes they are termed as pattern formation, dissipative structures, etc. Such nonequilibrium transitions in physical, chemical and biological systems are widely studied in the current literature (e.g, [1 – 17]). Unlike equilibrium statistical mechanics, where many powerful methods for studying phase transitions exist, the statistical mechanics of nonequilibrium phase transitions is quite primitive. There is still little understanding of the critical behavior, such as exponents, scaling, universality classes.

Difficult problems led to studies via simplified models. Historically, simple models for systems in equilibrium have played an instructive role in reaching the present level of understanding of the cooperative behavior. One might expect that simple models of nonequilibrium systems would lead to useful results as well. A class of such models assumes that the time evolution of the probability of finding the system in some "grossly" defined state is governed by a master equation of a Markov chain. As the efforts were turned to more detailed levels of description and to deeper understanding of the microscopic mechanisms determining the phase transitions, the kinetic Ising models were introduced in the sixties by R. Glauber [18] and K. Kawasaki [19]. In these models, the transition probabilities depend on the thermodynamic parameters describing the phase transition, and are so constucted that the system finds itself in the equilibrium state in the infinite future.

The driven diffusuve Ising model (DDIM), was introduced in 1983 by S. Katz, J. Lebowitz and H. Spohn [1]. It is one of the simplest examples of an interacting system displaying general properties of a nonequilibrium steady state nontrivial behavior. The system consists of spins (or particles) located at the lattice sites of a regular lattice and interacting via a nearest-neighbor pair potential J (i.e., the usual Ising model). The system evolves according to a stochastic spin conserving (Kawasaki or else spin exchange) type dynamics. The nonequilibrium state is caused by some external driving force, assumed to be uniform and time independent. The external force is modeled by an "electric" field $\vec{E}$, driving the "spins" as though they were charged. Specifically, $\vec{E}$ biases "+" spins to move along and "−" spins against it. When periodic boundary conditions are imposed, a steady state current may be set up, while $\vec{E}$ cannot be represented as a a gradient of a potential globally. In addition the system interacts stochastically with a heat reservoir at fixed temperature T. The reservoir absorbs the Joule heat due to the current, and eventually, a steady state is reached by the system.

This system is also proposed as a model of a special class of materials – the fast ionic coductors with very promising properties for tecnological applications.

In this work we introduce a mean-field method for studying this driven diffusive Ising model. Results of its application for attractive interactions, at the pair level of approximation, are presented.

Mean-field theory is one of the oldest known analytic methods. Mathematical simplicity and physical basis are its advantages, accounting for its continuing use in the current literature. Numerous applications to a wide variety of physical systems led to a deeper understanding and intuition of the processes occuring in these systems. While mean-field theory is expected to be inadequate in describing details in the critical region, it is quite valuable in predicting qualitative features, such as phase diagrams.

Prior to this study, there were two mean-field approaches to the DDIM. First, H. van Beijeren and L. Schulman [13] proposed a simplified version of the model. Known as fast rate limit, this version relies an extremely anisotropic dynamics, i.e. exchange rates in the field direction being infinite. Later, dynamic mean-field theory was applied to the original DDIM by R. Dickman [15]. It involves *a priori* assumptions (about the order of the phase transition and existence of a critical slowing down in nonequilibrium) and is applicable only in the high temperature region.

Here, we propose a method for generating a hierarchy of mean-field approximations for treating the original DDIM, based on the principle of maximum entropy. It is applicable to the low temperature phase coexistence regime, and has as well the potential for dealing with first-order transitions.

This work is organized as follows. A detailed description of the model system is given in chapter II. The familiar kinetic Ising models are introduced and the physical considerations which dictate the choice of the transition rates are discussed (for $E = 0$ and $E \neq 0$). Section 2.2 of this chapter is devoted to the real materials, for which this system is proposed. Some of these materials are enumerated and a short account is given of their properties which make them candidates for broad applications.

The system has been a subject of intense investigations - numerical (Monte Carlo simulations) as well analytical. The scope of the previous studies of the system is presented in section 2.3. The most important observations are the following :

- A second order phase transition takes place as the temperature T is lowered, for all values of the driving field strength E ;
- The critical temperature $T_c(E)$ increases with E ;
- In the ordered phase, the interface is oriented along the field;
- The average current has a break in its slope at $T_c(E)$;
- Critical exponents seem to take neither the Ising nor mean-field values.

The proposed method is outlined in chapters III through V. In chapter III, some preliminaries are recounted for the master equation approach. We show, under well defined mean-field assumptions, how a hierarchy of equations is derived for the macroscopic variables - average values of spins and products of spins (or the reduced probability distributions). These are the rate equations. Adopting a mean-field description of the system amounts to :

- considering explicitly the correlations in a chosen basic cluster and all its subclusters;

- neglecting the correlations in larger clusters and between nonintersecting clusters;
- assuming a certain homogeneity in the system .

At the pair level of approximation, an example is considered in order to illustrate the method. The anisotropy, induced by the electric field, is taken into account by allowing the pair probability distributions along the field and in direction perpendicular to it to be different. In equilibrium, they are of course the same. The equations of motion for the macroscopic variables are derived by considering the contributions of two type of clusters, each consisting of two adjacent sites and all their nearest neighbors but with axes parallel and perpendicular to the field respectively. The equations are identical to these of R. Dickman's dynamic mean-field theory. However, Dickman's approach has serious limitations, recounted briefly below. At a given level of approximation, described by n independent mean-field variables, one gets $n-1$ nonlinear algebraic equations from the statement that the system is in a steady state. The "last" equation is trivial, due to the fact that the system is diffusive and the local order parameter m is conserved. Thus $\frac{dm}{dt} \equiv 0$. At high temperatures, $m = 0$ can be assumed so that the system of equations is closed and can be solved numerically. At low temperatures, however, $m(T, E)$ is expected to be nonzero and the system of equations is not closed. One needs additional hypotheses in order to solve them. We overcome this problem by adopting the point of view that the relevant information for the system can be extracted by applying the principle of maximum entropy.

In chapter IV we present some background on the information theory approach to statistical mechanics, initiated by E. T. Jayenes [20]. The exact statement of the

PME, as well the basic steps involved in its application to nonequlibrium systems, are given. The simplifications which occur (and which make our problem manageable) in the case of DDIM in mean-field approximation are stressed. The best probability distribution, describing a nonequilibrium system in contact with a heat reservoir, is obtained by applying PME to the combined system to yield the minimization of a generalized free energy $\psi = u - Ts$ [21], subject to constraints coming from the dynamics and any additional data about the system . Here, u and s are the internal energy and the entropy per site of the system and T is the temperature of the reservoir. We adopted here the characterization of the contact and the reservoir, given by R. Bowers and A. McKerrel [21].

At a fixed E and T , the free energy ψ can be expressed in terms of the mean-field variables which are appropriate at the given level of approximation, The variational parameters are the mean-field variables. An expression is derived in chapter V in a purely combinatorial way, using a generalization of the familiar Kikuchi cluster variation method [22] for equilibrium cases . The general idea of the method is described in sec. 5.1. The specific derivation of ψ for DDIM is within the framework of Morita's formulation [23, 24] of the cluster variation method. His formulation offers a particularly clear and simple derivation, by making all the approximations explicit. It is independent of the underlying lattice structure. Only a slight modification is needed in order to account for the field. In order to extend the method to treat the antiferromagnetic case and higher level of approximations, all the variables were expressed in terms of independent correlation functions, following a scheme proposed in [25, 26] by J. Sanchez and D. de Fontaine.

Applying the general procedure, outlined in chapter IV, amounts to minimizing the free energy with respect to the mean-field variables. The rate equations, incorporating the dynamics and defining the steady state of the system, serve as constraints to the minimization procedure. By imposing these as constraints, the effect of the electric field is accounted for through the rates.

To test the method, the above procedure has been carried out numerically at a pair level of mean-field approximation for the two-dimensional DDIM on a square lattice with attractive interaction. The results are described and discussed in chapter VI. They reproduce quite well the basic properties and the qualitative behavior of the system as described in [1,2]. The dependence of various physical quantities as a functions of the temperature of the resrvoir T at fixed field E and as functions of E at fixed T are displayed graphically. The effect of different transition rates on the steady state properties of DDIM was also studied. Comparisons with the results from Monte Carlo simulations and R. Dickman's dynamic mean-field theory are made.

CHAPTER II

THE MODEL, REAL MATERIALS AND SCOPE OF

THE PRESENT RESULTS

2.1. Driven diffusive Ising model

The model under investigation was originally introduced by S. Katz, J. Lebowitz and H. Spohn [1] in order to study nonequilibrium steady state properties of a simple interacting system and also as a model for some fast ionic conductors (FIC). A very precise and elaborate definition is given in stochastic lattice gas form in [2]. Here the Ising spin version of the driven diffusive system is described.

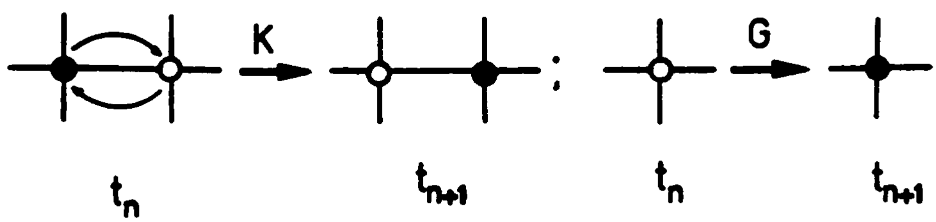
This idealized system consists of Ising spins σ_i $(\sigma_i = \pm 1)$ (particles or ions in lattice gas version) located at the sites, labeled by i , of a regular hypercubic d-dimensional lattice. In principle, we are interested in the properties only for a system with infinite volume. In practice, i.e., both physical systems and simulation studies, finite lattices $(\Lambda \subset Z^d)$ are inevitable. The phase space of the system is the set of all possible configurations $\{\sigma\}$, where the full spin configuration σ is given by specifying the spin of every lattice site $\sigma = \{\sigma_i\}_{i\in\Lambda}$. The internal interactions are specified via a Hamiltonian

$$H[\sigma] = -J \sum_{<ij>} \sigma_i \sigma_j \quad , \tag{2.1}$$

where J is the nearest-neighbor pair potential and $< ij >$ as usual denotes the summation only over nearest-neighbor sites. $J > 0$ describes ferromagnetic (attractive) and $J < 0$ antiferromagnetic (repulsive) interaction. The system is in thermal contact with a heat reservoir at temperature T. Static properties of the Ising model at equilibrium with a thermostat are well known. All can be derived from the time independent probability distribution,

$$\rho_{eq}(\sigma) = \frac{1}{Z}\exp(-H[\sigma]/k_B T) \quad ,$$

for finding a spin configuration σ in the system (Z denotes as usual the partition function : $Z = \sum_{\{\sigma\}} \exp\{-H[\sigma]/k_B T\}$). To model time evolution and transport properties at the mesoscopic level, the familiar kinetic Ising models have been introduced in the sixties (see the original papers by Glauber [18] and Kawasaki [19] and the review article by Kawasaki [27]). The different models are specified by different types of stochastic dynamics. For example, the system can evolve in time due to exchanging the spins at two lattice sites (Kawasaki type dynamics) or due to spin flips (Glauber type dynamics) performed with certain rates (see the picture below).



In this approach the time evolution of the probability distribution $\rho_t(\sigma)$ to find a spin configuration σ at discrete times t is derived from the assumption that the system can be modeled by a stationary Markov chain (no memory effects), and obeys a certain master equation. Derivation of the kinetic Ising models from the classical or quantum-mechanical Liouville equation is given by Heims (1965), under certain assumptions, on the basis of the existing general theory (Hubbard 1961) of relaxation of spins in contact with a heat reservoir.

Once the form of the dynamics is chosen, time evolution is completely specified by prescribing the transition rates (probabilities per unit time) for a configuration σ to evolve to σ' : $\Phi(\sigma \to \sigma')$. Though there are constraints on Φ , due to general physical considerations, there are infinitely many choices for Φ and some important properties of the NESS system may depend on the particular rates. Since we wish to model a system of charged ions, we must consider a particle–number conserving dynamics. In the spin language, this restricts us to a spin exchange (or Kawasaki) dynamics, which preserves the total spin of the system $S = \sum_i \sigma_i$. To reflect the existing symmetry in the system in the absence of a driving force it is convenient to require

$$\Phi(i,j,\sigma) = \Phi(j,i,\sigma) \geq 0$$

as the rate at which the spins at sites i and j are exchanged when the configuration of the system is σ . If $\sigma_i = \sigma_j$, then the exchange does not change the configuration of the system and $\Phi(i,j,\sigma)$ could be taken to be zero. Let σ^{ij} denotes the configuration obtained from σ by interchanging the spins at sites i and j, then:

$$(\sigma^{ij})_k = \begin{cases} \sigma_j, & \text{if } k = i \\ \sigma_i, & \text{if } k = j \\ \sigma_k, & \text{if } k \neq i,j. \end{cases}$$

The master equation for DDIM, in this notation , has the following form:

$$\begin{aligned} \frac{d}{dt}\rho_t(\sigma) &= \sum_{<ij>} \left[\Phi(i,j,\sigma^{ij})\rho_t(\sigma^{ij}) - \Phi(i,j,\sigma)\rho_t(\sigma)\right] \\ &\equiv \mathcal{L}\rho_t(\sigma) \end{aligned}$$

Usually the following constraints are imposed:

(i) For simplicity only nearest-neighbor exchanges are considered, i.e. $\Phi(i,j,\sigma)=0$ for $|i-j|>1$. $\Phi(i,j,\sigma)>0$ for $|i-j|=1$ and $\sigma_i \neq \sigma_j$ is usually required to ensure that the only conserved quantity is the total spin of the system $S=\sum_i \sigma_i$.

(ii) In the absence of an external force the rates should be such that, in the infinite future, the system should find itself in the canonical Gibbs equilibrium state

$$\rho_t(\sigma,S) \underset{t\to\infty}{\to} \rho_{eq}(\sigma)\,\delta\left(\sum_i \sigma_i - S\right) \quad .$$

This requirement is satisfied by imposing the detailed balance condition on the rates

$$\Phi(i,j,\sigma)=\Phi(i,j,\sigma^{ij})\exp(-\Delta H^{<ij>}/k_B T) \quad , \tag{2.2}$$

where

$$\Delta H^{<ij>} = H(\sigma)-H(\sigma^{ij}) \tag{2.3}$$

is the change in the energy of the system when a pair exchange has been performed.

(iii) Finally the rates are required to obey certain symmetry and homogeneity properties, i.e. they should be invariant under translations :

$$\Phi(i+n_1\hat{e}_1, j+n_2\hat{e}_2, \tau_{n_1 n_2}\sigma)=\Phi(i,j,\sigma) \quad .$$

Here, $\hat{e}_1$ and $\hat{e}_2$ are the lattice vectors (for simplicity it is assumed that the lattice constant $a=1$) and $\tau_{n_1 n_2}\sigma$ is a configuration, obtained by shifting σ by a vector $n_1\hat{e}_1+n_2\hat{e}_2$, modulo the periodicity of Λ .

Next, an external, uniform and time independent driving force is imposed on the system and the question of the boundary conditions becomes crucial. To model the effect of the driving force on an infinite system the finite lattice is assumed to have periodic boundary conditions. Eventually a steady current flows in the system and a nonequilibrium steady state is attained in the system. The driving force can be modeled by a hypothetical electric field $\vec{E}$ which acts on the particles (i.e."+" spins) as though they were charged. The field $\vec{E}$ cannot be a gradient of a potential globally, although it is so locally. An important remark should be made here. Because of the periodic boundary conditions the electric field could not be included in the Hamiltonian. A solution of the form:

$$\frac{1}{Z}\exp\left(-\beta H(\sigma)+\beta\sum E\cdot i\frac{(\sigma_i+1)}{2}\right) \quad , \quad \beta=\frac{1}{k_BT}$$

is a stationary solution of the master equation with free boundary conditions . However, this solution represents a gas in a uniform field in equilibrium with the heat reservoir with no transport; moreover it is inhomogeneous in space. We would like the field to bias the exchanges in a given direction and thus to produce a homogeneous current. Here, for simplicity $\vec{E}$ is taken to be parallel to one of the lattice vectors $\hat{e}_1, \hat{e}_2$ (e.g., $\vec{E} = E\hat{e}_1$). One can think of the field as produced by a uniformly increasing with the time magnetic flux through a loop (i.e. the system, represented by periodic boundary conditions). The heat reservoir absorbs the heat generated by the current and thus maintains the steady state.

Now, we must consider what kind of rate functions Φ will produce this physical situation. Physically it seems reasonable [2] to assume a local detailed balance condition including the local work done by the electric field in the exchange. This leads to :

$$\Phi(i,j,\sigma)=\Phi(i,j,\sigma^{ij})\exp\left(-\Delta H^{<ij>}/k_BT\right)\exp\left(E(i-j)(\sigma_i-\sigma_j)/2k_BT\right) \quad .$$

E stands actually for qEa (recall that $a = 1$), where q is the charge. Further, in addition to the requirements and symmetries, listed above, one can also add :

– invariance under spatial reflection of both configuration and the driving force;

– invariance under spin conjugation $(\sigma \to -\sigma)$ and reversal of the driving force $E \to -E$.

The most general form of the exchange rates consistent with these requirements are

$$\Phi_E(i,j,\sigma) = \begin{cases} \Gamma_{\parallel}\phi([\Delta H^{<ij>} + E(i-j)(\sigma_i - \sigma_j)/2]/k_BT)(1-\sigma_i\sigma_j)/2, & i-j = \pm\hat{e}_1 \\ \Gamma_{\perp}\phi(\Delta H^{<ij>}/k_BT)(1-\sigma_i\sigma_j)/2, & i-j = \pm\hat{e}_2 \end{cases} \tag{2.4}$$

Here $\Gamma_{\parallel}$ and $\Gamma_{\perp}$ have the units of inverse time and set the time scales for attempting exchanges of pairs of spins in direction parallel and perpendicular to the field $\vec{E}$ respectively (they are called sampling rates). The function ϕ satisfies $\phi(\lambda) = \phi(-\lambda)e^{-\lambda}$ according to detailed balance (2.2). The factor $(1 - \sigma_i\sigma_j)/2$ ensures that the condition (i) is implemented. $\Delta H^{<ij>}$ is given explicitly by :

$$\Delta H^{<ij>} = 2J\left(\sigma_i \sum_{<im>} \sigma_m + \sigma_j \sum_{<jm>} \sigma_m - 2\sigma_i\sigma_j\right) \quad . \tag{2.5}$$

From (2.1) and (2.3) it follows that $\Delta H^{<ij>}$ depends only on the local cluster configuration of (i,j) and its nearest neighbors.

The rates (2.3) with different choices of the ratio $\Gamma_{\parallel}/\Gamma_{\perp}$ and the particular form of $\phi(\lambda)$ define different variants of the DDIM.

The results of previous studies of this system are given in section 2.3 and the results of our treatment of the system on square lattice are described in chapter V.

2.2. Fast ionic conductors

Solids with high ionic conductivity below the melting point are known as "superionic solids", "solid electrolytes" or "fast ionic conductors". In order for a solid to be recognized as a FIC its ionic conductivity $\bar{\sigma}_i$ has to be comparable to (or even exceed) the ionic conductivities of molten salts and electrolyte solutions [28], [29] (usually $\bar{\sigma}_i \geq 5\ 10^{-2}[\Omega.cm]^{-1}$ as compared to $10^{-8}[\Omega.cm]^{-1}$ for $NaCl$ at 200°) and its electron conductivity $\bar{\sigma}_e$ has to be at least two orders of magnitude lower . The usual characterization of the superionic phase, according to M. B. Salamon [30], also includes low activation energy ($\leq 0.3\ eV$) and an open structure of the crystal with a network of vacant sites available to one of the ionic species. To make the list of the properties of the FIC more complete one has also to add some important dynamic and collective effects, which distinguish them from the other ionic crystals, like the absence of well defined optical lattice modes, phase transitions, an infrared peak in the frequency-dependent conductivity, unusual nuclear magnetic resonance prefactors, the presence of a pervasive, low energy excitation and a strong tendency for the mobile ion to be found between allowed states.

Ionic conductivity was reported by Faraday in 1834, but the ionic solids have received little attention in the past, the main reason for that being the lack of solids with high ionic conductivity. Interest revived in 1967 when a fast sodium-ion conductivity in β-alumina and silver-ion conduction in MAg_4I_5 (where $M =$ K, Rb, NH_4) was discovered. Since then a large number of such solids have been found and they have been subject of quite intensive (especially in the last fifteen years) investigation, both experimental and theoretical (see e.g. [28-32] and the references therein). The main focus is on several "clasic" superionic conductors –

$\alpha - AgI$, $\alpha - RbAg_4I_5$, $\beta-$alumina, the fluorites, the copper halides and few quasi one dimensional materials.

Since enough experimental data were gathered, several attempts have been made to classify the FIC (e.g O'Keefe in [29]) according to their properties and the kind of phase transition they exhibit. According to Pardee and Mahan [31], there are roughly three classes of FIC materials.

The type I materials are characterized by a first order (or discontinuous) phase transition. They exhibit discontinuity in conductivity at the transition temperature, a latent heat and change in lattice symmetry (a typical example is AgI with jump in the conductivity four orders of magnitude). The type II FIC undergo a second-order (or continuous) phase transition or very weak first-order transition. The materials in this group show a change (abrupt or more gradual) only in the slope of the conductivity versus temperature curve (examples are $AgCrS_2$, PbF_2 and others). They exhibit power law divergence in the specific heat at the transition temperature and no change in the lattice symmetry. Some studies of the critical properties of the FIC show that the critical behaviour of these materials is close to the equilibrium three-dimensional Ising model.

$Na - \beta - Al_2O_3$ is considered as being of type III FIC (considered to have a Faraday transition). The conductivity of these materials increases exponentially over a broad range of temperatures with no signals of a phase transition).

The strong interest in the superionic conductors has been initially motivated by the their promising properties for technological applications (e.g. for use in solid state batteries, fuel cells, memory devices, display panels, sodium heat engine etc.). But their very interesting physical properties have led to a more fundamental interest in the FIC, e.g. these materials may be thought of as providing a link between solids and liquids. One may think of a superionic conductor as a liquid of one type of ions moving through a lattice set up by different type of ions.

Lattice gas models have been proposed at early stages to model the properties of some of the FIC. The mobile ions are considered as "lattice gas"- particles which can hop to nearest-neighbor empty sites. The interaction between them can be modeled by Ising antiferromagnetic (repulsive) Hamiltonian with nearest-neighbor interactions only (due to a Debye screening)

$$H = -J \sum_{<ij>} n_i n_j \quad , \quad (J < 0)$$

For derivations of different lattice gas models and justification of their relevancy and applicability to particular classes of materials see [30] and [32] and references therein. In general, lattice gas models are appropriate for materials in which the average time ions spend in flight τ_f is small compared to the time they spend at the lattice site τ_{res} , i.e. $\tau_f/\tau_{res} \to 0$ and also their underoccupancy should be $\geq 10^{18}\ cm^{-3}$. (There are many superionic conductors for which this condition does not hold and different mechanisms are suggested to explain their high ionic conductivity.) It has to be stressed, however, that all of these studies concern the equilibrium situation or small electric fields and the proper treatment of the properties of the FIC should take into account that these are nonequilibrium properties. The influence of an arbitrary large external electric field was incorporated in the discrete lattice gas version of the fast ionic conductors and studied by Katz, Lebowitz, Spohn [1]. Thus FIC provide an example of relatively simple interacting system in nonequilibrium steady state.

There is another feature of FIC which makes them also an attractive object of investigation - i.e. the low dimensionality effects. There exhist FIC materials like KAg_4I_5 , hollandite ($K_{2x}Mg_xTi_{8-x}O_{16}$), 1-dimensional β-eucryptite, where the ions are restricted to moving in channels, or sodium β-alumina ($(1+x)Na_2 \cdot 11Al_2O_3$) in which conduction is restricted to a 2-dimensional plane whenever the applied electric field is parallel to the planes formed by the sodium (Na^+) ions [28]. $AgCrS_2$ is another material which also exhibits two dimensional properties.

Of course, one has always to keep in mind that a lattice gas is a quite crude and oversimplified model of the real physical system.

2.3. Scope of the present results

2.3.1. Results from Monte Carlo simulations

The first results about DDIM are obtained in 1983 from both Monte Carlo simulations and theoretical studies by S. Katz, J. Lebowitz and H. Spohn [1]. Since then it has become a subject of intense investigation. These early studies have concentrated on a half filled, two-dimensional square lattice with Metropolis transition rates, attractive ($J > 0$) interactions and periodic boundary conditions. The basic results [1,2] can be summarized as follows :

– there is a second order transition which persists at any field strength E ;

– the critical temperature increases with E ;

– the ordered phase is anisotropic, the system segregates in the direction perpendicular to the field, into $+m$- and $-m$-magnetization ("fluid" and "gas") phases. In contrast, for an equilibrium system ($E = 0$) on a square sample, segregation in either direction is possible below the Onsager critical temperature $T_c = 2.269|J|/k_B$;

– the critical exponents appear to be different from the $E = 0$ case;

– the average current has a break in its slope at the critical temperature.

Very little was known for the repulsive ($J < 0$) case besides the decrease of the critical temperature with E .

It was proved in this work that the Kubo formula for the bulk diffusivity also holds in the steady state with finite field E , which is the first rigorous proof of the Kubo relation for a steady state transport coefficient in an interacting system.

These results have been corroborated by more extensive runs performed by J. Marro, J. Lebowitz, H. Spohn and M. Kalos [3] and J. Valles and J. Marro [4] .

In [3] the three-dimensional DDIM has been studied and the same basic properties were found, but $T_c(E)$ increases with E substantially less strongly than in two dimensions. The numerical results suggested that the coexistence curve critical exponent is larger than the equilibrium value $\beta \approx 5/16$ and it is probably of mean-field type.

More detailed numerical studies for the $d = 2$ case by J. Marro and J. Valles [5,6] of the critical behaviour in two dimensions yield an order parameter exponent $\beta = 0.23$. Since the Onsager result is 0.125 and the mean-field value is 0.5 this exponent would place the model in a new universality class, distinct from Ising and mean-field classes.

The case of off-critical densities (i.e. $\rho \neq 1/2$) was treated in [7]. Computer simulations for $\rho = 0.05,\ 0.075,\ 0.1,\ 0.2,\ 0.35$ showed that the system segregates again into two phases, the ordered phase being highly anisotropic under the influence of the infinite electric field. Here the system undergoes a first-order phase transition, (or discontinuous) which is very similar to the one exhibited by the real materials. For $0.35 < \rho < 0.5$, the phase transition is weakly first order. Coexistence and spinodal lines are also measured, existence of metastable states very different in nature from the corresponding ones for the $\rho = 1/2$ are found. The calculations are performed for $L = 50, 100$ and the results seem to be largely independent of finite-size effects. Also, MC computations are limited to the case $J > 0$ and to Metropolis rates.

Comparisons with experimental observations of FIC are made. They seem to show that this oversimplified model captures many essential physical features of FIC (e.g. the current, the shape of specific heat in $AgCrS_2$). The most general behaviour of the type I of FIC seems to be well represented by the model. There is qualitative aggreement between the results found in the Monte Carlo simulations (which are on a two-dimensional lattice) and the properties of the real materials which are three dimensional.

2.3.2. Field theoretic studies

The continuum version of the DDIM has been also subjected to intense investigation. One starts by assuming that on a coarse time and length scale a Langevin description of the system can be set up. Let $\phi(x,t)$ denotes the local order parameter (magnetization) of the system. In the absence of a driving field, the equations of the motion for the system are

$$\frac{\partial}{\partial t}\phi + \nabla \cdot j = 0 \tag{2.6}$$

$$j = -D\nabla\left(\frac{\delta H}{\delta \phi}\right) + j_R \tag{2.7}$$

where j is the particle current, $D(\phi)$ is the diffusion coefficient, j_R is a white noise random current modeling the fast microscopic processes. $H[\phi]$ is the Ginsburg - Landau - Wilson energy functional

$$H[\phi] = \int d^d x \left\{ \frac{1}{2}(\nabla\phi)^2 + \frac{\tau}{2}\phi^2 + \frac{g}{4!}\phi^4 \right\} \quad ,$$

where τ is the reduced temperature variable (of the form $\sim T - T_c$), $g > 0$. The effect of the driving field is taken into account by adding to (2.2) the additional term :

$$j^{(1)} = \bar{\sigma} E \quad ,$$

where $\bar{\sigma}$ is the conductivity which in general is E and ϕ dependent. Note, the external field introduces anisotropy into the system, which may lead to anisotropic transport coefficients. This should be incorporated into the model from the start. In particular, two variables $(D\tau)_{\|}$ and $(D\tau)_{\perp}$, associated with the anisotropic ordering, need to be considered.

The high temperature long time behavior of the continuum version of the DDIM as defined by (2.1), (2.2) and (2.3) for $\bar{\sigma} = \phi^2$ was first investigated by van Beijeren, R. Kutner and H. Spohn in [8]. Their results are derived, based on the assumption of isotropic diffusion coefficient, by a mode-coupling approximation. For systems with dimension $d \leq 2$ it was found that the density fluctuation spread faster (e.g. as $t^{2/3}$ for $d = 1$) than as predicted by an ordinary diffusion law. For $d = 2$ the spread is diffusive $\sim t^{1/2}$.

The same problem was studied by H.K. Janssen and B. Schmittmann [9] by the means of more powerful renormalization group formalism. In a systematic way (allowing the transport coefficients to be anisotropic) they showed that the assumption made in [8] is justified and that the obtained prediction for the scaling behavior of the system is correct. The exact scaling form of the density - density correlation function was found and the obtained universal amplitude for $d = 1$ is in excellent agreement with the MC results.

The supersymmetric formulation was used by K. Gawedski and A. Kupianen [10] to find that the upper critical dimension of the system is 3 and 5 for $\bar{\sigma}(\phi)$ odd and even respectively (as compared to $d_c = 4$ for $E = 0$).

A field theoretic renormalization group study of the universal aspect of the critical behavior of the DDIM was undertaken by K. Leung and J. Cardy [11] and H. Janssen and B. Schmittmann [12]. An infrared fixed point stable below $d_c = 5$ was found to govern the transition to transverse order (strip-like configurations oriented along the field). The scaling forms for the density correlation functions and the critical exponents to all orders in $\epsilon = 5 - d$ were derived. The transition to trasverse order is continuous and of mean-field type for $d > 2$.

However, while renormalized field theory is very suitable for studying universal properties of the continuum version it cannot provide information about nonuniversal quantities such as the critical temperature.

2.3.3. Van Beijeren and Schulman's mean-field theory for the fast-rate limit of the DDIM

It is of great interest to devise a mean-field theory for the DDIM. While such a theory is expected to be inadequate for describing the critical behaviour, it could be quite valuable in predicting a rough phase diagram, contributing to the understanding of the mechanism of cooperative behaviour in nonequilibrium situations.

A mean-field type theory was first proposed by van Beijeren and Schulman [13] for a simplified version of the DDIM. In their version the jumps in the field direction are very fast compared to the jumps orthogonal to it. This was achieved by choosing the sampling rates $\Gamma_{\|}$ and $\Gamma_{\perp}$, which set the time-scale in these directions, so that $\Gamma_{\|}/\Gamma_{\perp} \gg 1$. The driving field was considered to be infinite, i.e. no jumps opposite to the field were allowed. In the fast-rate limit (i.e. $\Gamma_{\|}/\Gamma_{\perp} \rightarrow \infty$) the spatial dimension of the system effectively reduces by one. In this limit the DDIM is analytically solvable and exhibits a critical point of the mean-field variety. Below T_c , van Beijeren and Schulman used the Maxwell construction to derive their results. They also considered jump rate function other than Metropolis, e.g. ,

$$\phi_{vBS}(\Delta H) = \exp\left(-\frac{\Delta H}{2k_BT}\right). \tag{2.8}$$

For the equilibrium case the choice of the rates is not important as long as they satisfy the detailed balance condition. But a steady state distribution depends in general on the specific jump rates, since it is defined as the stationary solution of a certain master equation. One can explore if some features of the system, e.g. the phase diagram and the critical exponents, are independent of the specific choice of the rates.

The van Bejeren – Schulman's model corresponds to a quasi one-dimensional conductivity, which resembles the situation in some materials such as hollandite.

The rate dependence of the critical temperature for the fast-rate limit of the DDIM was investigated in [14] yielding the following results:

- in the $d = 2$ case for all choices of rates (for exchange in direction perpendicular to the field) the corresponding critical temperatures are higher than the equilibrium one, varying in the range $0.14 \leq \beta_c J \leq 0.44$. The fast-rate limit (for Metropolis rates) yields critical temperature lower than the corresponding one for the original DDIM;
- in the $d \geq 3$ case the fast-rate limit with Metropolis rates gives T_c lower than the equilibrium one and vBS rates yield higher critical temperature.

MC simulations by Marro and Valles [5] for $\gamma = \Gamma_{\|}/\Gamma_{\perp} = 1, 5, 20, 80$ confirmed that the fast-rate limit lowers T_c found in [1] and that T_c decreases as a function of γ . It was observed that the nonequilibrium steady state of the system depends on the transition mechanisms (Kawasaki, Metropolis and vBS rates were used) and system shapes ($L \times K$, $L \ll K$ and $\rho = 1/2$). States with several strips persist during the evolution of the system below T_c (metastable states), but these decay finally into one-strip stationary state for finite γ .

Further study of the vBS model by a field-theoretic formulation has been pursued by J. Krug, J. Lebowitz et al. [14] . They proposed a dynamical method of finding the phase separation by requiring the existence of a stable kink profile with asymptotic densities lying on the phase coexistence curve. The low-temperature dynamics was treated by the Freidlin - Wentzel theory of small random perturbations of dynamical systems.

2.3.4. Dynamic mean-field theory

The original DDIM (i.e. with isotropic hopping rates) has been studied by R. Dickman [15] via a dynamic mean-field theory and for the first time the detailed dependence of the critical temperature and short range correlations on the driving field strength has been explored.

The mean-field description of the system is given in terms of the site- and pair-occupation fractions (on the level of pair approximation) and in terms of site- ,pair- and square-occupation fractions (on the level of square approximation) generalizing the familiar Kikuchi cluster variation method for equilibrium case. Evolution equations for the independent macroscopic variables (the so-called rate equations for the probabilities of broken bonds) has been derived, which are approximations of a hierarchy of equations derivable from the master equation. In the spirit of the equilibrium kinetic Ising model with conserved global magnetization (first introduced and studied by Kawasaki) R. Dickman investigates the steady-state response of the system to a small uniform gradient in the magnetization at the critical density $\rho_c = 1/2$ (or equivalently $S = 0$). The transition temperature has been determined by assuming that there is a second order phase transition which is accompanied by a critical slowing down (a concept familiar from the equilibrium case, known since van Hove), though there is some evidence that this is not always the case in nonequilibrium situations (M. Suzuki [33,34]). The qualitative dependence of T_c on the strength of the electric field E obtained in [15] seems to agree quite well with the one obtained from MC simulations. For example the critical temperature for infinitely strong electric field is $T_c(\infty) = 3.206$ as compared to $T_c = 3.075 \pm 0.007$ in MC simulations.

The dynamic MF theory proposed by R. Dickman has one major difficulty – it is applicable only to the disordered phase ($m = 0$). It is not clear how to extend this method to include investigation of the low-temperature phase, as well as $\rho \neq 1/2$ cases.

In the present work we propose a mean-field method which is applicable to the low temperature region as well.

CHAPTER III

MASTER EQUATION APPROACH AND THE DDIM

3.1. Master equation approach

In a vast majority of physical systems, time dependence is extremely complicated, typically far beyond possibility of calculation and detailed observation. Nevertheless some average features can be observed, which obey relatively simple laws. Our experience shows that, in spite of the lack of knowledge of the exact values of most of the microscopic variables, it is still possible to detect regularities in the overall macroscopic behavior and to formulate them in terms of general laws.

To take advantage of the situation described above, the master equation approach was developed, providing a description of the system on the mesoscopic or "coarse - grained" level. It has been applied to numerous problems in physics (e.g. laser physics, Brownian motion, to problems in physics of fluids and semiconductors etc.), chemistry (reaction - diffusion systems) and biology (population dynamics), to enumarate only a few cases.

Generally speaking, the master equation is the equation which governs the time evolution of a probability distribution in a certain specified phase space for stochastic processes in which the memory effects can be neglected. More specifically, in this approach one assumes that the most detailed description of a state of the system under consideration is provided by specifying the values of a certain set of "interesting " physical quantities Y_j , which represents a small fraction of the total degrees of freedom of the system. It is considered that any more detailed knowledge of the state of the system is irrelevant for describing the time evolution of the state. The particular choice of the set Y_j depends upon the particular system under investigation and also on the adopted level of description. For instance, the set Y_j can consist of the momenta of all the particles in the system or, as it is the case of the DDIM, it can be the set of spins located on every site of the lattice. To proceed further, let us suppose that a state α of the system is completely specified by the set of values $Y_j(\alpha)$ for the variables Y_j chosen to describe the state of the system.(A state α corresponds to a volume in the entire phase space of the system.) For a real system it is not known exactly what the state of the system is. It is known only that with a certain probability it is one of the points in the phase space. Thus, the state point (or respectively the set of variables Y_j) can be regarded as a random variable and one can assign a probability distribution to the points in phase space according to the information available on the state of the system. If $P(\alpha, t)$ denotes the probability that the system is found in the state α at time t , then the time evolution of a state is determined by the following equation of motion for $P(\alpha, t)$

$$\frac{\partial P(\alpha,t)}{\partial t} = \sum_{\beta} W_{\alpha\beta} P(\beta,t) - P(\alpha,t) \sum_{\beta} W_{\beta\alpha} \quad , \tag{3.1}$$

This is the master equation. Here $W_{\alpha\beta}$ is the transition probability from the state β to the state α . The meaning of this equation is very simple and clear. The first term in (3.1) is the gain due to transitions from other states β and the second term is the loss due to transitions from the given state into other states. The transition probabilities are in most cases determined phenomenologically and thus the master equation and the related Fokker - Planck equation may be considered as phenomenological equations.

The master equation can be derived for a system with Markov property, i.e. no memory effects.(For examples of derivation in the literature see [35,36]. Here only few definitions will be given for the sake of completeness.) More precisely a stochastic process is called a Markov process if it has the property, that for any set of n successive times $t_1 < t_2 < \cdots < t_n$ the following equality holds,

$$P_{1|n-1}(y_n, t_n | y_1, t_1; \ldots; y_{n-1}, t_{n-1}) = P_{1|1}(y_n, t_n | y_{n-1}, t_{n-1}) \quad . \tag{3.2}$$

Here, $P_{1|n-1}$ is the probability of the variable Y taking value y_n (at t_n) conditioned on its taking the other $n-1$ values at previous times. Thus, (3.2) expresses that the conditional probability at t_n , given the value y_{n-1} at t_{n-1} , is uniquely determined and does not depend on any knowledge of the values of the random variable (which in most cases is actually a multicomponent variable) at earlier times. Note that $P_{1|1}$ is the transition probability.

A very important property of the Markov processes, which makes them more manageable and because of that with wide range of applicability in physics and chemistry, is that they are actually fully determined by specifying $P_1(y_1, t_1)$ – the probability distribution at time t_1 and the transition probability – $P_{1|1}(y_2, t_2; y_1, t_1)$. Then the whole (in general infinite) hierarchy of the joint probability distributions $P_n(y_1, t_1; y_2, t_2; \ldots; y_n, t_n)$, $n = 1, 2 \ldots$, that Y has value (y_1 at t_1 , y_2 at $t_2, \ldots,$ y_n at t_n) can be reconstructed from P_1 and $P_{1|1}$. Thus, for example, one can write for P_3 and $t_1 < t_2 < t_3$

$$\begin{aligned} P_3(y_1, t_1; y_2, t_2; y_3, t_3) &= P_2(y_1, t_1; y_2, t_2) P_{1|1}(y_3, t_3 | y_1, t_1; y_2, t_2) \\ &= P_1(y_1, t_1) P_{1|1}(y_2, t_2 | y_1, t_1) P_{1|1}(y_3, t_3 | y_2, t_2) \end{aligned} \tag{3.3}$$

By repeated application of this step many times one can get P_n for all n . For two nonnegative functions P_1 and $P_{1|1}$ to define a Markov process uniquely, they must satisfy two consistency conditions. The first is the Chapman - Kolmogorov equation, expressed through the following identity :

$$P_{1|1}(y_3,t_3|y_1,t_1) = \int P_{1|1}(y_3,t_3|y_2,t_2)P_{1|1}(y_2,t_2|y_1,t_1)\,dy_2 \quad , \tag{3.4}$$

where $t_1 < t_2 < t_3$ (the time ordering is essential). The second identity relates the transition probability $P_{1|1}$ and the probability distribution at later time P_1 , i.e.

$$P_1(y_2,t_2) = \int P_{1|1}(y_2,t_2|y_1,t_1)P_1(y_1,t_1)\,dy_1 \ . \tag{3.5}$$

The master equation (3.1) is actually a more convenient form of the Chapman - Kolmogorov equation , which is easier to handle in specific applications. It is the differential version of this equation, obtained by taking the limit of going to zero time difference (i. e. $\tau = t_2 - t_1$ and $\tau \to 0$).

The kinetic Ising models (and respectively the DDIM) are now obtained as a special cases where the variables Y_j are the Ising spin variables $\{\sigma\} = \{\sigma_1, \sigma_2, \dots\}$ and $\sigma_i = \pm 1$. Specializing to this case, we write

$$W_{\alpha\beta} \to \Phi(i,j,\sigma) \quad , \quad P(\alpha,t) \to \rho_t(\sigma) \quad . \tag{3.6}$$

The assumption that time evolution of the probability density $\rho_t(\sigma)$ in configuration space of all possible spin arrangements for the DDIM (as defined in sec. 2.1) is governed by a stochastic equation of Markovian nature for chains is a very strong one. For any system it is not at all obvious and not an easy task to show that $P(\alpha,t)$ for a chosen set Y_j satisfies the master equation (3.1) and the goal of numerous investigations has been the derivation of the master equation starting from a more fundamental equation for the density matrix or the phase space distribution function of the entire system. More generally speaking, the master equation has been derived only in the cases where one can consider the change occuring in the variables Y_j to proceed very slowly compared to the rate of change in other degrees of freedom. This restriction excludes many of the interesting systems displaying phase transitions from being treated this way.

The physicist's problem is to find these variables that are needed to make the description approximately Markovian. (According to van Kampen [35], any closed isolated physical system can be described as a Markov process by introducing all microscopic variables as components of a multicomponenet stochastic process.) The well known experimental fact is that one can do this for most many-body systems in nature. Of course, such a description is at best approximate and restricted to some "coarse-grained" level.

The justification of this approximation is still subject to many investigations and theoretical discussions. Nevertheless, even in the cases where it is not possible to derive the master equation from more fundamental principles, it can still be regarded as a useful trial model that will hopefully reflect some gross features of the real system and bring some insight to the cooperative processes occuring in these systems.

3.2. Dynamic mean-field method

In most cases (as it is also in our case) explicit solution of the master equation is impossible. For that reason one has to resort to approximate solutions and various approximate methods have been suggested in the literature.

The solution of the master equation $\rho_t(\sigma)$ (as it was already noted in sec. 3.1) provide the most complete information about the system, available on the adopted level of description. Although it is desirable to know these functions, it has to be noted also, that in fact, they contain much more information than is needed for practical purposes. To answer the most familiar physical questions about the system it usually suffices to know the probabilities with which configurations of certain clusters appear in the system (site, pair or larger clusters of lattice sites). In practice, the main use of the full probability density is to find expectation values or correlation functions for various physical quantities, since these are measured in the experiment and also with these one deals in thermodynamics.

To proceed further, let us now define the n-point reduced probability functions $\rho_t^{(n)}$ to find a configuration $\{\sigma_{i_1},\ldots,\sigma_{i_N}\}$ of spins at time t on a cluster of points $i_1,\ldots,i_n$ ($n < N$) , i.e. a subgraph of the entire lattice. These are given by the following expression

$$\rho_t^{(n)}(\sigma_{i_1},\ldots,\sigma_{i_n}) = \sum_{\sigma'_1\in\Theta_1}\cdots\sum_{\sigma'_N\in\Theta_N}\prod_{l=1}^{n}\delta_{\sigma_{i_l},\sigma'_{i_l}}\,\rho_t^{(N)}(\sigma'_1,\ldots,\sigma'_N)\,.$$

where Θ_i , $i = 1,2,\ldots,N$, denotes the set of all possible configurations of the i-th point. For the DDIM $\Theta = \{-1,+1\}$.

On a given level of approximation one considers explicitly the correlations in a given basic cluster and all its subclusters, neglecting the correlations in larger clusters and between the clusters which do not intersect. (See sec. 5.2 for more detailes.)

In the mean-field approximation one assumes homogeneity in the system, which simplifies the considerations a great deal. This is implemented by requiring

$$\rho_i^{(k)}(\sigma_{i_1}, \sigma_{i_2}, \ldots, \sigma_{i_k}) = \rho_i^{(k)}(\sigma_1, \sigma_2, \ldots, \sigma_k) \quad , \quad k = 1, 2, \ldots \quad . \tag{3.7}$$

From the master equation one can derive a hierarchy of equations for the macroscopic variables – average values of spins and products of spins. A systematic method is developed by van Kampen [35] in a form of a power series expansion in a parameter Ω , related to the size of the system. Thus it provides the answer to the question how the deterministic macroscopic equations emerge from the stochastic description in terms of a master equation.

On the other hand, there is a simple and practical way for arriving at the equations of motion for the macroscopic variables (also called rate equations). These are used in, e.g., the study of the kinetics of homogeneous short range order by I. Kidin and M. Shtremel [37]. R. Dickman has applied this method for several systems in nonequilibrium steady state [15 - 17].

Such equations are derived by considering explicitly all the configurations on a certain small cluster, their respective probabilities $P(\text{conf.})$ of occurring, and the corresponding transition probabilities when performing exchange $\Phi(\Delta H)$. Let $\rho^{(k)}$ be one of the reduced probability functions (3.7). Then the general structure of the corresponding rate equation is as follows

$$\begin{aligned}\frac{d\rho^{(k)}}{dt} &= G^{(k)}(\rho^{(1)}, \rho^{(2)}, \ldots, \rho^{(n)}) \\ &= \sum_{conf} \Delta\rho^{(k)}\, \Phi(\Delta H) P(\text{conf}) \quad ,\end{aligned}$$

where $\Delta\rho^{(k)}$ is the corresponding change in $\rho^{(k)}$ when exchange occurs. $P(\text{conf.})$ is estimated approximately by assuming noninterference of nonintersecting clusters, which is an extension of the idea of the quasi-chemical approximation. Explicit implementation of this equation is in the next section.

These two approaches can be related to each other for sytems in equilibrium. On the pair level of approximation, van Baal [38,39] has suggested a systematic coarse-graining procedure for the master equation for both Kawasaki and Glauber kinetic Ising models using van Kampen's Ω - expansion. The resulting rate equations are the same as those, obtained in [37]. For nonequilibrium systems, no such link has been established. In this thesis, we adopt the second, more heuristic and manageable method.

3.3. Pair level of approximation

Here, we concentrate on the pair level of approximation. It is the simplest approximation to carry out and accounts for the most important correlations in the system.

At this level, the system is decribed in terms of the single site and nearest-neighbor pair probability distributions $\rho^{(1)}(\sigma_i)$ and $\rho^{(2)}(\sigma_i, \sigma_j)$ respectively. In equilibrium, the mean-field homogeneity assumption is expressed by taking all the probability distributions for single spins and nearest-neighbor pairs of spins to be the same

$$
\begin{aligned}
\rho^{(1)}(\sigma_i) &= \rho^{(1)}(\sigma) \qquad \text{for all } i \in \Lambda \quad , \\
\rho^{(2)}(\sigma_i, \sigma_j) &= \rho^{(2)}(\sigma_1, \sigma_2) \qquad \text{for all } i \in \Lambda \text{ and } j = i + \hat{e}_{1,2}
\end{aligned}
\tag{3.8}
$$

However, in the presence of an electric field along $\hat{e}_1$ this certainly would not be true. At the least, we must account for anisotropy introduced by the field. We assume that there are two different probability distributions over bonds of nearest neighbors, i.e. one for bonds along the electric field and second one for bonds perpendicular to the field :

$$
\begin{aligned}
\rho^{(2)}(\sigma_i, \sigma_{i+\hat{e}_1}) &= \rho_1^{(2)}(\sigma_1, \sigma_{1+\hat{e}_1}) \quad , \quad i \in \Lambda \\
\rho^{(2)}(\sigma_i, \sigma_{i+\hat{e}_2}) &= \rho_2^{(2)}(\sigma_1, \sigma_{1+\hat{e}_2}) \quad , \quad i \in \Lambda
\end{aligned}
\tag{3.9}
$$

Thus one has

It is convenient to introduce the following notation

$$\left.\begin{aligned} &\rho^{(1)}(+1) = x\ , \quad \rho^{(1)}(-1) = y \\ &\rho_i^{(2)}(+1,+1) = z_i \\ &\rho_i^{(2)}(+1,-1) = \rho_i^{(2)}(-1,+1) = b_i \\ &\rho_i^{(2)}(-1,-1) = w_i \end{aligned}\right\} \quad i = 1,2 \tag{3.10}$$

where, of course

$$x + y = 1 \ \text{ and } \ z_i + 2b_i + w_i = 1 \quad , \quad i = 1,2 \tag{3.11}$$

Among these eight variables only three are independent. For example, we can consider x, b_1 and b_2 to be the independent variables. These are the fraction of up spins, the fractions of up - down nearest-neighbor pairs of spins in direction parallel to the field and those perpendicular to the field respectively. The rest of the variables can be expressed in terms of these :

$y = 1 - x$ fraction of down spins,

$z_i = b_i + x$ fraction of up - up spins,

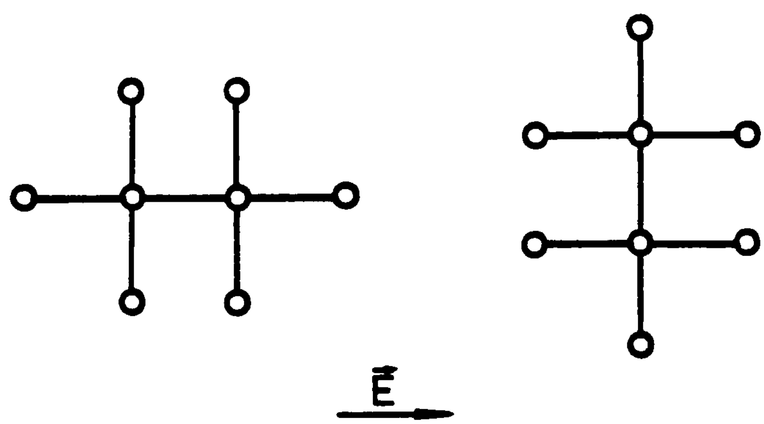
$w_i = b_i + y$ fractions of down -down spins for $i = 1,2$.

In the standard way x and y can be expressed in terms of m , the magnetization per site, i.e.

$$x = \frac{1+m}{2} \quad , \quad y = \frac{1-m}{2} \quad . \tag{3.12}$$

When an elementary exchange process occurs, the local magnetization m does not change. Thus only equations of motion for b_1 and b_2 can be derived. According to the model (as described in sec. 2.1) exchanges occur only between the spins of nearest-neighbor lattice sites. The change in energy associated with such exchange depends only on the surroundings of the given pair (see (2.3) and also (2.5)).

Therefore, to derive the rate equations for b_1 and b_2 we need to consider only a cluster consisting of a bond and all its nearest neighbors. Since every spin can attempt exchange with equal probability, both in direction parallel and in direction perpendicular to the field, we have to consider the contributions from the following two clusters :



Then the general stucture of the rate equations in the presence of a driving force for b_1 and b_2 is

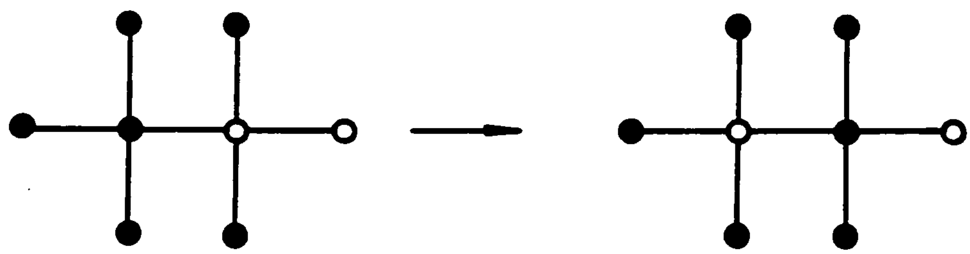
$$\frac{db_i}{dt} = \left[G_i^{(1)}(m, b_1, b_2; T, E) + G_i^{(2)}(m, b_1, b_2; T, E)\right] \quad i = 1, 2 \qquad (3.13)$$

Here, $G_i^{(k)}$ are the contributions from the two clusters. Their dependence on T and E through the rates is also explicitly displayed

$$G_i^{(k)}(m, b_1, b_2; T, E) = \sum_{\alpha} \Delta b_i \, \phi\left(\Delta H_\alpha + \epsilon_\alpha^{(k)} E\right) \, P_\alpha^{(k)} \quad , \quad k = 1, 2 \quad . \qquad (3.14)$$

The summation over α refers to all configurations appearing in the clusters. $P_\alpha^{(k)}$ is the probability for an α to occur in cluster k . Once α is specified, the spin-exchange direction (and final configuration) is also fixed. Thus, $\epsilon_\alpha^{(k)}$ is ± 1 or 0 , depending on whether the exchange is parallel or perpendicular to E .

To illustrate the derivation, let us consider a particular configuration of spins on the first cluster and calculate explicitly its contribution to the equations of motion.



$$\Delta H = 4J \qquad \Delta b_1 = 2 \qquad \Delta b_2 = 0 \qquad \Delta m = 0$$

In this approximation (quasi chemical) the probability for this particular configuration to occur is given by

$$P_\alpha = \frac{z_1 b_1 w_1 z_2^2 b_2^2}{x^3 y^3}.$$

Therefore the contribution from this configuration to $G_1^{(1)}$ and $G_2^{(1)}$ are

$$2\phi(4J - E)\frac{z_1 b_1 w_1 z_2^2 b_2 w_2}{x^3 y^3} \quad \text{and} \quad 0$$

respectively. The contribution of the same configuration of spins from the second cluster, oriented perpendicular to the field, can be obtained from this one simply by interchanging the indeces, i.e.

$$b_1 \longleftrightarrow b_2 \text{ corresp. } \Delta b_1 \longleftrightarrow \Delta b_2$$

$$z_1 \longleftrightarrow z_2$$

$$w_1 \longleftrightarrow w_2$$

and by putting $E = 0$ into the rates.

Some simplifications occur when symmetries are taken into account. Thus, configurations that can be obtained from each other by a reflection with respect to the axes, passing through the middle of the bond connecting the two central spins, and perpendicular to the principle axes of the cluster have the same P but different Φ . The full expressions for G_i , $i = 1,2$ are very long and cumbersome. They may be found in app. A.

3.4. Limitations of the dynamic mean-field method

The model system we are considering is diffusive, i.e. it evolves according to a spin exchange dynamics. This effectively means that the local order parameter m is conserved when exchange is performed and therefore its time evolution contributes a trivial algebraic equation at nonequilibrium steady state. In general, on a given level of mean-field approximation, one gets $n-1$ rate equations for n independent mean-field variables, describing the nonequilibrium steady state of the system. In the high temperature regime the spontaneous magnetization is zero (completely disordered phase). The system of equations is closed and can be solved numerically. However, at low enough temperatures $m \neq 0$ and the sytem of equations is incomplete. By using only the rate equations it is not possible to obtain any information, concerning the transition temperature $T_c(E)$ or the low temperature properties of the system. One needs additional hypothesis in order to proceed further. In the treatment of the DDIM by R. Dickman within the framework of the dynamic mean-field theory, $T_c(E)$ was determined by the vanishing of the diffusion coefficient D when a small uniform gradient in the magnetization is imposed. This involves two *a priori* assumptions :

(i) there is a second order phase transition,

(ii) there is a critical slowing down in the nonequilibrium state.

The limitations of this approach are clear. If a first order transition occurs, this method fails. There is evidence for such transitions, both in physical fast ionic conductors and in MC simulations of the driven antiferromagnetic Ising model [40]. Even for our system, where a second order transition is expected, this method cannot be extended below T_c . If pushed blindly, it will find the spinodal, instead of the co-existence curve. Of course, this difficulty merely reflects the first order nature of phase transitions for $T < T_c$.

To overcome this limitations, we adopt the view point that the relevant information of the system can be obtained by applying the principle of maximum entropy. By appling the principle of maximum entropy (see chapter IV) to a system in a contact with a heat reservoir, one finds that this is equivalent to minimizing the generalized free energy of the system. This gives one more equation at low temperatures for determining the order parameter m .

CHAPTER IV

INFORMATION THEORY APPROACH TO STATISTICAL MECHANICS AND PRINCIPLE OF MAXIMUM ENTROPY

4.1. Introduction

The application of information theory to statistical mechanics, initiated by E. T. Jaynes (1957) and subsequently developed (see e.g. [41 - 43] and references therein), proved to be quite successful in treating sytems in equilibrium. Further, it appears to be rather promising for treating nonequilibrium systems as well.

The starting point is the adoption of the view point that a probability distribution is a means of describing certain state of knowledge, as opposed to the frequentist view point. This line of thought could be traced back to Bernoulli, Laplace, Jeffreys and others and has led to many applications in physics as well outside the field of physics.

Another important observation is the following. For most nontrivial problems of physical interest the available information is far from being sufficient in order to determine a unique probability distribution, but nevertheless one can still answer some macroscopic questions. For example, in the usual situation in the laboratory the experimenter has control over certain macroscopic quantities X_i , defining the thermodynamic state of the sytem under investigation. If knowledge of the values of the parameters X_i is sufficient to determine reproducible results (these are termed by E. T. Jaynes as experimentally reproducible phenomena) then it must follow that information about these macroscopic conditions should transmit enough information about the microscopic states for the theoretical prediction of that result. Rather naturally one comes to the following question: of all the probability distributions over the set of all microstates of the system capable of reproducing the given data, which one is the most sensible to choose?

The answer is provided by the Principle of Maximum Entropy (PME), introduced by E. T. Jaynes [20]. PME asserts that, when only incomplete data are available, one should choose a probability assignment which is maximally noncommittal with respect to the missing information in order to avoid introducing unjustified bias. But in order to do that one needs some adequate measure of the intrinsic ucertainty contained in a probability assignment. The existence of such measure was first demonstrated by C. Shannon, who called it the entropy of a probability distribution:

$$S_I(p_1, \ldots, p_n) = -K \sum_{i=1}^{n} p_i \log p_i \quad (K > 0)$$

S has the subscript I in order to be stressed that this is a measure coming from the information theory and K is a constant determined in the particular context of an application.

Jaynes' informational approach views the laws of statistical mechanics as inferences based entirely on the laws of mechanics and additional hypotheses are not needed. To emphasize the difference between this approach and the established one, the new approach was given the name Predictive Statistical Mechanics. Previously known results , e,g., Onsager relations, Kubo's transport coefficients, etc., have been reproduced in this way with great formal economy and as a special cases for particular kinds of information (see [41,42,44]). There are many applications of PME outside the field of statistical thermodynamics. A survey of the results of applications of PME to spectral anlysis and inverse problems can be found in the proceedings of several workshops on the subject (e.g. [45,46]). Successful applications of PME in biology, economics, oceanography etc., also exist.

Since the Shannon information measure (which is the negative of S_I) is a quantity of fundamental interest in the information theory approach to statistical mechanics, it will be considered in more detail in the next section.

4.2. Information measures

4.2.1. Shannon information measure

Let a set of n events which are exhaustive and mutually exclusive be given, i.e. they form a complete disjunction. This is the most common case of interest. The events can be represented, without serious restrictions of the considerations, as the possible results of an experiment. If a probability distribution P is given by a set of probabilities p_i for the n events $i = 1, 2, \ldots, n$ of the whole sample set, then the corresponding information measure of the lack of communication (or the lack of knowledge) is given by the mean value of the bit number $\mathbf{b}_i = -\log p_i$ necessary to communicate the occurrence of the elementary event i

$$S(P) = -K \sum_{i=1}^{n} p_i \log p_i$$

The negative of this $I(P) = -S(P)$ is an adequate measure for the knowledge contained in the probability distribution $P = (p_1, p_2, \ldots, p_n)$ with respect to the question which event i of the n events of the sample set will occur. This measure, $I(P)$, is called "Shannon information".

Shannon's information can be defined in a formal way as the unique solution satisfying Khinchin's axioms (for ref. see [43]). These axioms express our expectations, in a formal and selfconsistent form, the properties which the information $I(P)$ should have. They state:

Axiom I : $I(P) = I(p_1, p_2, \ldots, p_n)$

Axiom II : $I(1/n, 1/n, \ldots, 1/n) \leq I(p_1, p_2, \ldots, p_n)$

Axiom III: $I(p_1, p_2, \ldots, p_n) = I(p_1, p_2, \ldots, p_n, 0)$

Axiom IV : $I(\tilde{P}) = I(P) + \sum_i p_i I(q|i)$, where $\tilde{P}$ and $I(q|i)$ will be defined below.

The first axiom just expresses the fact that the information measure is a function only of the probabilities. For simplicity it is assumed that $I(P)$ is a continuous function with continuous derivatives. The second axiom requires that the homogeneous distribution is the one which has minimum information as compared to the information which any other distribution has over the same sample set. The third axiom gives the relation between the information measures of two distributions over two different sets, where the second distribution is obtained from the first by adding one more event with zero probability.

If one has two different sample sets $i = 1, 2, \ldots, n$ and $j = 1, 2, \ldots, m$ of events, then one can form a Cartesian set of both sets by considering the events (i, j) for simultaneous occurrence of the events i and j. The probability distribution on this new set is given by

$$\tilde{p}_{ij} = q(j|i)p_i \quad ; \quad \tilde{P} = \{\tilde{p}_{ij}\} \quad , \quad Q \equiv \{q((j|i)\} \quad ,$$

i.e. the probability that i and j occur simultaneously is factored into the probability that p_i occurs times the conditional probability $q(j|i)$ that the event j occurs given that i occurs. $I(q|i)$ in axiom IV denotes the information measure of the conditional distribution $q(j|i)$ for fixed i. The meaning of axiom IV is that the information measure does not depend on the way information has been supplied (by $\tilde{P}$ or in separate steps by P and Q).

Other measures, generalizing Shannon's measure have been introduced also – they are often called convex measures and they are defined as follows:

$$\Im(P) = \sum_{i=1}^{n} g(p_i) \quad ,$$

where $g(x)$ is a convex function for positive x. They always fulfill axioms I, II and III. Among the convex measures the Shannon information is the only one satisfying axiom IV. In the special case when the events i and j are independent, axiom IV reduces to a requirement of additivity of $I(P)$, i. e.

$$I(\tilde{P}) = I(P) + I(Q) \quad .$$

When the number of alternatives form a continuum ($n \to \infty$) we may write $\rho(x)$ in place of P_i. Naively, the Shannon entropy diverges when one attempts to deduce it as the limiting case of some finite distribution. However, apart from an infinite (ρ independent) constant, the finite measure

$$S(\rho) = -\int \rho(x) \log \rho(x)\, dx \quad ,$$

still serves as an adequate measure of the missing information under the condition that the parameter space x is the one in which the lack of any knowledge is expressed by the uniform distribution. A further difficulty of this entropy is that, under a volume non-conserving change of variables, it does not remain invariant.

A somewhat different renormalization procedure was suggested by Jaynes, which leaves the expression of the entropy invariant under change of variables. One approaches the continuous case as the limit of a discrete one and by introducing a measure function $m(x)$, which is proportional to the limiting density of discrete points

$$\lim_{n\to\infty} \frac{1}{n}[\text{number of points in } (a,b)] = \int_a^b m(x)\,dx \quad .$$

Then the following expression for the renormalized entropy is obtained :

$$S = -\int_a^b \rho(x) \log \frac{\rho(x)}{m(x)}\,dx \quad .$$

But there is no unambigous way (except in the case when there is some obvious limiting process) of determining $m(x)$. This is still an open problem in probability theory, though it does not arise when one uses instead a quantity called Kullback information.

4.2.2. Kullback information

Kullback formulated an extension of Shannon's measure. To define this quantity let us suppose that two probability distributions P^0 (a prior probability distribution) and P (a posterior probability distribution) are given on the same sample set of events i . The amount of information necessary to change the expectations expressed by P^0 to those expressed by P is used to define the measure for the relative information of P with respect to P^0

$$\Delta S(P,P^0) = K \sum_i p_i \log(\frac{p_i}{p_i^0}) \quad , \quad K \geq 0 \quad .$$

This measure is called Kullback information, known also as "cross-entropy", "information gain", "entropy deficiency" etc. of P with respect to P_i^0 . The distinction of P as the posterior or correct distribution has made ΔS nonsymmetric in both distributions. ΔS is a non-negative (which can be seen immediately by employing the inequality $\log x \geq 1 - 1/x$, $x \geq 0$) convex function of P . If the p_i are changed into $p_i + \delta p_i$, then the change of ΔS to second order of δp_i is non-negative

$$\begin{aligned}\delta^2 \Delta S &= \frac{1}{2} \sum_i (\delta p_i)^2 \frac{\partial^2}{\partial {p_i}^2} \left[p_i \log \left((\frac{p_i}{p_i^0} \right) \right] \\ &= \frac{1}{2} \sum_i (\delta p_i)^2 / p_i > 0 \quad .\end{aligned}$$

The Shannon information measure is obtained (up to unimportant additive constant) from $\Delta S(P, P^0)$ as a special case when P^0 is the homogeneous distribution h (i. e. all $p_i^0 = 1/n$) :

$$\Delta S(P, h) = I(P) + \log n$$

A major advantage of Kullback's measure is the straightforward generalization to the case of continuous distributions, in that there is no divergence problem and no ambiguity regarding the basic measure. The corresponding expression is given by

$$\Delta S(\rho, \rho^0) = \int \log \frac{\rho(x)}{\rho^0(x)} \, dx$$

There are several studies concerned with constructing a variational principle involving the Kullback information. It was shown that a principle of minimum cross-entropy, subject to the same constraints, is equivalent to a maximum entropy principle (at least for processes without memory) see e.g. [47].

4.3. Principle of maximum entropy of Jaynes

The development of information theory enabled Jaynes to formulate his principle of maximum entropy and to expand the calculation methods, introduced in statistical mechanics by Gibbs, as a general formalism for inductive reasoning which emerges from probability theory. Indeed, its validity is not restricted to physics only.

The exact statement of PME (which is called also principle of unbiased guess) is as follows : *the least biased probability assignment is that which maximizes the entropy subject to the constraints imposed by the available information.*

In order to yield a well posed problem the data (or more generally the information) $\mathcal{I}$ cannot have a completely arbitrary form. It should be "testable" (in Jaynes' terminology), i.e. for any proposed distribution $P = \{p_1, p_2, \ldots, p_n\}$ one must be able to determine unambiguously whether it agrees with $\mathcal{I}$. For the same physical system, one may measure different quantities, so that different constraints must be imposed on the probability distribution.

Applying the maximum entropy formalism to statistical mechanics offers a unified framework within which any particular equilibrium ensemble (or equivalently any particular reservoir) is just a special case. This can be seen by considering the very important class of problems (the general solution for which was given by Gibbs) in which the information $\mathcal{I}$ is given by specifying the mean values of certain macroscopic observables. To proceed further let $a_1(x), \ldots, a_m(x)$ be the set of macroscopic variables, $\mathcal{I} = \{A_1, \ldots, A_m\}$ be the set of corresponding mean values ($A_k = \langle a_k \rangle$, $k = 1, 2, \ldots, m$) and x be a real variable taking values x_i for each microscopic state i ($i = 1, 2, \ldots, n$) of the system. One needs to find a probability distribution $P = \{p_i\}$ which maximizes the entropy $S_I = -K\sum_i p_i \log p_i$ subject to the follwing constraints :

$$\sum_{i=1}^{n} p_i = 1 \quad ,$$

$$A_k = \sum_{i=1}^{n} p_i a_k(x_i) \quad , \quad 1 \leq k \leq m \quad .$$

By applying the Lagrange multiplier technique for this standard variational problem one gets the formal solution

$$p_i = exp\left[-\lambda_0 - \sum_{k=1}^{m} \lambda_k a_k(x_i)\right]$$

where the $m+1$ Lagrange multipliers λ_k are determined by the condition that the $m+1$ constraints are satisfied. This is the case if

$$\lambda_0 = \ln Z(\lambda) \quad , \quad \lambda = (\lambda_1, \ldots, \lambda_m) \quad ,$$

where

$$Z(\lambda) = \sum_{i=1}^{n} exp\left\{-\sum_{k=1}^{m} \lambda_k a_k(x_i)\right\}$$

is the partition function, and

$$A_k = -\frac{\partial}{\partial \lambda_k} \ln Z(\lambda) \quad .$$

Substituting back in the expression for S_I one gets the maximal value for the entropy consistent with the data

$$S = K \ln Z + K \sum_{k=1}^{n} \lambda_k A_k$$

Now if the system is coupled to a heat bath, the only constraint on the equilibrium state is then on the mean energy of the system, i.e. $\langle u \rangle = U$. One has only one Lagrange multiplier and the corresponding probability distribution is the well known canonical distibution of Gibbs

$$p_i = \frac{1}{Z} exp\left[-\frac{u_i}{k_B T}\right] \quad .$$

When the system is exchanging both energy and matter with a reservoir, then the corresponding Lagrange multipliers for the average number of particles of every component are the chemical potentials $\lambda_k = \mu_k / k_B T$ per particle and one arrives at the familiar grand canonical distribution

$$p_i = \frac{1}{Z} exp\left\{-\frac{[u_i - \sum_i \mu_k N_k(i)]}{k_B T}\right\} \quad .$$

If some information is redundant (that is, it could be predicted from the available data), then the corresponding Lagrange multiplier will disappear. If there is information which contradicts the rest of the data, then the PME will fail as it should be expected. There are situations when such a failure could be in fact beneficial. When the best predictions provided by PME based on the available information consistently disagree with the experimental observations, one can conclude that there are additional constraints, missing from the original set, yet essential for the given problem.

4.4. Nonequilibrium system in contact with a heat reservoir

The calculation for an irreversible process in the general framework of Predictive Statistical Mechanics, according to E. T. Jaynes [20], must necessarily pass through three distinct stages . They are :

(i) Setting up an "ensemble", i. e. choosing an N- particle distribution function P^0 (or a statistical operator $\hat{\rho}(t_0)$) which has to describe our initial knowledge about the state of the system of interest and which maximizes the entropy;

(ii) Utilizing the microscopic dynamics in order to obtain the time-evolving probability distribution (or respectively $\rho(t)$);

(iii) Making predictions from the time depending distribution $P(t)$ for the macroscopic physical quantities of interest.

It has to be stressed again that in the nonequilibrium case one is interested in experimentally reproducible phenomena. The above described procedure is addressing the problem of how a many body system in nonequilibrium responds to external forces, the application of which as well as the macroscopic evolution of the system should be reproducible if one starts with the same initial macroscopic state.

Stage (iii) does not pose procedural difficulties (while its justification is still debated). One employs the prescription familiar from the equilibrium case, i.e. to predict the quantity $A(x)$ one uses the expectation value $\langle A\rangle = \sum_i p_i A(x_i)$.

Stage (ii) is usually the most difficult part of this procedure to carry out. Its realization depends on the particular physical system. Many investigations focus on this stage and different techniques are suggested.

The problem of stage (i), in the nonequilibrium case, has received little attention. Here, a much more general form of Gibbs' algorithm is needed, which has been suggested by E. T. Jayenes. An arbitrary physical process, in general, may depend not only on the present values of the macroscopic quantities, but also on the previous history of the system. The local expectation values may not suffice to predict the future behavior of the system. If one has macroscopic information about the observables $A_k(x,t)$ throughout information gathering space-time regions R_k (which may be different for different A_k) then the generalized procedure involves maximization of the entropy S_I , subject to the constraints imposed by the values $\langle A_k(x,t)\rangle$ over the regions R_k . (For justification of this procedure see e.g. [42] and references therein.) The formal solution to this variational problem is given by :

$$\rho = \frac{1}{Z} \exp\left\{ \sum_k \int_{R_k} dt\, d^3x\, \lambda_k(x,t)\, A_k(x,t) \right\}$$

where $\lambda_k(x,t)$ are now *Lagrange multiplier functions*, to be determined from the constraints, and $Z = Z\left[\lambda_1(x,t), \ldots, \lambda_k(x,t), \ldots\right]$ is *the partition functional*.

For most systems the time dependent variational problem is formidable if not impossible to solve. In the case of the DDIM, though, the degree of difficulty involved is reduced enormously due to the following :

- The DDIM is a system without memory. Moreover, we are interested in the steady state properties of the system. Thus, one does not have to include the previous history of the system as a constraint;
- Adopting a mean-field description of the system (3.8,9), which is equivalent to considering a spatially uniform system, removes the necessity to integrate over the space variables.

Finally, recall that the time evolution of the DDIM on the mesoscopic level is modeled by the master equation. Thus, stage (ii) has been already incorporated.

The application of PME to nonequilibrium spatially uniform, without memory, systems has been the subject of many studies (see e.g. [21,43,48 - 50]). In [47 - 50] where the data consists of mean values of some macroscopic quantities $A_k(t)$, the first stage was treated in a way similar to the equilibrium one. A nonequilibrium macroscopic state is reflectd by a nonequilibrium distribution function $P_t(n)$ on the microscopic states of the system. At any given time t the best probability distribution was determined by maximizing the entropy, subject to the constraints imposed by the available data (representing different reservoirs). The corresponding Lagrange multipliers $\lambda_k(t)$ are also time-dependent.

R. Bowers and A. McKerrel [21] derived the probability distribution which best represent a system in nonequilibrium in contact with a heat reservoir by using the information theory approach. Applying the PME of Jayenes to the combined system (see also [43]), in a way consistent with any additional data, yielded minimization of a quantity which is a generalization of the thermodynamic Helmholtz free energy

$$\psi = u - Ts \quad ,$$

where T is the temperature of the reservoir.

In the spirit of these studies the PME will be applied in the next section to the DDIM.

4.5. Application of the PME to DDIM

In applying the fundamental variational principle of Jayenes we will follow basicaly the derivation of R. Bowers and A. McKerrel [21] of the probability distribution which best represents a system in contact with a heat reservoir. The following considerations and assumptions enable us to accomplish this goal. The system of interest is in thermal contact and under the influence of a time-independent, uniform electric field E . The work done by the electric field is changing the population of configurations with different energies. As a result the density of the mean energy of the system u is changing with time. Part of the work is released into the reservoir as Joule heat, due to the current induced in the system. After a sufficiently long time, the system reaches a nonequilibrium steady state, which is well known in MC simulations. This state is characterized by stationary values of the probability distribution . At the pair level of approximation, these are given in terms of mean-field variables x, y, z_i, w_i *and* b_i as introduced in sec. 3.3. As a consequence all macroscopic variables of the system do not change with time. In particular, the density of the mean energy has a fixed value and there is a steady average current flowing into the system. In the model system (as realized in the MC simulations) it is assumed that the heat generated by the electric current is immediately absorbed by the heat reservoir. The contact of the heat bath with the system in the steady state influences the population of configurations with different energies through the rates. In these rates T does not change even when the field is incorporated. For convenience, one can imagine a second heat reservoir at the same T , whose only role is to absorb the Joule heat. The crucial point is characterization of the contact and the heat reservoir. Here, we adopt the one given by R. Bowers and A. McKerrel

[21], which is reproduced below for convenience.

A system R is called a heat resrervoir in thermal contact with a system A if it has the following properties :

(i) The system R is so large that the exchange of energy with the system does not change its macroscopic equilibrium state. A specification (see also [43] or [47]) of the reservoir is given by the corresponding Lagrange multiplier $\frac{1}{T}$, characterizing the state of a system in equilibrium with R ;

(ii) All equilibrium states which may play an effective role (due to conservation laws) can be labeled by the energy of the reservoir u_R ;

(iii) The absolute temperature $T(u_R)$ of the reservoir is defined by

$$\frac{ds_R}{du_R} = \frac{1}{T(u_R)} \quad , \tag{4.1}$$

where s_R is the equilibrium entropy of the reservoir (the probability assignment which corresponds to equilibrium in the information theory approach is identified with the thermodynamic entropy). The first property then implies that $T(u_R)$ is essentially constant at T , for changes in u_R arising in the interaction of R with A . To leading order in size, one can assume that the thermal state of the bath is independent of the thermal state of the system. The statistical independence is expressed in terms of subadditivity of the statistical entropy

$$s_{tot} = s_R + s \quad .$$

Applying the PME to the combined system, it follows that for all allowable changes in δP_n

$$\delta(s_R + s) = 0 \quad . \tag{4.2}$$

At the steady state, in the view of the remarks made above, and to leading order in size, $u_R + u = u_{tot}$, where u_{tot} does not change. Using this and (4.1), from (4.2) one gets

$$ds + \frac{1}{T} du_R = 0. \tag{4.3}$$

One can now define $\psi = u - Ts$ and since T is a constant (4.3) can be written as

$$d(\psi) = 0.$$

ψ is the generalized free energy. (For more details see [21].)

One last remark is in order here. A useful physical interpretation exists [49,50] for the cross entropy $\Delta S(P, P^0)$. $T\Delta S$ provides a measure of the maximal amount of work available from the system coupled to a reservoir when it relaxes from a given nonequilibrium state P_n to the equilibrium one P^0 . Since the system is coupled to a reservoir, different choices of reservoir result in different explicit expressions for the available work. In the particular case of a heat reservoir, P^0 is the cannonical Gibbs distribution $\frac{1}{Z_0}\exp(-\beta u_n)$ and upon substitution in ΔS one gets that the cross entropy is proportional to the generalized free energy up to an additive constant, i.e.

$$\Delta S(P, P^0) \approx \beta\psi + \ln Z_0 \quad .$$

According to R. Levine [47] minimizing ΔS , when the mean energy of the system is known, is equivalent to maximizing the entropy under the same constraint.

Thus, the best probability distribution representing our system in a contact with a heat resrvoir is the one which minimizes the generalized free energy $\psi = u - Ts$ in a way consistent with the dynamics and any additional data. On a given level of mean-field description of the system, the variational parameters are the mean-field variables as defined in sec. 3.2. The rate equations (recall they are $n-1$ for n independent variables), incorporating the dynamics of the system, serve as additional constraints. Note also that by imposing the rate equations as constraints, the effect of the electric field is taken into aacount. At the pair level, the variational parameters are m, b_1 and b_2 respectively (see 3.9-12). The rate equations, $\frac{db_i}{dt} = 0$ (3.13-14), defining the steady state of the system are the corresponding constraints. An expression for the generalized free energy ψ on every level of approximation is derived in the next chapter using a cluster variation method.

CHAPTER V

EVALUATION OF THE GENERALIZED HELMHOLTZ FREE ENERGY BY A CLUSTER VARIATION METHOD

5.1. Cluster variation method

In order to apply the maximum entropy principle and thus to accomplish the general scheme (as outlined in ch.IV) for constructing the phase diagram for the DDIM in mean-field approximation, one needs to derive an expression for the generalized Helmholtz free energy Ψ. This goal can be achieved by employing a generalization of the cluster variation approach devised by Kikuchi [22] to generate systematic approximations for the free energy of order–disorder systems at equilibrium.

The CVM is one of the most successful of closed form approximation schemes. Often used in statistical physics, it is powerful and accurate in determining phase diagrams involving both first order and second order transitions. As with most methods aimed at a systematically improving series of approximations, the CVM, uses basically the same approach to attain the goal, i.e. constructing an approximation based on a small basic cluster and improving the approximation by making the cluster larger and larger. In principle, one can arrive at as accurate a solution as desired. While the simplest approxomations usually can be evaluated explicitly, when a large clusters are used the solution of the resulting equations requires the use of computers.

In Kikuchi's original formulation of the CVM, the state of the system is described in terms of some macroscopic parameters $\alpha_1, \alpha_2 \ldots$ which are chosen to be the fractions with which the configurations on certain clusters of lattice sites appear in the system. Next, for the free energy, an expression for the energy portion is easy to write down, while an expression for the entropy is less clear. In CVM one generates an approximate expression for the entropy through Boltzmann's relation $S = k_B \ln G$ in a purely combinatorial way (i.e. by counting the thermodynamic weight G approximately). The general method considers an ensemble of n lattices each containing N sites and computes the number of ways of arranging specified small clusters on this ensemble of lattices. This is obtained by adding the sites one at a time and when the number of ways has been calculated the approximation to the entropy S is obtained. Minimizing the free energy F with respect to the α_i's, one arrives at a set of non-linear algebraic equation. When solved, substitution back into either the free energy or directly into the physical quantities gives a complete description of the model.

It was shown by Kikuchi that by a suitable choice of the variables this technique leads to the approximations of Bethe and the "variation method" of Kramers and Wannier. Also an improved version for the 3-dimensional Ising model on a simple cubic lattice was compared with the rigorous expansion of the partition function by Kirkwood's method of moments, with agreement up to the fourth moment (for the disordered phase). But in the original Kikuchi formulation, CVM becomes difficult to follow for large clusters because of the complex combinatorial reasoning involved for each lattice and each basic figure. To overcome this problem CVM has been reformulated and improved schemes have been proposed several times.

Barker's formulation [51] has a relative computational simplicity. It is essentially a generalization of the quasi-chemical approximation. Later Morita [23,24] reformulated the CVM using a generalized cumulant expansion for the entropy in terms of reduced probability functions for both classical and quantum cases. It is conceptually more favorable than the previous formulations.

The fundamental question whether the CVM approximations converge towards the rigorous solution in the thermodynamic limit of an infinitely extended lattice has been addressed by A. Schlijper [52]. He has proven that a suitably chosen hierarchy of CVM approximations underestimates the free enrgy per lattice site and monotonously converges to some limit. He established that this limiting value equals to some exact result under slightly more restrictive conditions on the hierarchy of approximations. He noticed that Morita's expansion is a Möbius inversion. This aspect has been exploited further by G. An [53], reaching a very clear and mathematically simple formulation of the CVM as the truncation of a Möbius inversion.

5.2. Morita's formulation and application to the DDIM

In this section the expression for the free energy will be generalized for the DDIM. We essentially follow Morita since his formulation requires only slight modifications to include the effect of the electric field. Also, in this formulation and notation, the connection between the CVM approximation and the coarse-graining of the master equation is very clearly seen, allowing different levels of approximations to be generated by the proposed method. Finally Morita's formulation is independent of the underlying lattice structure (which is not true for the most of the other existing formulations), so that it is applicable to cases with longer range interactions.

Consider the exact and most general expression for the free energy, which is given by the minimum value of:

$$\begin{aligned}\Psi = &\sum_{\sigma_1\in\Theta_1}\cdots\sum_{\sigma_N\in\Theta_N}\rho_t^{(N)}(\sigma_1,\ldots,\sigma_N)\times H(\sigma_1,\ldots,\sigma_N)\\ &+k_BT\sum_{\sigma_1\in\Theta_1}\cdots\sum_{\sigma_N\in\Theta_N}\rho_t^{(N)}(\sigma_1,\ldots,\sigma_N)\times\ln\rho_t^{(N)}(\sigma_1,\ldots,\sigma_N)\quad,\end{aligned}\tag{5.1}$$

for the variation of the joint probability distribution function $\rho_t = \rho_t^{(N)}(\sigma_1,\ldots,\sigma_N)$ for the entire lattice, subject to the normalization constraint

$$\sum_{\sigma_1\in\Theta_1}\cdots\sum_{\sigma_N\in\Theta_N}\rho_t^{(N)}(\sigma_1,\ldots,\sigma_N)=1\quad.$$

The energy of the system $H(\sigma_1,\ldots,\sigma_N)$ in general could be a quite complicated expression but in our case it has the simple form given by (2.1).

Following Morita one can define a hierarchy of n-spin functions $\eta_t^{(n)}$ that are a measure of the correlation between the n spins by

$$\eta_t^{(2)}(\sigma_i,\sigma_j) = \frac{\rho_t^{(2)}(\sigma_i,\sigma_j)}{\rho_t^{(1)}(\sigma_i)\rho_t^{(1)}(\sigma_j)}$$

$$\vdots$$

$$\eta_t^{(n)}(\sigma_1,\ldots,\sigma_n) = \frac{\rho_t^{(n)}(\sigma_1,\ldots,\sigma_n)}{\prod_{i=1}^n \rho_t^{(1)}(\sigma_i)\prod_{i>j}\eta_t^{(2)}(\sigma_i,\sigma_j)\cdots\prod_{i_1<\cdots<i_{n-1}}\eta_t^{(n-1)}(\sigma_{i_1},\ldots,\sigma_{i_{n-1}})}\,, \tag{5.2}$$

where $\rho^{(n)}$, $n = 1,2\ldots$ are the reduced probability functions, defined in sec. 3.2. Then the joint probability distribution for the entire system can be written in terms of these correlation functions as

$$\rho_t(\sigma_1,\ldots,\sigma_N) = \prod_i \rho_t^{(1)}(\sigma_i)\prod_{i<j}\eta_t^{(2)}(\sigma_i,\sigma_j)\ldots\eta_t^{(N)}(\sigma_1,\ldots,\sigma_N)\,.$$

Next step is to define functions $G_t^{(n)}(i_1,\ldots,i_n)$ via $\ln G$, which serves naturally as the entropy for cluster $(i_1,\ldots,i_N)$

$$\ln G_t^{(n)}(i_1,\ldots,i_n) = -\sum_{\sigma_{i_1}\in\Theta_{i_1}}\cdots\sum_{\sigma_{i_n}\in\Theta_{i_n}}\rho_t^{(n)}(\sigma_{i_1},\ldots,\sigma_{i_n})\times\ln\rho_t^{(n)}(\sigma_{i_1},\ldots,\sigma_{i_n})\,. \tag{5.3}$$

Then in a way similar to the way η_t functions were defined one can also introduce the correlation functions $F_t^{(n)}$

$$F_t^{(2)}(i,j) = \frac{G_t^{(2)}(i,j)}{G_t^{(1)}(i)G_t^{(1)}(j)}$$

$$\vdots$$

$$F_t^{(n)}(i_1,\ldots,i_n) = \frac{G_t^{(n)}(i_1,\ldots,i_n)}{\prod_{l=1}^n G_t^{(n)}(i_l)\prod_{l_1<l_2}F_t^{(2)}(i_{l_1},i_{l_2})\cdots\prod_{l_1<\cdots<l_n}F_t^{(n-1)}(i_{l_1},\ldots,i_{l_{n-1}})} \tag{5.4}$$

In terms of $\rho_t^{(n)}$, $G_t^{(n)}$ and $F_t^{(n)}$, we arrive at the following expression for the free energy, which is still exact :

$$\begin{aligned}\Psi = &\sum_{<ij>}^{N} \rho_t^{(2)}(\sigma_i,\sigma_j)H(\sigma_i,\sigma_j)\\ &+ k_BT\Big[\sum_{i=1}^{N}\ln G_t^{(1)}(i) + \sum_{i>j}\ln F_t^{(2)}(i,j) + \sum_{i>j>k}\ln F_t^{(2)}(i,j,k) + \cdots +\\ &+ \ldots \ln F_t^{(N)}(1,\ldots,N)\Big]\end{aligned} \tag{5.5}$$

Here, in the first term, we have used that the Hamiltonian has only nearest-neighbor interactions. The minimum value of this expression cannot be found unless some approximations are made. As is shown by Morita, the various levels of approximations in the framework of the CVM correspond to different choices of families of indecomposable small clusters (or "preserved clusters" in the terminology introduced by Morita). The approximation is implemented by requiring that

$$\eta_t^{(n)}(\sigma_1,\ldots,\sigma_n) = 1 \quad \text{and} \quad F_t^{(N)}(i_1,\ldots,i_n) = 1$$

for all n-point clusters that do not belong to some family of indecomposable clusters. The physical meaning of this assumption is neglecting all correlations other than in the indecomposable clusters. Of course, to get a meaningful result one has to choose the family of indecomposable clusters from appropriate physical considerations, i.e. the family of the indecomposable clusters should be chosen in a such way as to take into account the most important correlations in the system. The higher the level of approximation the larger is the subset of indecomposable clusters. The approximation usually improves as larger indecomposable clusters are introduced.

For the case of an Ising ferromagnet on a square lattice with nearest-neighbor interactions only, the simplest scheme is the pair level approximation. In this case the indecomposable clusters are the lattice points themselves and pairs of nearest-neighbor lattice points (sometimes called the bond approximation). Therefore, one has

$$\begin{aligned} \eta_t^{(n)}(\sigma_{i_1}, \ldots, \sigma_{i_n}) = 1 \qquad & \text{for} \quad n > 2 \quad , \\ \eta_t^{(2)}(\sigma_i, \sigma_j) = 1 \qquad & \text{for} \quad |\hat{i} - \hat{j}| > 1 \quad . \end{aligned} \tag{5.6}$$

The same assumption is made for the correlation functions $F_t^{(n)}$:

$$\begin{aligned} F_t^{(n)}(i_1, \ldots, i_n) = 1 \qquad & \text{for} \quad n > 2 \quad , \\ F_t^{(2)}(i, j) = 1 \qquad & \text{for} \quad |\hat{i} - \hat{j}| > 1 \; . \end{aligned} \tag{5.7}$$

A simple way to account for site and bond contributions is to associate two bonds to each site. Using (5.3) for G and (5.4) for $F_t^{(2)}(i,j)$ and the approximations (5.6,7), one obtaines an expression for the free energy by summing over the site index alone :

$$\begin{aligned} \Psi = & - J \sum_{i=1}^{N} \left(\rho_t^{(2)}(i, i + \hat{e}_1) + \rho_t^{(2)}(i, i + \hat{e}_2) \right) \\ & - k_B T \left[3 \sum_{i=1}^{N} \ln G_t^{(1)}(i) - \sum_{i=1}^{N} \left(\ln G_t^{(2)}(i, i + \hat{e}_1) + \ln G_t^{(2)}(i, i + \hat{e}_2) \right) \right] \; . \end{aligned} \tag{5.8}$$

But still the problem of minimizing (5.8) is quite untractable. The homogeneity assumption (3.8,9), in addition to the approximations made above, simplifies enormously the minimization procedure. Using the notation (3.10) introduced in sec. 3.3 and after some manipulations over (5.8) one gets the final expression for the free energy of Ising ferromagnet in the presence of an electric field along one of the principal axes ($\hat{e}_1$) :

$$\begin{aligned} & \Psi = N\psi \; , \; \text{where} \\ & \psi = J(4b_1 - 1) + (4b_2 - 1) + \\ & - k_B T \left[3(x \ln x + y \ln y) - \sum_{i=1}^{2} (z_i \ln z_i + 2b_i \ln b_i + w_i \ln w_i) \right] \; . \end{aligned} \tag{5.9}$$

5.3. Formulation in terms of the correlation functions

The site probabilities x and y and the pair probabiliies z_i, b_i and w_i , $i = 1,2$ are not independent variables. They are connected through relations (3.11). A scheme for determining a set of independent cluster variables for characterizing the concentration of the different cluster configurations was presented by J. Sanchez and D. de Fontaine [25,26]. Using this scheme simplifies considerably the minimization of the free energy. This is especially important if one would like to go to higher levels of approximation, where the degree of difficulty involved in the minimization of the free energy grows fast with the size of the basic cluster because of the linear constraints existing between different cluster configurations. Also, adopting this scheme will enable us to generalize in a straightforward manner our approach for treating the antiferromagnetic case (some preliminary calculations are in progress).

The most convenient set of independent variables appears to be the set of correlation functions. The total number of independent variables associated with a given cluster variation approximation is determined (see in [25,26]) by the total number of distinct clusters in which the basic cluster, consisting of r points, can be decomposed. A correlation function $\xi(r,t)$ is associated with every such cluster (r refers to the number of lattice sites in the cluster and t enumaretes the distinct clusters).

On the pair level of cluster approximation, for the ferromagnetic case, one has to consider the following set of clusters and subclusters :

- pairs of nearest-neighbor lattice sites in direction parallel and in direction perpendicular to the electric field;
- the single lattice sites.

The corresponding correlation functions are defined as follows

$$\begin{aligned}\xi(1,1) &= \langle\sigma(i)\rangle \quad , \\ \xi(2,1) &= \langle\sigma(i)\sigma(i+\hat{e}_1)\rangle \\ &\equiv \langle\sigma(i)\sigma(i-\hat{e}_1)\rangle \quad , \\ \xi(2,2) &= \langle\sigma(i)\sigma(i+\hat{e}_2)\rangle \\ &\equiv \langle\sigma(i)\sigma(i-\hat{e}_2)\rangle \quad i\in\Lambda \ .\end{aligned} \tag{5.10}$$

From the definition, the single site correlation function, $\xi(1,1) = m$, the ferromagnetic order parameter (total magnetization per site).(Note, for the antiferromagnetic case one has to consider two different sublattices and correspondingly two site correlation functions $\xi(1,1)$ and $\xi(1,2)$, and two more pair correlation functions. $\xi(1,1)$ and $\xi(1,2)$ define the magnetization per lattice site belonging to different sublattices.)

The site and pair probabilities are expressed through the correlation functions $\xi(r,t)$ in the following way

$$\begin{aligned}\rho^{(1)}(i) &= \frac{1}{2}[1+i\xi(1,1)] \quad , \\ \rho_1^{(2)}(i,j) &= \frac{1}{4}[1+(i+j)\xi(1,1)+ij\xi(2,1)] \quad , \quad i,j=1,2 \\ \rho_2^{(2)}(i,j) &= \frac{1}{4}[1+(i+j)\xi(1,1)+ij\xi(2,2)] \quad ,\end{aligned} \tag{5.11}$$

Substituting these expressions into the equations of motion and the expression for the generalized free energy (5.8) we have the problem defined in terms of the independent variables.

CHAPTER VI

MEAN-FIELD RESULTS FOR DDIM

6.1. Numerical realization

In this chapter the results from the numerical realization of the procedure, outlined in chapters III – V, on the pair level of approximation are described.

Ther are many ways to minimize the free energy of the DDIM

$$\psi = u - Ts \quad , \tag{6.1}$$

where

$$u = -J\left(\xi(2,1) + \xi(2,2)\right) \quad ,$$

$$s = 3\sum_{i=\pm 1} \rho^{(1)}(i) \ln \rho^{(1)}(i) - \left(\sum_{i,j=\pm 1} \rho_1^{(2)}(i,j) \ln \rho_1^{(2)}(i,j) + \sum_{i,j=\pm 1} \rho_2^{(2)}(i,j) \ln \rho_2^{(2)}(i,j) \right)$$

with respect to the independent mean-field variables $m \equiv \xi(1,1)$, $\xi(2,1)$ and $\xi(2,2)$ (see (5.9 – 11)). The constraints of being in a nonequilibrium steady state are defined by setting the rate equations for $\xi(2,1)$ and $\xi(2,2)$ equal to zero :

$$\begin{aligned} \frac{d\xi(2,1)}{dt} &\equiv G_1(m, \xi(2,1), \xi(2,2); T, E) = 0 \\ \frac{d\xi(2,1)}{dt} &\equiv G_2(m, \xi(2,1), \xi(2,2); T, E) = 0 \quad . \end{aligned} \tag{6.2}$$

We have tried several methods. For example, one can use the Lagrange multipliers technique. But it is more difficult numerically than the one we have adopted. Also, in this approach, it is unclear how to give a physical interpretation to the Lagrange multipliers corresponding to the constraints. Indeed, we found that the simplest and more accurate way is the following. At fixed temperature of the reservoir T

and fixed driving field strength E for every given value of the magnetization per site m , the rate equations (6.2) can be solved numerically for $\xi(2,1)$ and $\xi(2,2)$:

$$\xi(2,1) = \xi_1(m;T,E)$$
$$\xi(2,2) = \xi_2(m;T,E) \quad .$$

Upon substitution in the expression for the generalized free energy ψ (6.1), one gets the latter only as a function of m , i.e.

$$\begin{aligned} \psi &= \psi(m, \xi_1(m;T,E), \xi_2(m;T,E); T, E) \\ &\equiv \psi(m;T,E) \quad . \end{aligned} \tag{6.3}$$

This way, since the constraints are taken into account, we have to minimize ψ (6.3) with respect to the only variational parameter left, m , to find the best probability distribution in terms of the mean-field variables .

This procedure has been carried out independently in two different programs. In the first, (given in app. B) all quantities are expressed in terms of m, b_i, z_i and w_i $i = 1,2$ (3.10). There also, analytic expressions for the cluster probabilities and the rate equations are used. It is designed to treat the ferromagnetic case ($J > 0$) only.

The second program is more general. It could be used to treat the antiferromagnetic case and off-critical densities as well. The effect of a driving field in arbitrary direction could be studied. There, all the variables are expressed in terms of the correlation functions (5.10).(Treating the antiferromagnetic case requires several new variables to be introduced. In particular, one has to introduce the natural order parameter for the antiferromagnetic, i.e. the staggered magnetization, for which a rate equation can be derived in a way similar as for the fractions b_i, $i = 1,2$.) All the following steps are carried out numerically :

- construction of the probabilities for all clusters;
- evaluation of the energy change ΔH and the coresponding changes in $\xi(2,1)$ and $\xi(2,2)$ when exchange occurs for every particular cluster;
- construction of the rate equations, taking into account the contributions of the different clusters.

The ferromagnetic and antiferromagnetic case are obtained by appropriate choices of the variables.

In the equilibrium case ($E = 0$) there is only one rate equation ($b_1 = b_2$), which can be solved analytically. In fact, it is a redundant constraint. One can get the same result by minimizing ψ with respect to both b and m . Of course, both ways give the same result.

6.2. Description and discussion for Metropolis rates

Here, the results from the study of the nonequilibrium steady state of the two dimensional DDIM on square lattice with $\Gamma_{\|}$ and $\Gamma_{\perp}$ are presented. The calculations were performed with the rate used in most MC simulations, since it provides comparatively fast convergence to the steady state, i.e. the Metropolis rate :

$$\phi(\lambda) = \begin{cases} \exp(-\lambda), & \lambda > 0 \\ 1, & \lambda \leq 0. \end{cases}$$

We started by exploring first the dependence of the generalized free energy $\psi = u - Ts$ on the magnetization per site m . We plot $\psi(m)$, using T , the temperature of the reservoir, and E , the driving field strength, as parameters. Since the equations of motion are invariant under the exchange of m with $-m$ and the expression (6.2) for ψ is an even function of m , we have restricted our calculations to nonnegative values of m . It appears that there exists a certain temperature depending on the electic field $T_c(E)$, such that the behavior of the $\psi(m)$ changes. Above $T_c(E)$ ψ is a convex function and it has a single minimum at $m = 0$, i.e. there is a single disordered phase. Below $T_c(E)$, $\psi(m)$ has the familiar doublehump shape with two minima at $m_{1,2} = \pm\bar{m}(T, E)$ and a maximum at $m = 0$. This indicates that a spontaneous symmetry breaking takes place at low enough temperatures. Thus m emerges as the natural order parameter of the phase transition. ψ is plotted versus m for $E \to \infty$ at three different temperatures in fig. 6.1. The behavior is typical for all values of the driving field strength. Since we studied the system in mean-field theory, the result here is applicable only for homogeneous phases. In simulations, the total magnetization is usually fixed to be zero and the phase transition is signalled by the system's separating into two bulk phases with the "spontaneous" magnetization $\pm\bar{m}$. To describe such phenomena, we need to use the Maxwell constuction in conjuction with our result. Krug, et al. [14] have investigated this kind of behavior, seeking a solution to the master equation, but only in the fast-rate limit. Here, in this context, the Maxwell constuction appears in a natural way as an extension of the PME.

The dependence of the spontaneous magnetization $\bar{m}$ on the temperature for fixed value of the field E was studied next. It was found that $\bar{m}$ goes continuously to zero as T approaches a certain critical temperature $T_c(E)$ – a clear indication that a second order phase transition is taking place. The result is in complete accordance with the order of the phase transition found in the MC simulations [2,4 – 7]. To ensure more accurate determination of the $T_c(E)$, the energy ψ was fitted at every step in T around $m = 0$, with an even polynomial in m. The change of sign of the coefficient of m^2 was used to find the temperature at which the $m = 0$ turns from a maximum to a minimum. The dependence of $\bar{m}$ on T is displayed in fig. 6.2 for the equilibrium case, $E = 10$ and infinitely strong field. It is clearly seen that for fixed T, the corresponding $\bar{m}(E)$ increases with E, showing that the presence of a driving field favors the ordered phase. This can also be well seen in fig. 6.3, where the dependence of $\bar{m}$ on E is displayed. For $T = 3.0$, which lies between the equilibrium critical temperature $T_c(0)$ and the critical temperature for infinitely strong field $T_c(E \to \infty)$, $\bar{m}$ increases from zero (disordered phase) rapidly towards the saturation value ≈ 0.6. For $T = 2.0$ ($T < T_c(0)$) the increase from the equilibrium value to the saturation one is less pronounced – only 2% . In fig. 6.4, a larger scale is used so that details could be seen. The discontinuities in the slope of $\bar{m}$ are due to corners in the Metropolis rates at $E = 4, 8, 12$. They do not have any physical significance.

The free energy after the minimiztion is depicted in fig. 6.5 as a function of the temperature.

We have studied how the existence of a phase transition in the steady state depends on the driving field E . We found out, in accordance with MC simulations [1,2,6], that the phase transition persists at all values of the electric field. The critical temperature increases monotonically with E and for $E > 15$ (in units of J) $T_c(E)$ does not change appreceably. For these strong fields, jumps against the field practically never occur. The calculation for the equilibrium case yields $T_c(0) = 2.885$, which is the well known Bethe mean-field result. In the limit of an infinitely strong field the critical temperature reaches the saturation value $T_c(E \to \infty) = 3.3228$ (for Metropolis rates). The total change in T_c when the electric field is varied from zero to infinity is $\approx 15\%$. Early MC simulations yielded $T_c(E \to \infty) = 3.125$ [1,2]. More extensive runs with larger size of the lattice [5,6] give $T_c(E \to \infty) = 3.075 \pm 0.007$ which is 35.5% increase over the exact (Onsager) $T_c(0) = 2.269$. The dynamic mean-field theory of Dickman [15] estimates $T_c(E \to \infty) \approx 3.206$ (11% increase) on the same level of approximation.

The error due to the mean-field approximation is $\approx 27\%$ for $E = 0$ as compared to $\approx 8\%$ for $E \to \infty$. Why the pair approximation is "better" for this nonequilibrium system is unclear.

The detailed dependence of T_c on E is shown in fig. 6.6. The overall shape of the curve seems to reproduce well the qualitative behavior of $T_c(E)$ as described in [2]. For comparison see also fig. 5 in ref. [15].

There is evidence [15] that if one goes to square level of approximation $T_c(E)$

for small E is actually a linear function of E (not quadratic as it is at pair level). Since $T_c(E)$ is an even function of E this implies that at $T = 0$ it is nonanalytic (at least for Metropolis rates). Thus an extension of our theory to a higher level is desirable.

It is interesting to see how the nearest-neighbor pair probabilities b_i, z_i, w_i, $i = 1, 2$ are affected by the presence of a driving field. As expected, the field E induces anisotropy and the probabilities in directions parallel and transverse to the field are no longer equal. Though unequal, they have quite close values. In fig. 6.7 , the difference between the fractions of up-down spin pairs, $b_2 - b_1$, as a function of the temperature of the reservoir T , are displayed for two different values of the driving field. As $T \rightarrow 0$ both b_1 and b_2 approach zero (see fig. 6.8) corresponding to a completely ordered phase. The maximum is attained at $T_c(E)$. In the limit of $T \rightarrow \infty$ b_1 and b_2 are expected to approach $1/4$ coresponding to a completely disordered phase. The number of broken bonds (in both directions) in the ordered phase increases rapidly as T increases (fig. 6.8) until the transition temperature is reached. In the disordered phase the increase towards the saturazation value of $1/4$ is much slower. This qualitative behavior holds for both $E = 0$ and $E \neq 0$. For $T < T_c(0)$, $b_i(E) < b_i(0)$ corresponding to a higher level of ordering, induced by the field. In the high temperature regime, however, the field stimulates higher level of disorder.

In the next figure (6.9) we show the dependence of the b_1 and b_2 versus the driving field strength at $T = 3$ ($T_c(0) < T < T_c(E \rightarrow \infty)$). The maximum is at $E \approx 5$ and the saturation values are practically achieved for $E \geq 15$. For $E \leq 6.5$ the system is in the homogeneus phase (see also fig. 6.3).

For completeness, the dependence of the fraction of up-up nearest-neighbor pairs (z_1) and down-down (w_1) pairs on T at fixed E and on E at fixed T are shown in fig. 6.10 and 6.11 respectively.

The internal energy per lattice site u (in units of T) and the entropy s at nonequilibrium steady state of the system are plotted in fig. 6.12 and 6.13 (see also fig. 6.23 where their dependence on E is displayed). u and s have the same qualitative behavior as b_1 and b_2 . The difference between the internal energy per site for $E \to \infty$ and $E = 0$ versus T is shown in fig. 6.14. The two extrema correspond to $T_c(0)$ and $T_c(E \to \infty)$. For comparison see [4] where a similar plot for u is displayed.

The nearest-neighbor pair (short range) correlations ξ_1 and ξ_2 are depicted in fig. 6.15 for $E \to \infty$ versus the reduced temperature $T/T_c(0)$ in order to be compared with a similar plot in [54]. In the disordered phase the effect of the field reduces the correlations in both directions. Th effect is more pronounced in transverse direction. This is in complete accordance with the results reported from MC simulations [4,5], as well as the prediction of the dynamic mean-field theory [15].

The anisotropy induced by the field can be measured by the ratio [15] :

$$\zeta = \frac{z_1(T, E \to \infty) - z_2(T, E \to \infty)}{z(T, E = 0)} \quad .$$

At $T = 3.3$ (i.e., $T \approx T_c(E \to \infty)$ our theory gives $\zeta = 0.0537$ as compared to 0.057 given in [15].

At first sight the results and the plots are alike. In a strong field the anisotropy of the short-range correlations persists at quite high temperatures. We find, for $T = 100$, $\xi_2/\xi_1 \approx 0.617$. In the limit of $T \to \infty$, though, both ξ_1 and ξ_2 should go to zero, while according to [54] and from high temperature expansion show that even as $T \to 0$ $\xi_2/\xi_1 \to 0.41$. This discrepancy could be due to the adopted level of decription or to the mean-field approximation itself.

Another quantity of interest, which is readily computed in our theory, is the average steady state current in direction of the field j . The current for the bond $(i, i+\hat{e}_1)$ is defined by :

$$j(i;\sigma) = \Phi_E(i, i+\hat{e}_1, \sigma)(\sigma_i - \sigma_{i+\hat{e}_1})/2 \quad ,$$

i.e. this is the expected jump rate from i to $i+\hat{e}_1$ in a configuration σ . In mean-field theory it is assumed that this is the same for all i . By averaging over all possible configurations appearing on a cluster consisting of a given bond and all its nearest neighbors (with axis parallel to the field) one gets the average current j at a pair level of approximation. It could be written in the following form

$$j = n_+ - n_- \quad ,$$

where n_+ and n_- are the average number of jumps performed along and opposite to the field respectively. These are given by the following expression

$$n_\pm = \sum_k \phi(\Delta H(k) \mp E) P_k \quad .$$

The summation here is only over the bonds for which $\sigma_i \neq \sigma_{i+\hat{e}_1}$, since they are the only ones who have nonzero contribution. The explicit expression can be found in app. A.

We plot j versus E at fixed T in fig. 6.16. For $T = 2$, j first increases linearly with E and then saturates rapidly after $E = 5$. At this temperature the system is in the ordered phase for all values of E and the current is strongly supressed.

At higher temperatures ($T = 3$, which is between $T_c(0)$ and $T_c(E \to \infty)$), however, j increases considerably for $E \in [0, 6.5]$. For these values of E the system is in the disordered phase (see fig. 6.3). The saturation of the current for $E \geq 6.5$ corresponds to the saturation of the magnetization $\bar{m}$ and the fraction of up-down pairs of spins along the field b_1 . At high temperatures and strong field $j \approx b_1$. The temperature dependence of j is shown in fig. 6.17. The average current has a break in its slope at $T_c(E)$, consistent with the MC results [1,2,4]. This is a reported feature of some of the FIC, e.g. AgI , which are modeled by the DDIM. For $T \to 0$, $j \to 0$ since the system orders and b_1 is going to zero as well. At infinite electric field j saturates as $T \to \infty$, while for all finite fields , after reaching a maximum value in the homogeneuos phase , j decreases slowly towards zero as $T \to \infty$. However, this is an artifact of the order in which the limits $E \to \infty$ and $T \to \infty$ are taken. Physically, there are only finite fields and temperatures.

Since the system is not in equilibrium with the heat reservoir, it could be expected that it may be characterized by some effective temperature different from that of the reservoir. If, in analogy with the equilibrium case, one defines a quantity $\tilde{T}_s = \frac{\partial u}{\partial s}$, one can try to interpret this as the temperature of the system. Such an interpretation follows from the assumption that the entropy of the nonequilibrium distribution can be identified with the thermodynamic entropy, even though such a relation has not been proved to hold in nonequilibrium. As it can be seen from fig. 6.18 $\tilde{T}_s(E) > T$ for $E > 0$. Of course, for $E = 0$ $\tilde{T}_s = T$. This result is consistent with the fact that there is a constant flow of heat from the system to the reservoir. Aside from this, there is no other evidence that $\tilde{T}_s$ could indeed be viewed as the temperature of the system. The dependence of $\tilde{T}_S(E)$ on E is shown on fig. 6.24. It has the typical behavior displayed by other quantities of interest, i.e., saturation as $E \to \infty$.

6.3. Effects of different rates

We have also studied how the properties of the DDIM in nonequilibrium steady state depend on the choice of transition rates. In addition to Metropolis rates (6.1) we have employed also van Beijeren - Schulman rates (2.7) and the original Kawasaki rates. The transition probability for Kawasaki rates is defined as follows

$$\phi_k(\lambda) = \frac{1}{1 + \exp\left[\left(\Delta H \pm E\right)/T\right]} \quad . \tag{6.4}$$

As previously mentioned, the choice of rates is immaterial for studying equilibrium properties, as long as they satisfy the detailed balance condition. In the presence of a driving field, however, the properties of the system are expectedto depend on the choice of rates. This is our motivation to study the effect of rates in mean-field approximation.

There are several previous results on the effect of different rates. Unfortunately these are for the fast-rate limit of DDIM [3,4], so that direct comparison is not possible.

The dependence of various quantities of interest as functions of T at fixed E and as functions of E at fixed T are displayed in fig. 6.19 – 24. The basic observations are :

(i) For Kawasaki rates the results are very close to these obtained with Metropolis rates. This is expected, since the Kawasaki rates are essentially smoothed versions of the Metropolis one. All physical quantities have the same qualitative behavior and values close to these computed with Metropolis rates. There are no breaks in the slope of the physical quantities as for the Metropolis rates since (6.4) is a smooth function. Our calculations indicate that the differences are unessential. For example, $T_c(E \to \infty)$ with Kawasaki rates is ≈ 3.326 which gives negligible change over the result with Metropolis rates. The square level of approximation of Dickaman's dynamic mean-field theory estimates $T_c^K(E \to \infty) \approx 3.1904$ (as compared to the square level Metropolis result 3.134 , given by the same theory). $T_c(E \to \infty)$ with Kawasaki rates has not yet been determined in MC simulations.

(ii) The effects of van Beijeren - Schulman rates, on the other hand, are dramatically different. Except for the existence of a steady state current, all other nonequilibrium steady state quantities are identical to their equilibrium values. These results can be traced to the specific form of the van Beijeren - Schulman rates and the way the driving field enters into the dynamical equations for ξ . In other words, at the pair level, in which contributions from two clusters are summed, E enters through the same overall factor in both rate equations. Such a factor can be absorbed into a change of time scale.

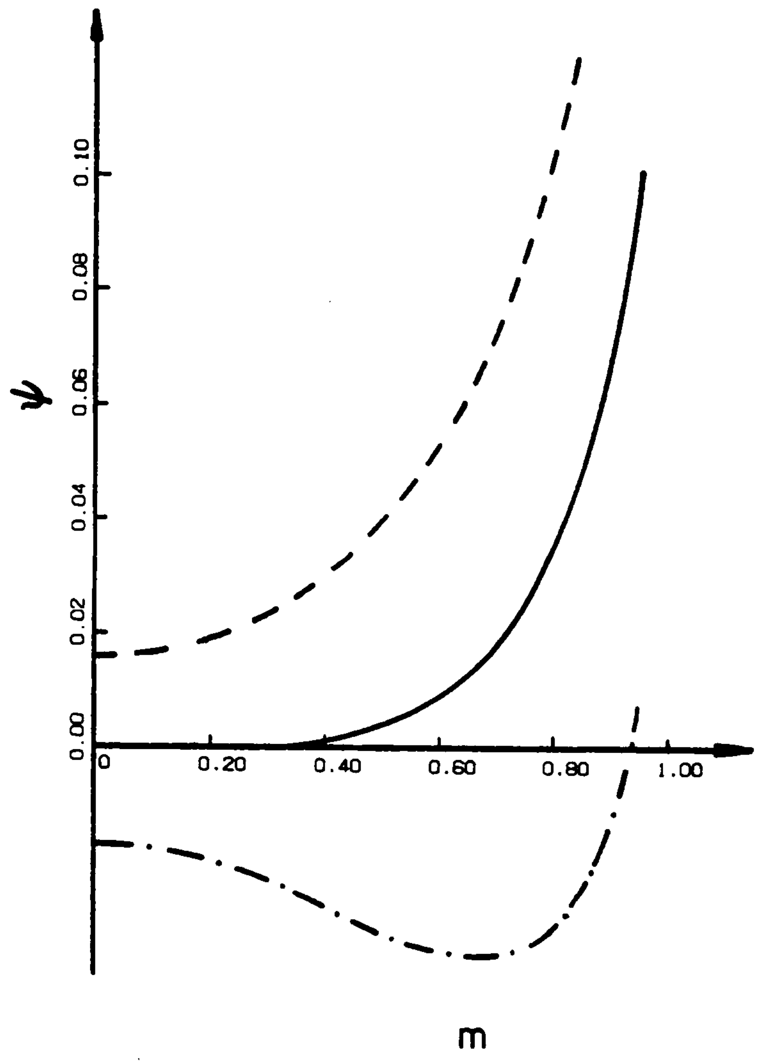


Fig. 6.1. The dependence of the free energy per site ψ versus the order parameter m is displayed for $E \to \infty$ for three different temperatures : $T > T_c$ (dashed line) ; $T = T_c$ (solid line) ; $T < T_c$ (dash-dotted line) .

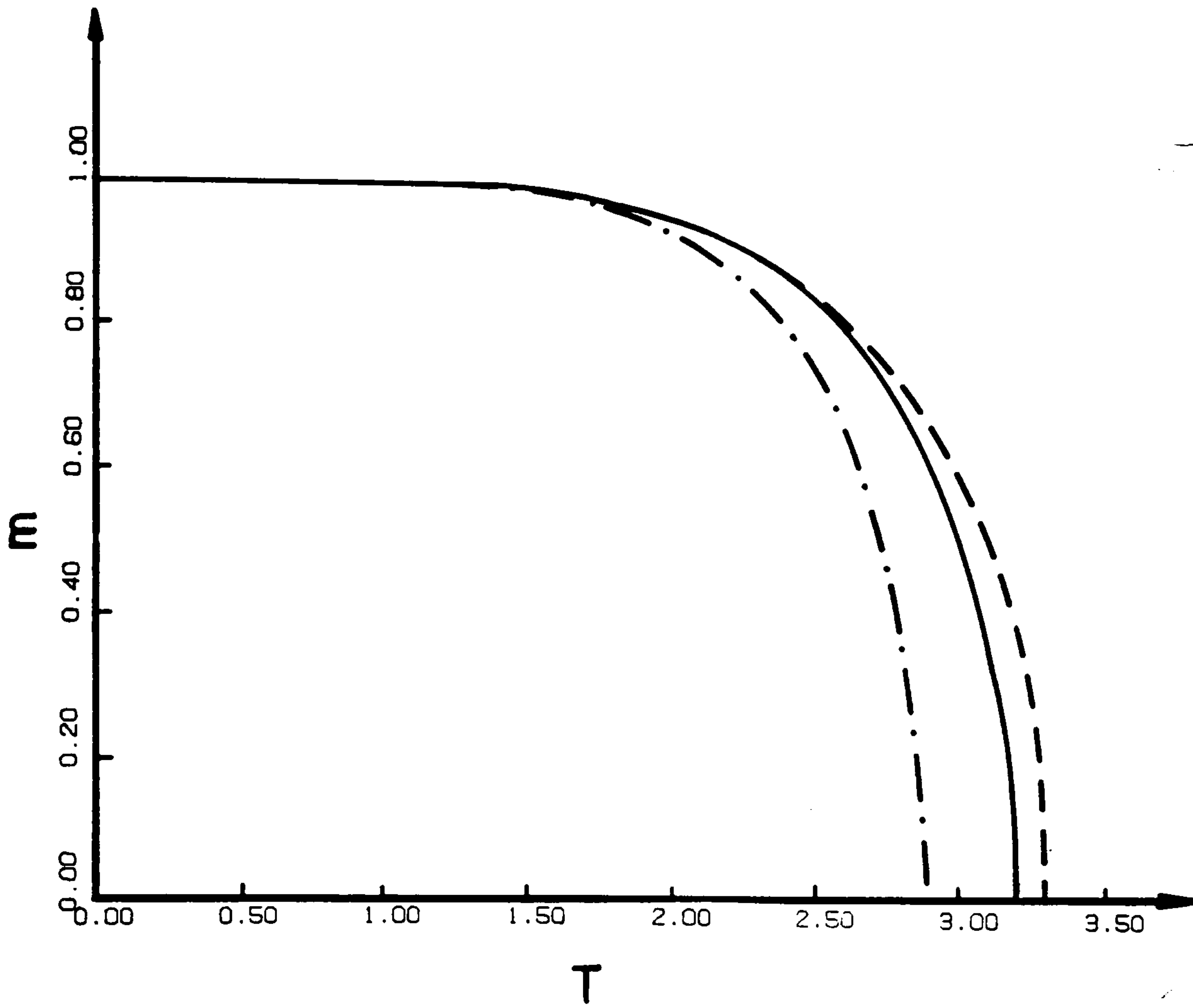


Fig. 6.2. Order - disorder phase diagram . The spontaneous magnetization m as a function of the temperature T is plotted for $E = 0$ (dash-dotted line), for $E = 10$ (solid line) and $E \to \infty$ (dashed line).

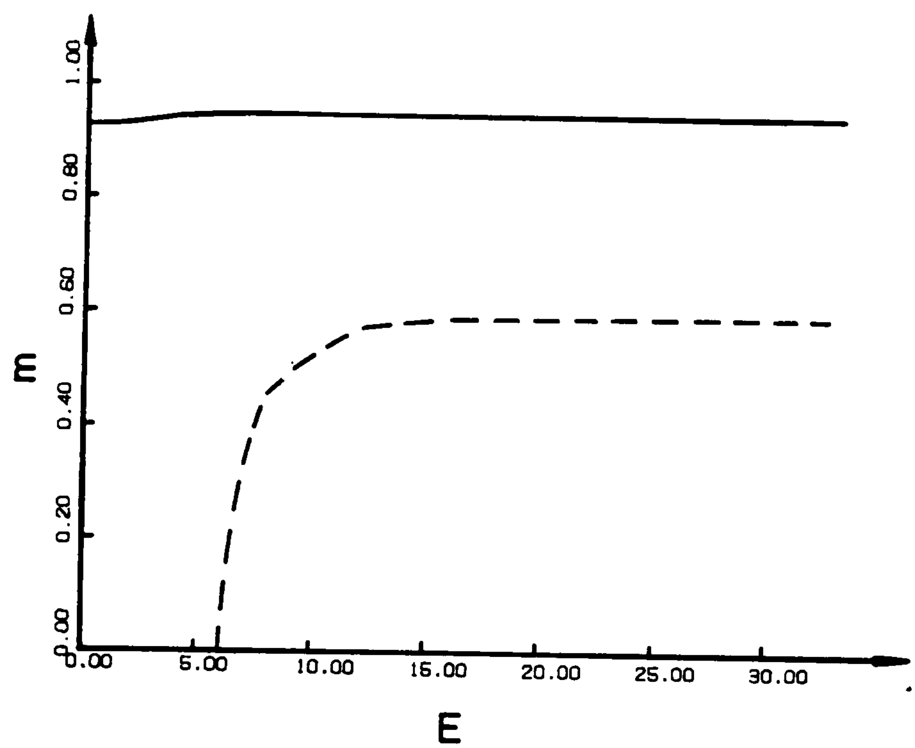


Fig. 6.3. The dependence of the order parameter m on the strength of the electric field E is shown for $T = 3.0$ ($T_c(0) < T < T_c(\infty)$) (dashed line) and for $T = 2.0$ ($T < T_c(0)$) (solid line).

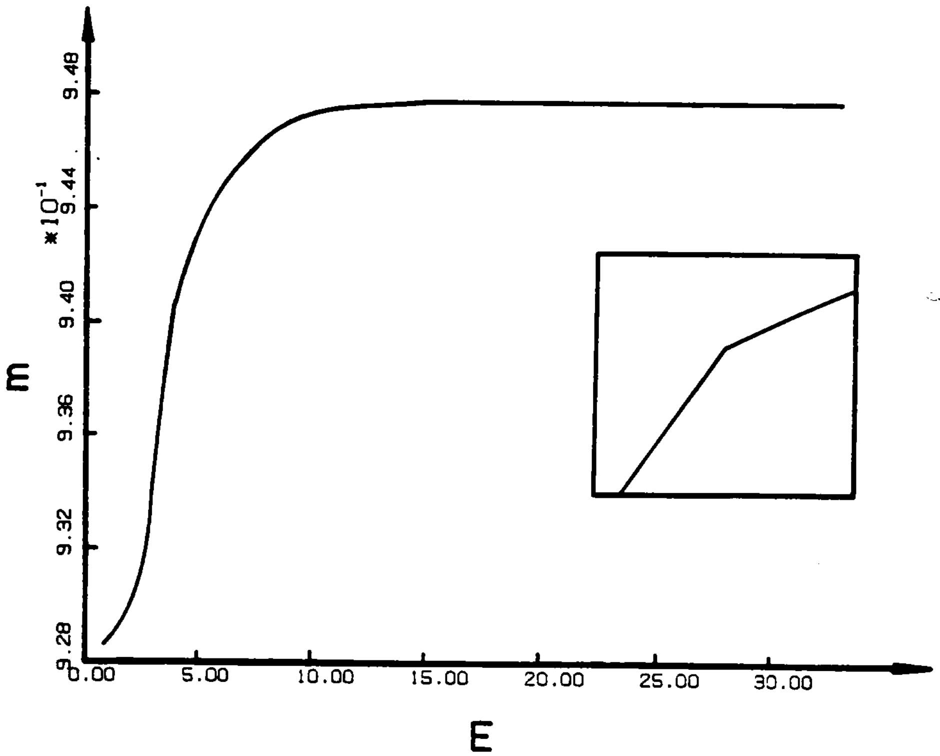


Fig. 6.4. The dependence of the order parameter at $T = 2$ (i.e. $T < T_c(0)$) is shown on a larger scale so that some details could be seen. The inset is a further enlargement showing the discontinuity in the slope of m versus E at $E = 4$. Similar discontinuities exist for $E = 8$ and $E = 12$ due to singularities in Metropolis rates. The same type of irregularities can also be seen in the graphs of the other physical quantities versus E .

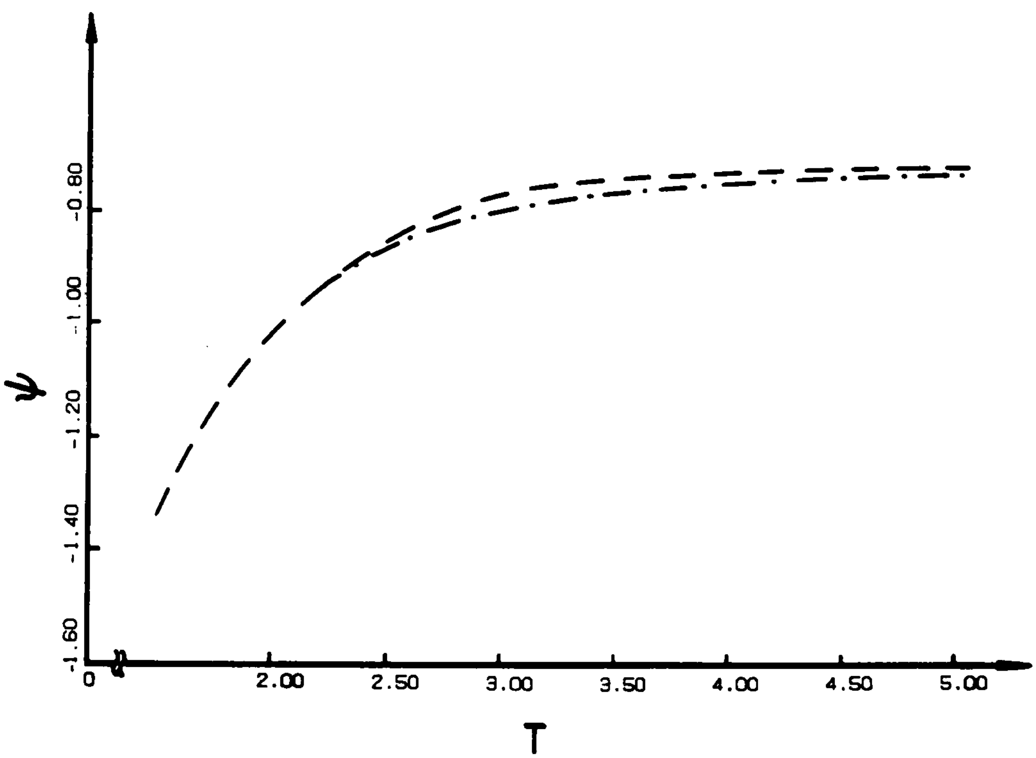


Fig. 6.5. The free energy of the system ψ (in units of T) after the minimization is plotted versus the temperature T for $E = 0$ (dash-dotted line) and for $E \to \infty$ (dashed line).

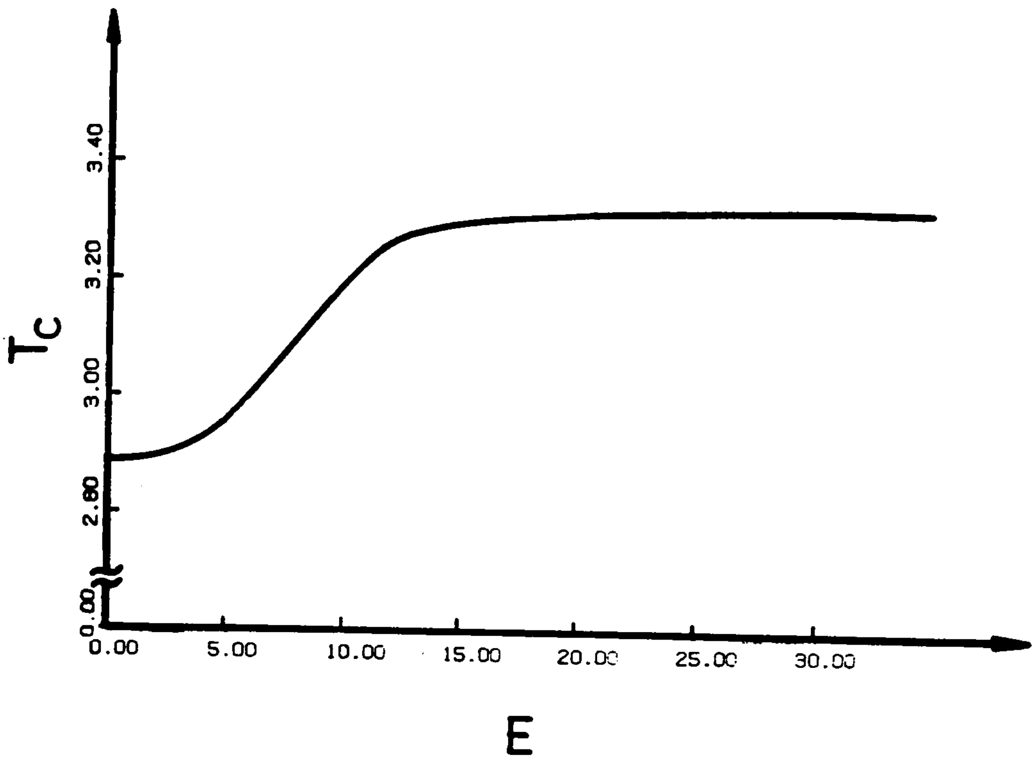


Fig. 6.6. The critical temperature T_c versus the driving field strength E (in units of J) for the DDIM ($J > 0$) in steady state, 2 dimensions, square lattice, Metropolis rates, pair level of cluster approximation.

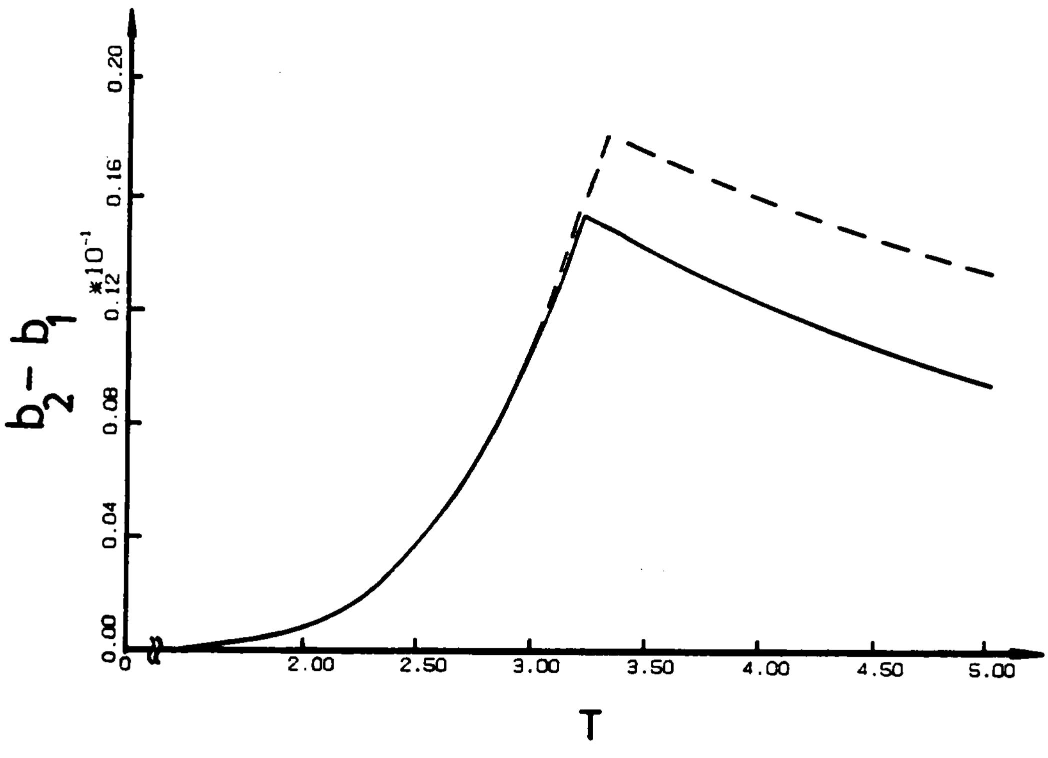


Fig. 6.7. The difference between the fraction of $(+,-)$ pairs in direction perpendicular to the field b_2 and along the field b_1 is displayed as a function of the temperature T for $E = 10$ (solid line) and for $E \to \infty$ (dashed line).

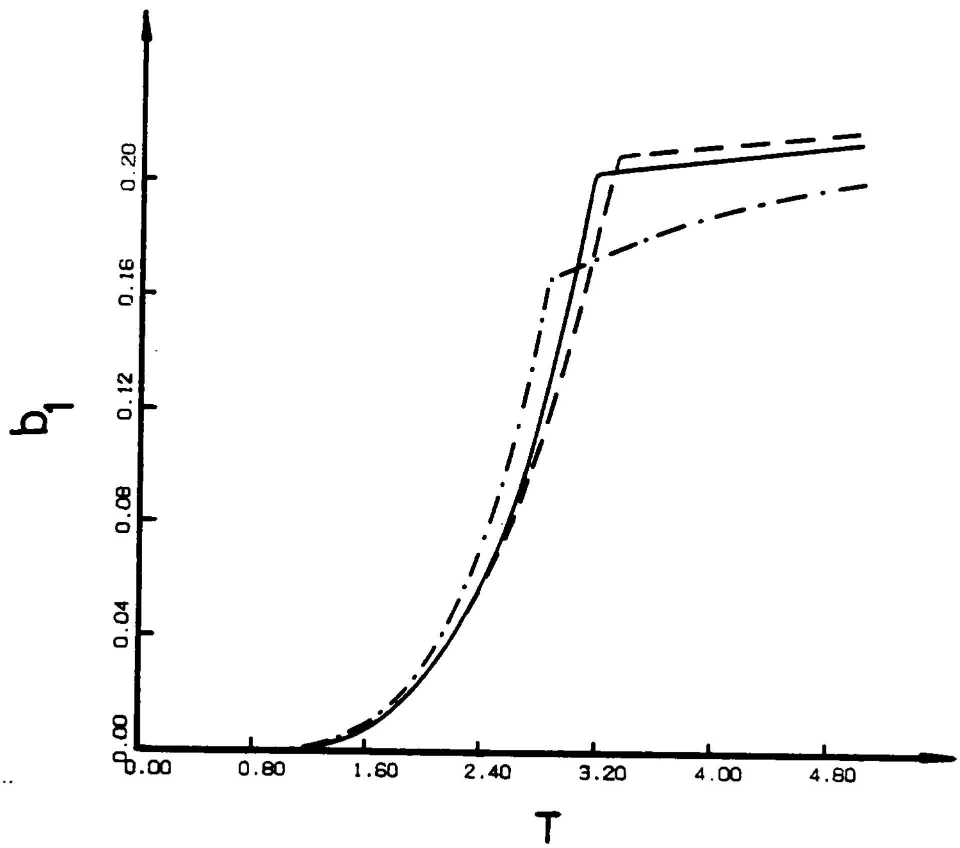


Fig. 6.8. The temperature dependence of the nearest-neighbor pair probability in direction of the field b_1 is displayed for the equilibrium case $E = 0$ (dash-dotted line), for $E = 10$ (solid line) and for $E \to \infty$ (dashed line). b_2 has similar behavior as a function of T .

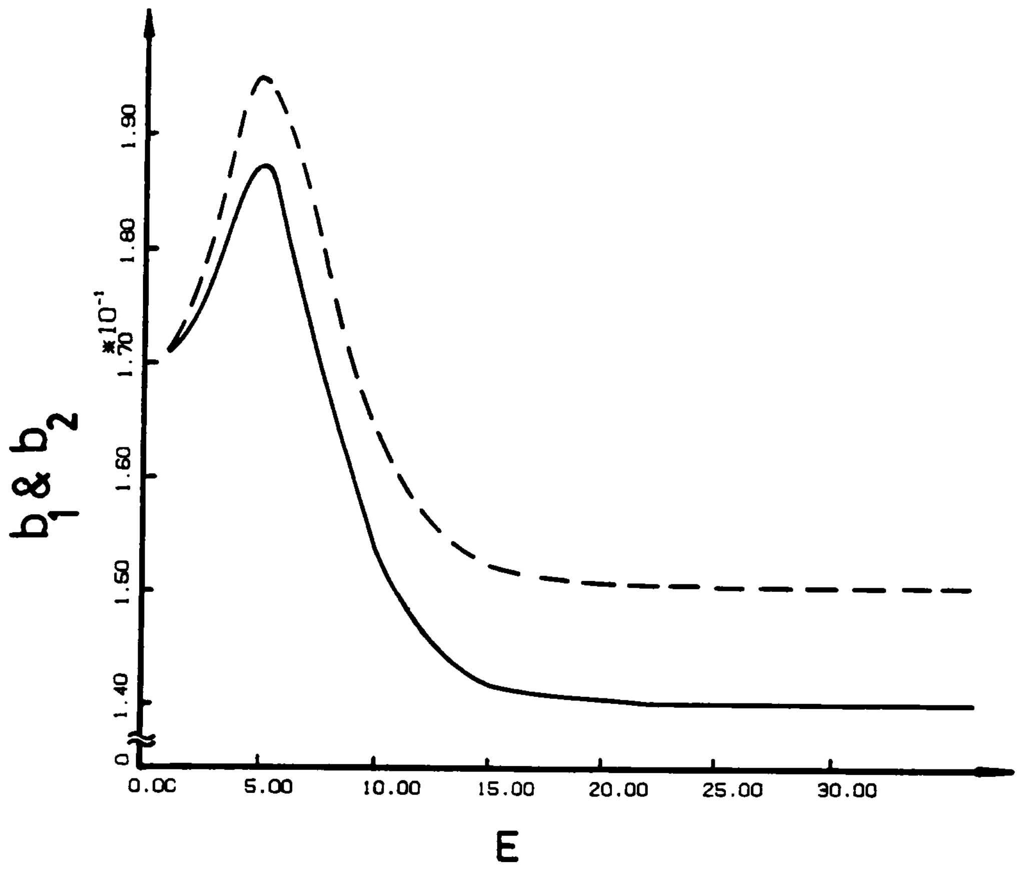


Fig. 6.9. The dependence of the pair probabilities along the field b_1 (solid line) and in direction perpendicular to the field b_2 (dashed line) on the strength of the electric field E is displayed for $T = 3$ ($T_c(0) < T < T_c(E \to \infty)$).

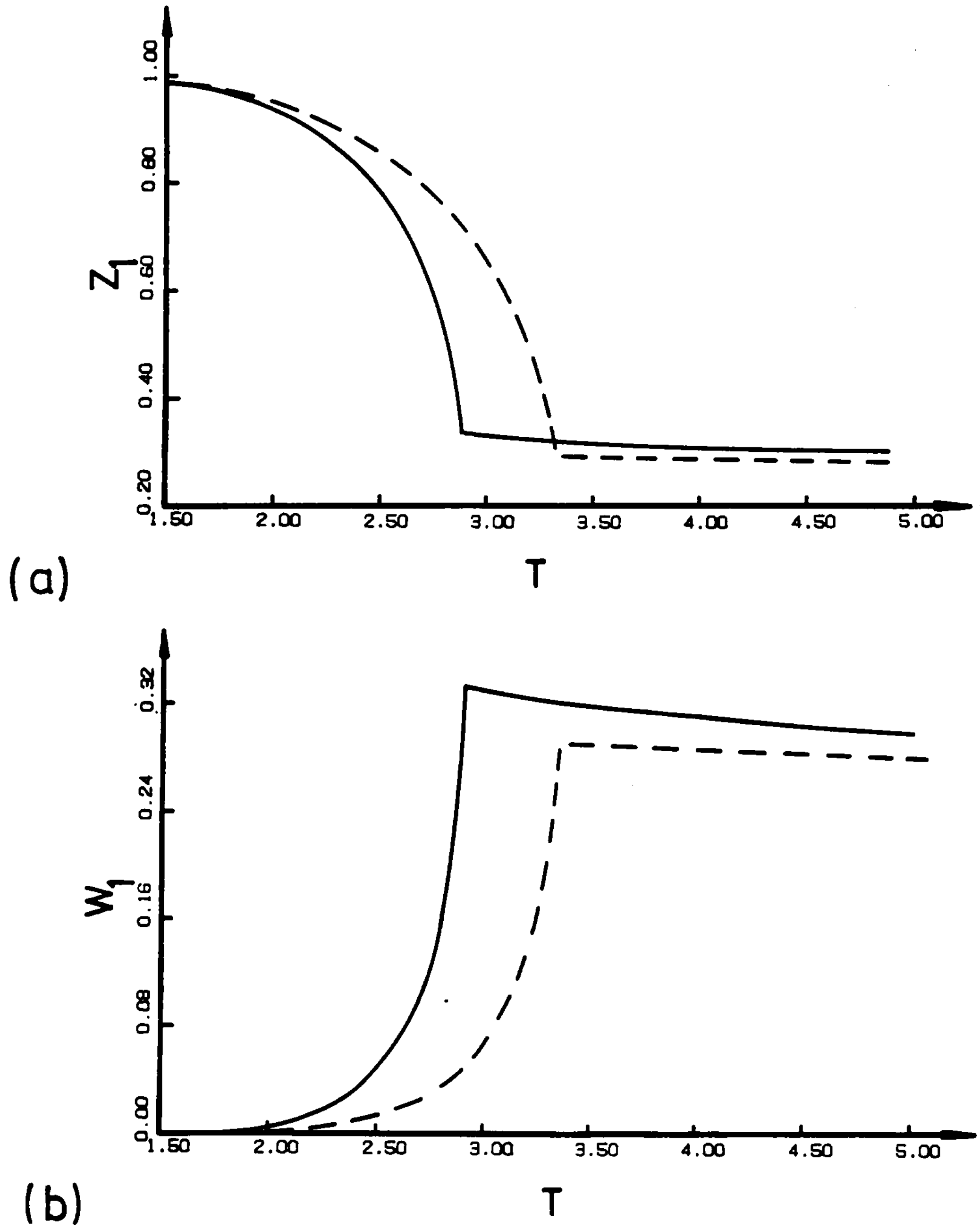


Fig. 6.10. Temperature dependence of the nearest-neighbor pair probabilities along the field for spins up z_1 - (a) and spins down w_1 - (b) are displayed. The solid line presents the results for $E = 0$ and the dashed line for $E \to \infty$.

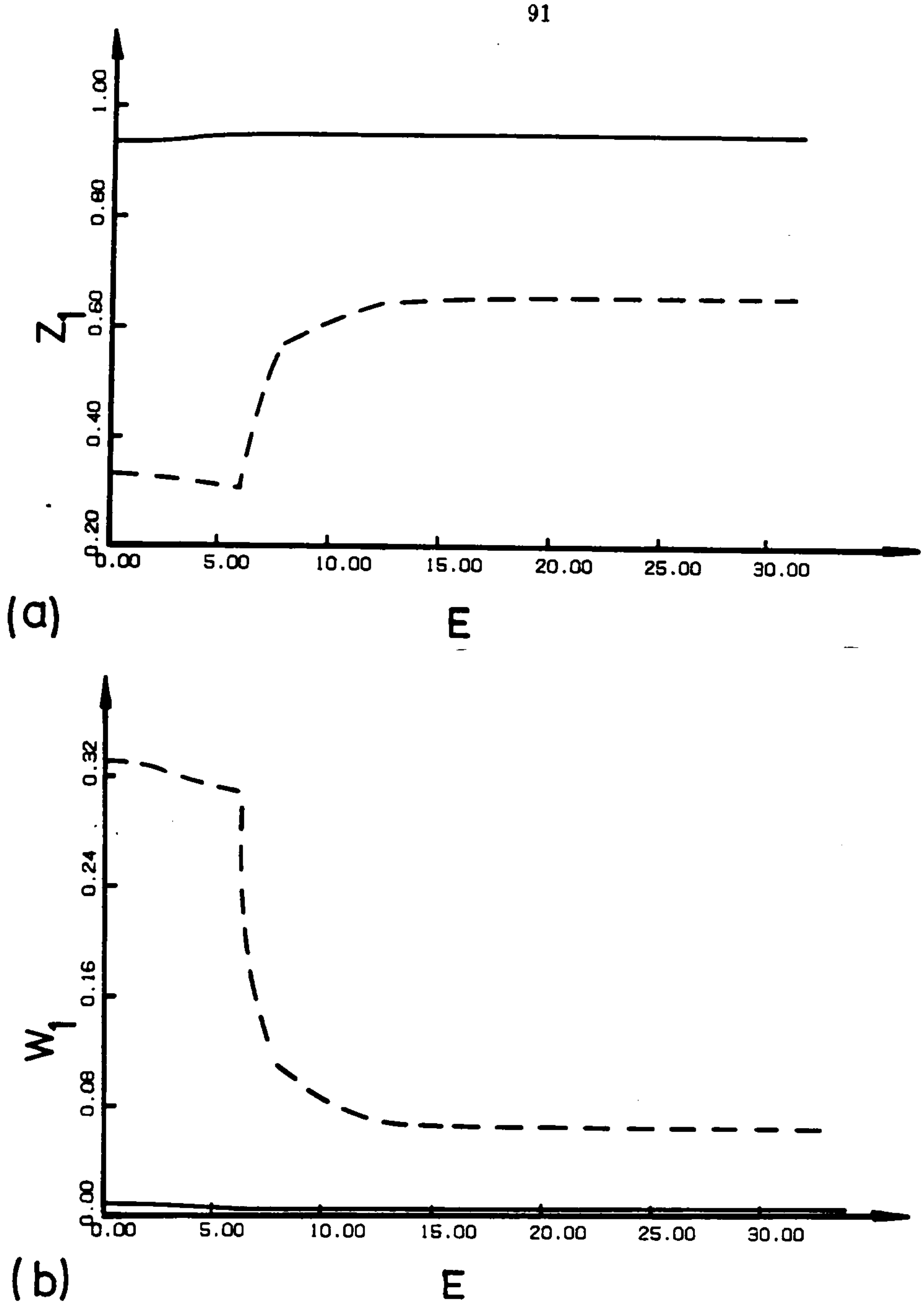


Fig. 6.11. The pair probabilities along the field for spins up z_1 – (a) and for spins down w_1 – (b) are plotted versus the strength of the electric field E. The solid line presents the result for $T = 2$ ($T < T_c(0)$) and the dashed line for $T = 3$ ($T_c(0) < T < T_c(E \to \infty)$).

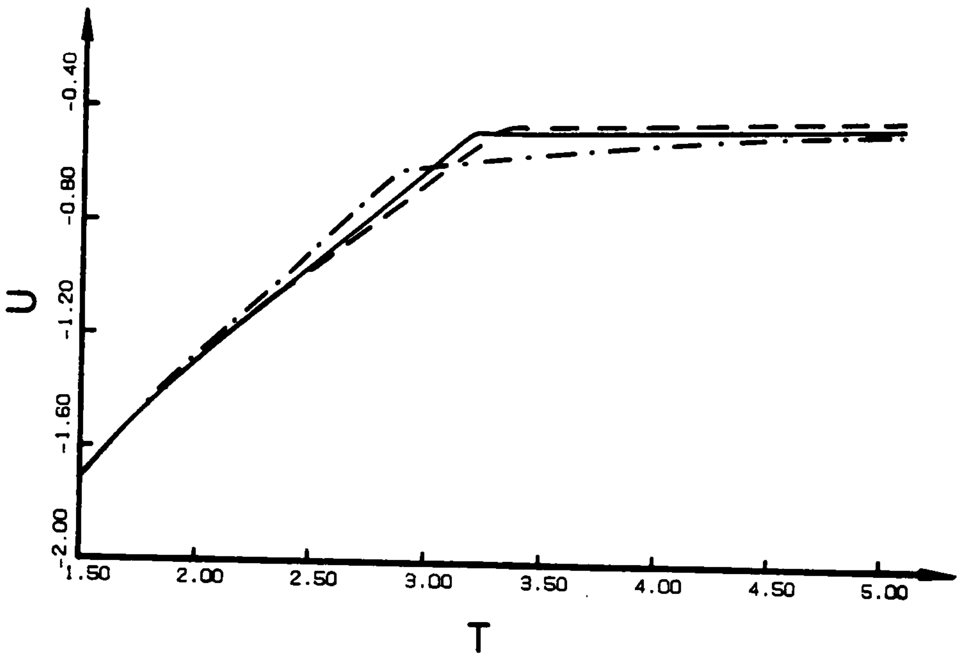


Fig. 6.12. The dependence of the internal energy per site u (in units of T) on the temperature T is shown for three different values of the strength of the electric field: $E = 0$ (dash- dotted line), $E = 10$ (solid line) and $E \to \infty$ (dashed line) .

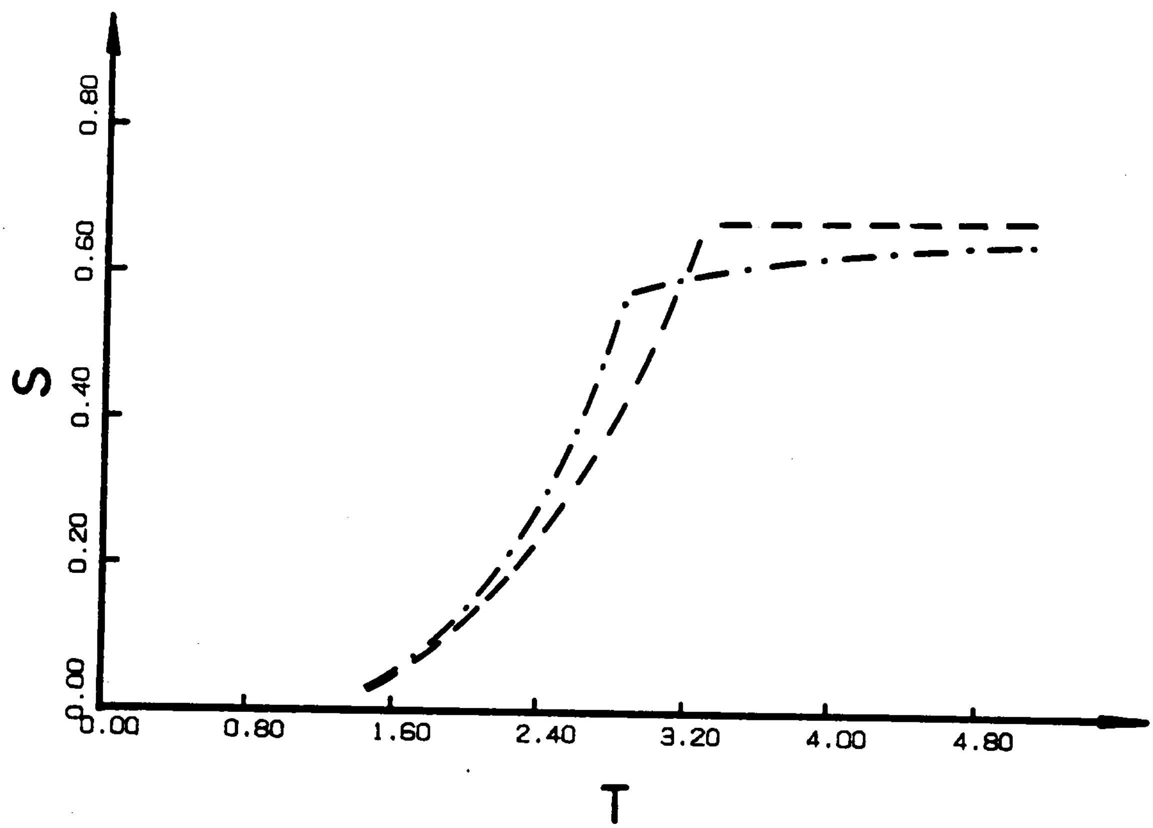


Fig. 6.13. The entropy per site s as a function of the temperature T is shown for $E = 0$ (dash-dotted line) and for $E \to \infty$ (dashed line).

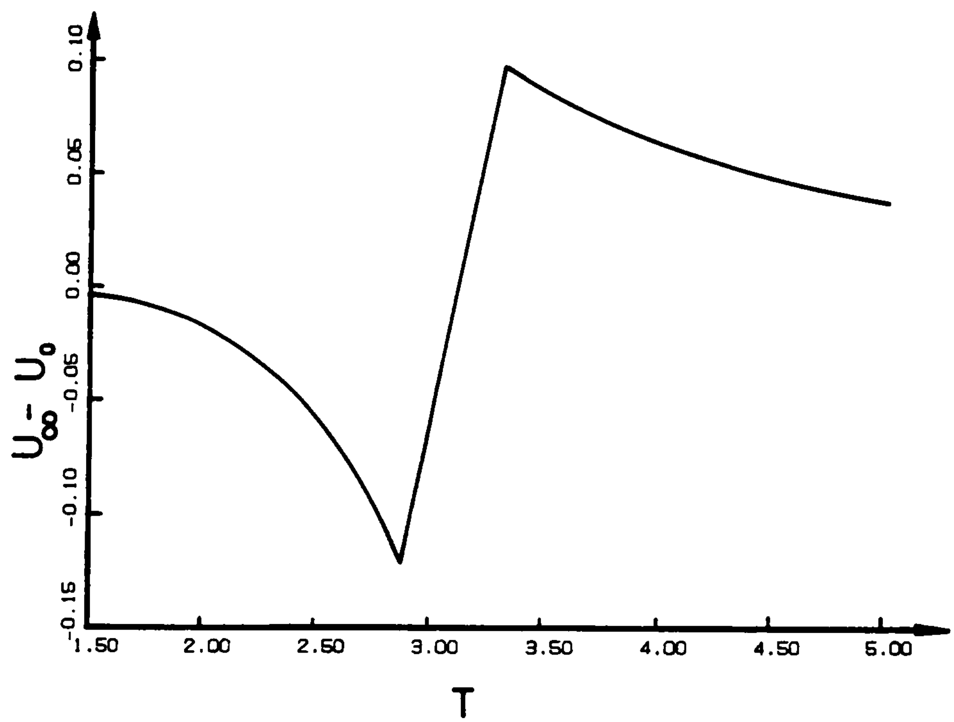


Fig. 6.14. The difference between the internal energy per site for $E \to \infty$ and $E = 0$ (in units of T) is plotted versus the temperature T .

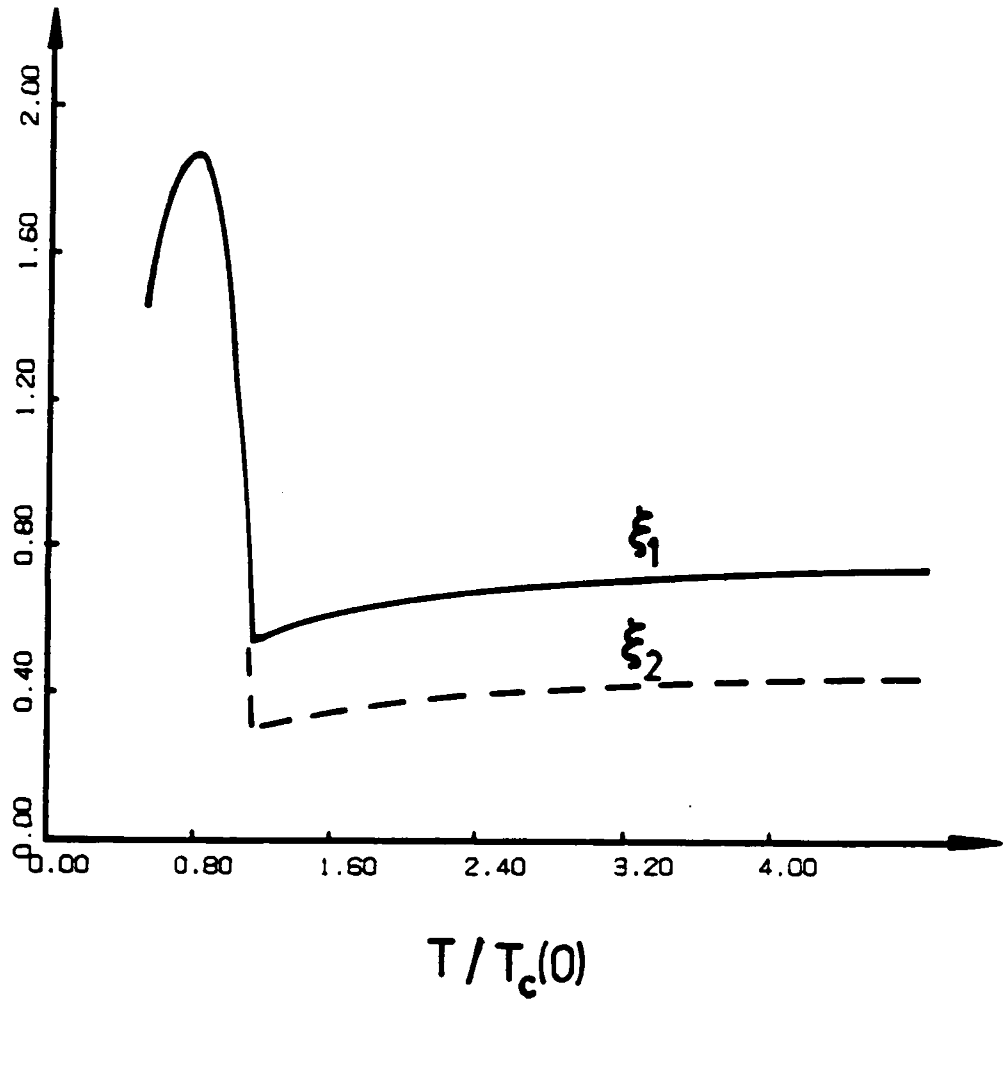


Fig. 6.15. The nearest-neighbor pair correlations along the field ξ_1 and perpendicular to it ξ_2 (multiplied by T) are plotted versus the reduced temperature $T/T_c(0)$.

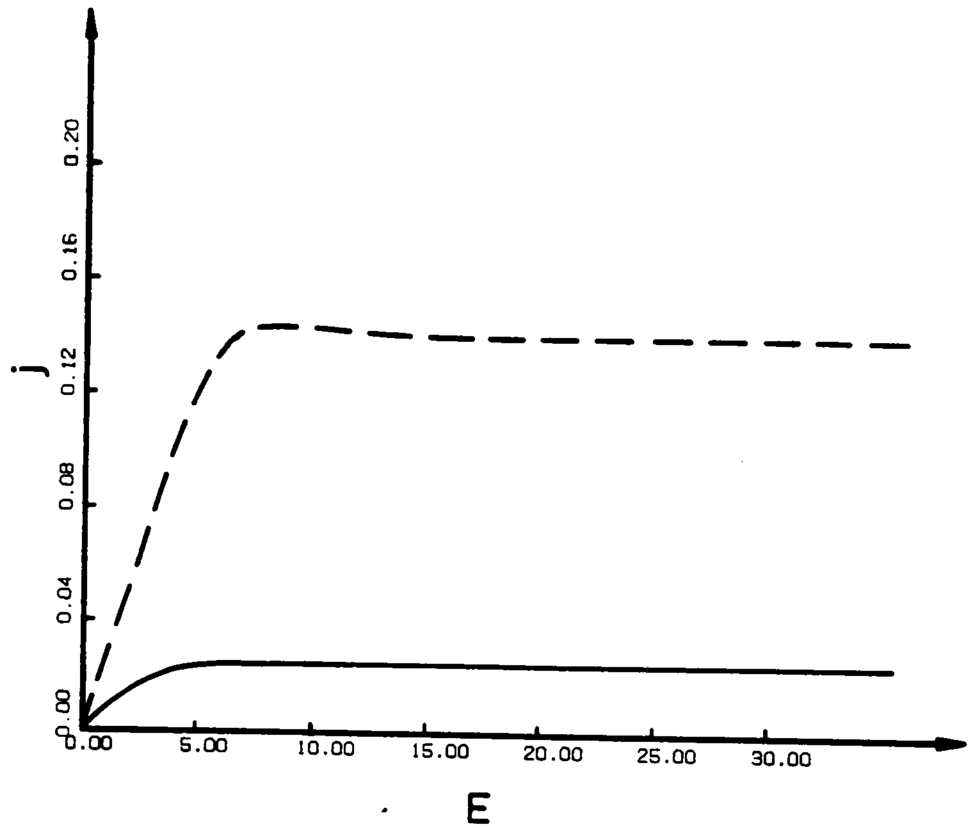


Fig. 6.16. The average electric current j in the steady state is plotted versus the strength of the electric field E for two different temperatures : $T < T_c(0)$ (solid line) and $T_c(0) < T < T(E \to \infty$ (dashed line) .

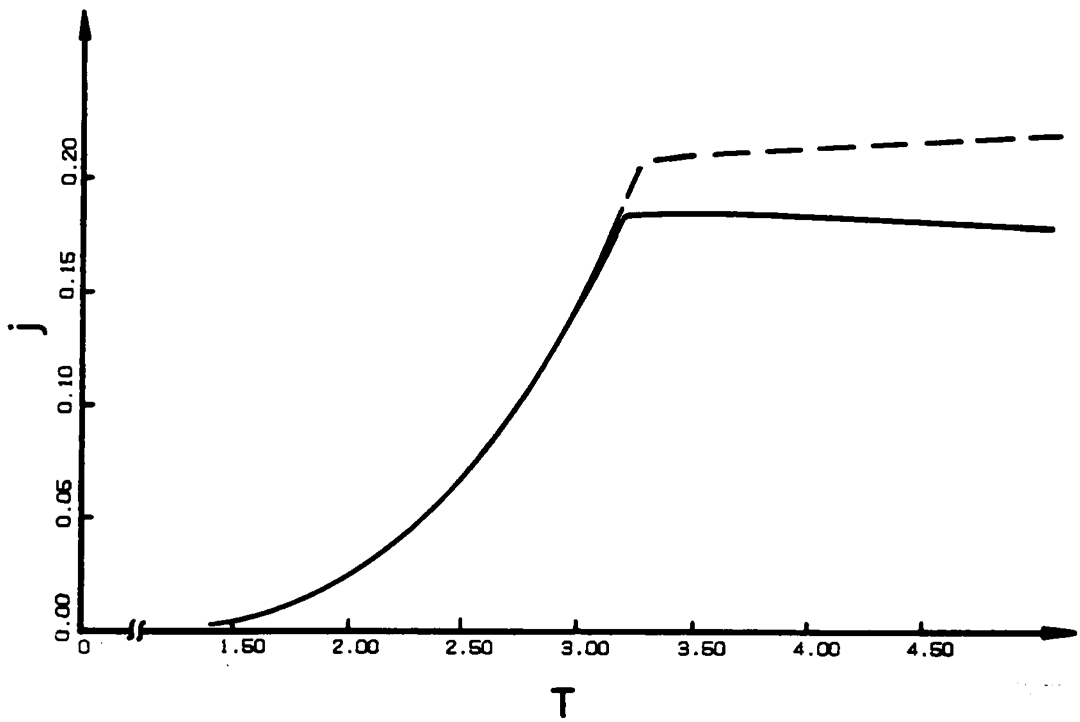


Fig. 6.17. The average electric current j in the direction of the field as a function of the temperature T for two values of the driving field : $E = 10$ (solid line) and $E \to \infty$ (dashed line).

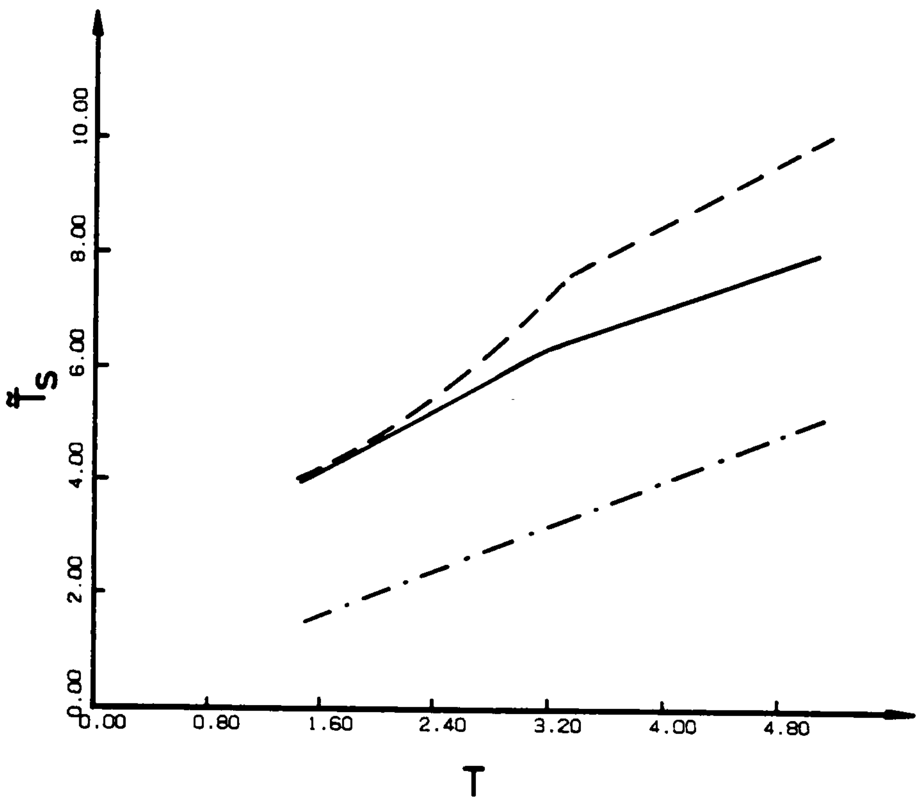


Fig. 6.18. The temperature dependence of the derivative of the internal energy with respect to the entropy (for fixed difference $b_2 - b_1$) in the steady state of the system is displayed for $E = 0$ (dash-dotted line), for $E = 10$ (solid line) and for $E \to \infty$ (dashed line). (For $E = 0$ this quantity is the temperature of the system in equilibrium with the heat bath) .

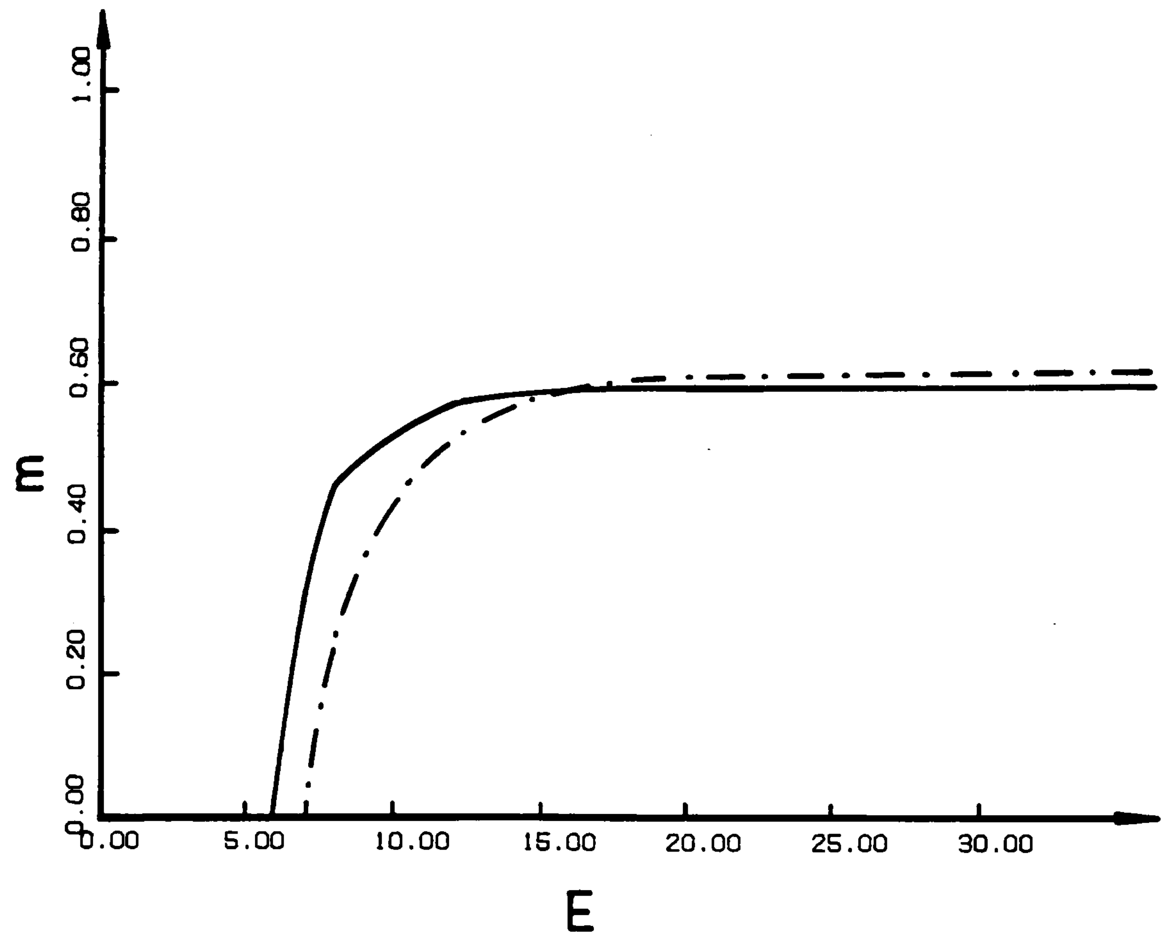


Fig. 6.19. The spontaneous magnetization at $T = 3$ ($T_c(0) < T < T_c(\infty)$) as a function of the strength of the driving field E is shown for Metropolis rates (solid line) and for Kawasaki rates (dash-dotted line). For van Beijeren - Schulman rates m is the same as in the equilibrium (i.e. it is zero) .

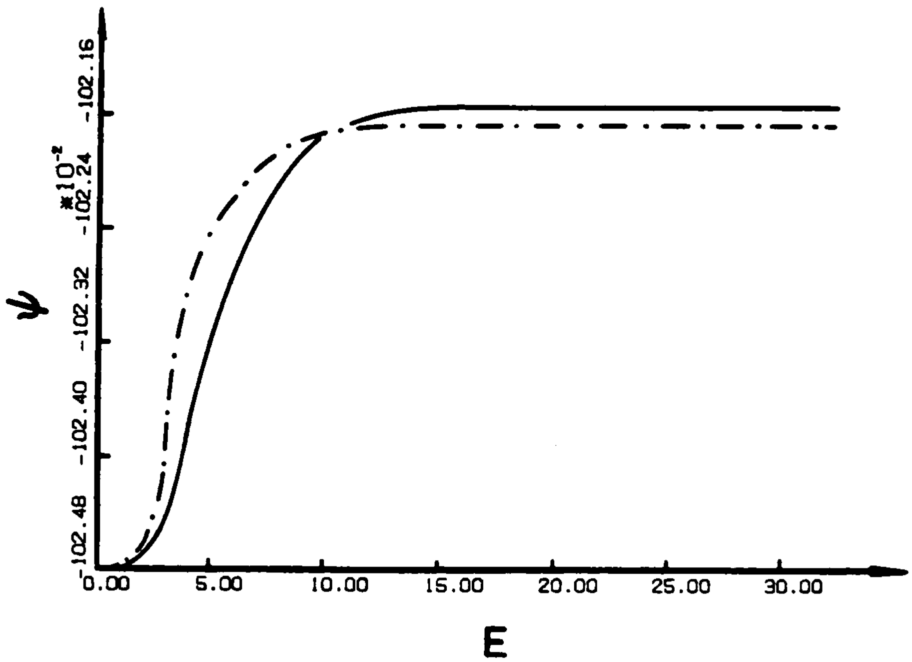


Fig. 6.20. The free energy of the system ψ (in units of T) after the minimization is plotted versus the strength of the electric field E at $T = 2$ for Metropolis rates (solid line) and Kawasaki rates (dashed line) .

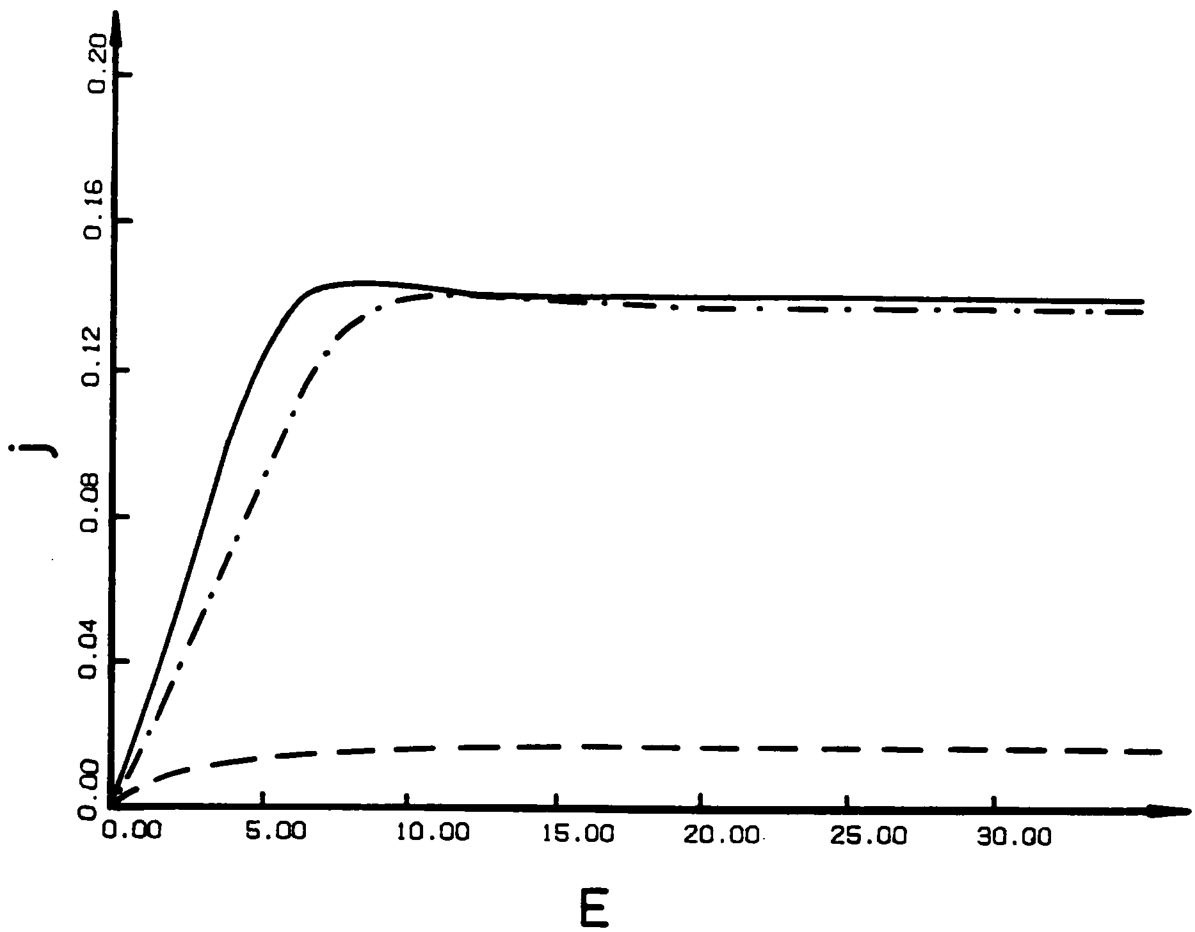


Fig. 6.21. The average electric current j in the direction of the field is plotted versus the strength of the driving field E for Metropolis rates (solid line), Kawasaki rates (dash-dotted line) and van Beijeren - Schulman rates (dashed line) .

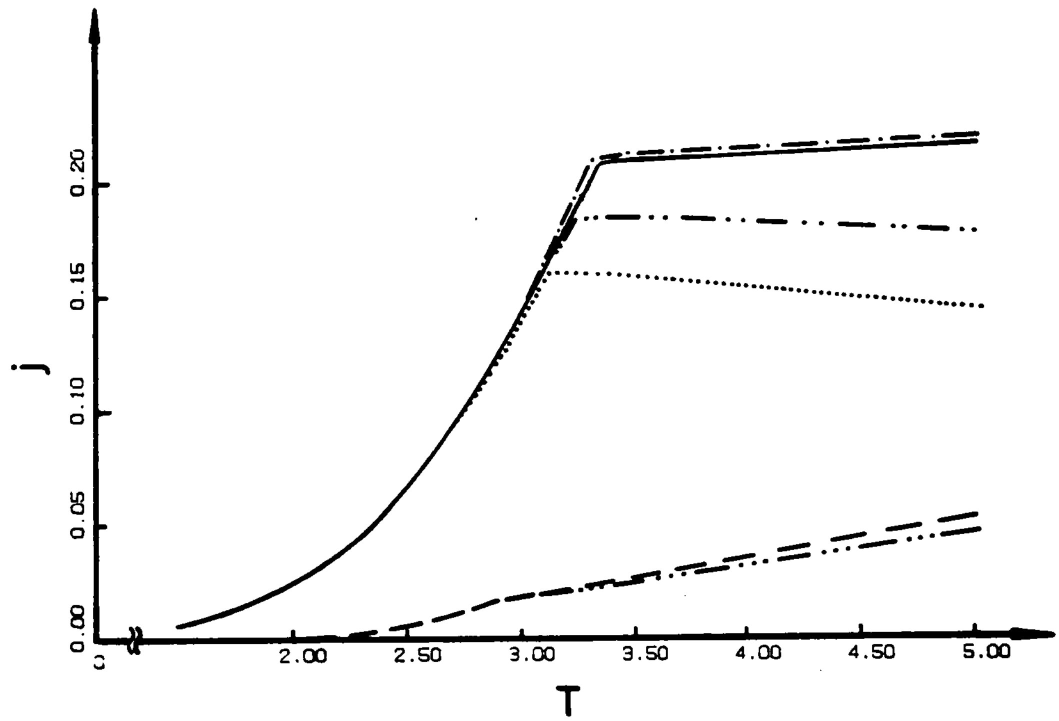


Fig. 6.22. The average electric current j in the direction of the field is plotted versus the temperature T for comparison for different values of the driving field and different rates : $E \to \infty$ – Metropolis rates (solid line), Kawasaki rates (dash-dotted line) and van Beijeren - Schulman rates (dashed line); $E = 10$ – Metropolis rates (dotted line), Kawasaki rates (dash-two-dots line) and van Beijeren - Schulman rates (dash-three-dots line) .

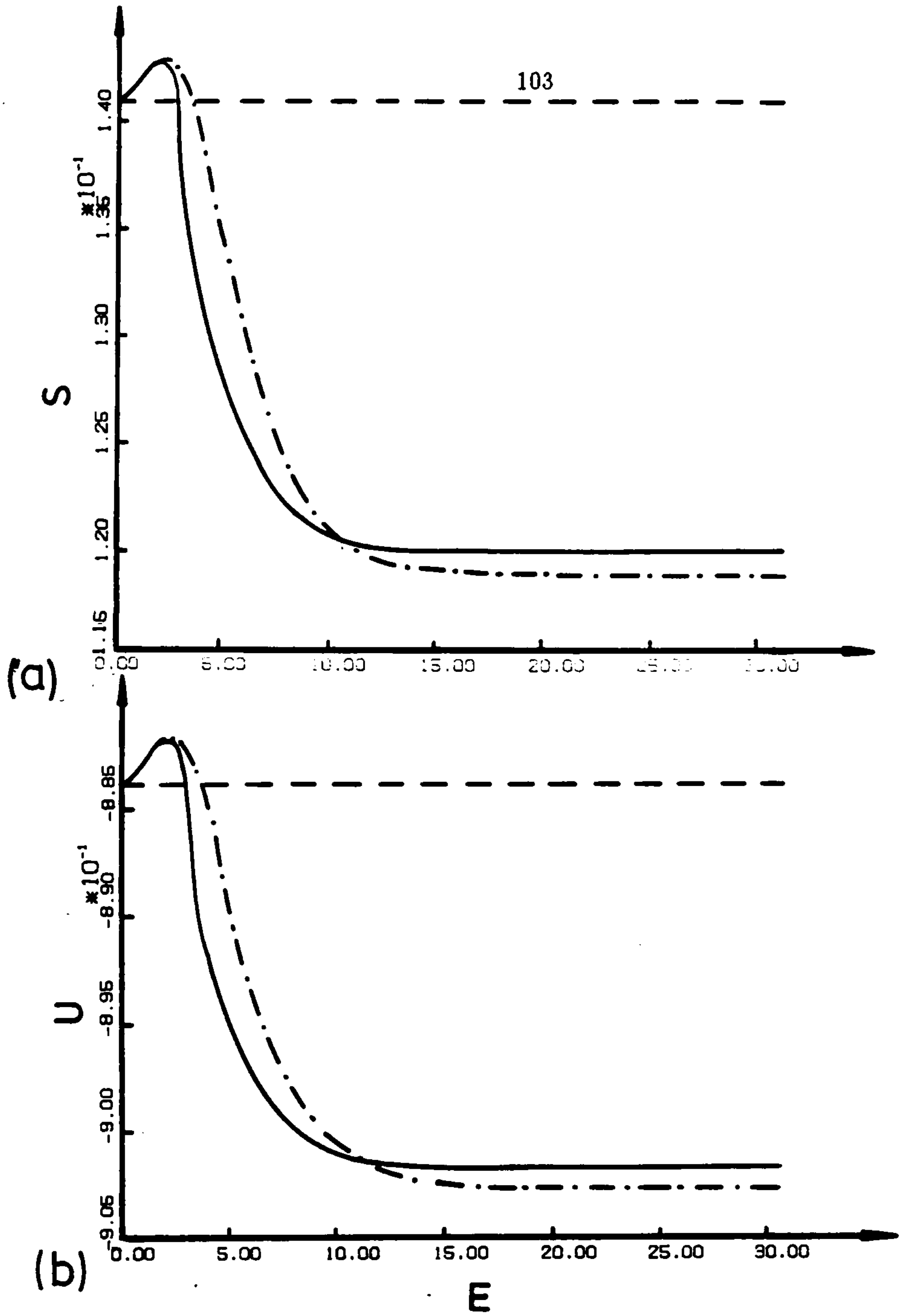


Fig. 6.23. The entropy s and the internal energy u of the system in the steady state are shown as functions of the strength of the driving field in (a) and (b) respectively. The results are presented for Metropolis rates by the solid line, for Kawasaki rates by the dash-dotted line and for van Beijeren - Schulman rates by the dashed line.

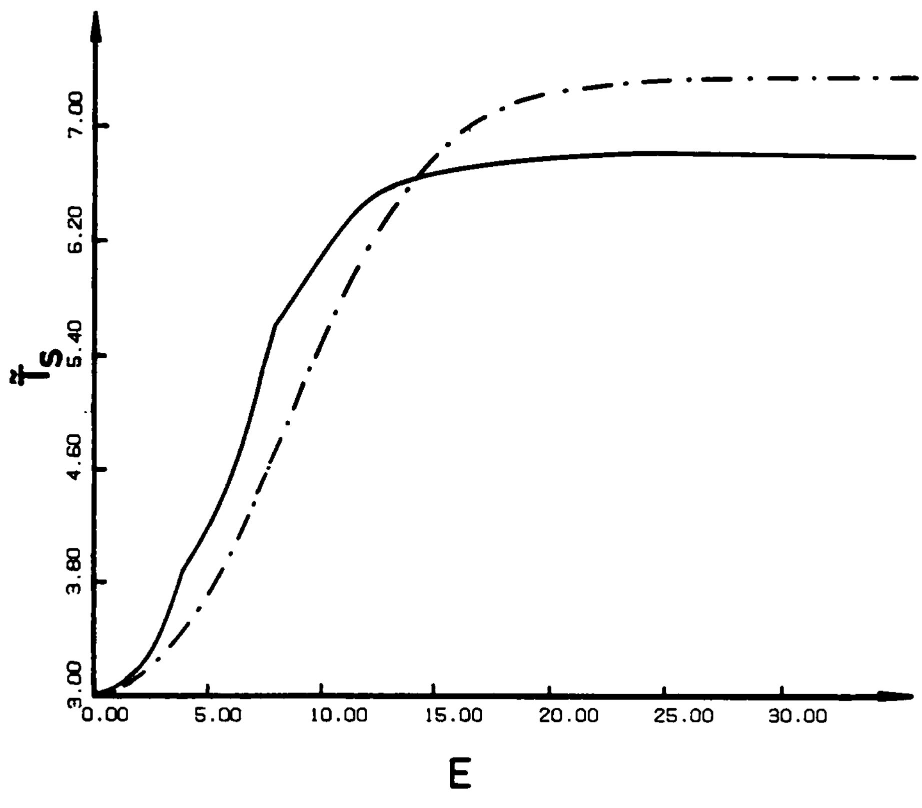


Fig. 6.24. The derivative of the internal energy with respect to the entropy (for fixed difference $b_2 - b_1$) in the steady state as a function of the driving field strength E is shown for Metropolis rates (solid line) and for Kawasaki rates (dash-dotted line).

APPENDIX A

EXPRESSIONS FOR THE RATE EQUATIONS AND THE CURRENT

At the pair level of mean-field approximation, one gets the following expressions for the rate equations:

$$\frac{db_1}{dt} = G_1^{(1)}(m, b_1, b_2; T, E) + G_2^{(2)}(m, b_1, b_2; T, E) \quad ,$$

where $G_1^{(1)}$ is the contribution of the first cluster to $\frac{db_1}{dt}$:

$$\begin{aligned} G_1^{(1)} =& \frac{b_1}{x^3 y^3}\Big[(\phi(12-E)+\phi(12+E))z_1 w_1 z_2^2 w_2^2 - (\phi(-12-E)+\phi(-12+E))\, b_1^2 b_2^4 \\ &+ 2(\phi(8-E)+\phi(8+E))\, z_1 w_1 z_2 w_2 (z_2+w_2) b_2 \\ &- 2(\phi(-8-E)+\phi(-8+E))\, b_1^2 b_2^2 (z_2+w_2) b_2 \\ &+ (\phi(4-E)+\phi(4+E))\left(z_1 w_1 b_2^2((z_2+w_2)^2 + 2z_2 w_2) - b_1^2 z_2^2 w_2^2\right) \\ &- (\phi(-4-E)+\phi(-4+E))\, b_2^2\left(b_1^2((z_2+w_2)^2 + 2z_2 w_2) - z_1 w_1 b_2^2\right) \\ &+ 2(\phi(-E)+\phi(E))\left(-b_1^2 z_2 w_2 + z_1 w_1 b_2^2\right)(z_2+w_2) b_2\Big] \quad , \end{aligned}$$

and $G_1^{(2)}$ is the contribution of the second cluster to $\frac{db_1}{dt}$:

$$\begin{aligned} G_1^{(2)} =& \frac{4b_2}{x^3 y^3}\Big[\phi(12) z_1^2 w_1^2 z_2 w_2 - \phi(-12) b_1^4 b_2^2 \\ &+ \phi(8)(z_1 b_1 w_1 z_2 w_2 (z_2+w_2) + z_1^2 w_1^2 b_2 (z_2+w_2)) \\ &- \phi(-8)(b_1^3 b_2^2 (z_2+w_2) + b_1^4 b_2 (z_2+w_2)) \\ &+ \phi(4)(z_1 b_1 w_1 b_2 (z_1+w_1)(z_2+w_2) + z_1^2 w_1^2 b_2^2) \\ &- \phi(-4)(b_1^3 b_2 (z_1+w_1)(z_2+w_2) + b_1^4 z_2 w_2) \\ &+ (z_1 b_1 w_1 b_2^2 (z_2+w2) - b_1^3 z_2 w_2 (z_1+w_1))\Big] \quad . \end{aligned}$$

In analogous way one has :

$$\frac{db_2}{dt} = G_2^{(1)}(m, b_1, b_2; T, E) + G_2^{(2)}(m, b_1, b_2; T, E) \quad ,$$

where $G_2^{(1)}$ is the contribution of the first cluster to $\frac{db_2}{dt}$:

$$\begin{aligned} G_2^{(1)} =& \frac{2b_1}{x^3y^3}\Big[(\phi(12-E)+\phi(12+E))z_1w_1z_2^2w_2^2 - (\phi(-12-E)+\phi(-12+E))b_1^2b_2^4 \\ &+(\phi(8-E)+\phi(8+E))z_2w_2(z_1w_1b_2(z_2+w_2)+b_1z_2w_2(z_1+w_1)) \\ &-(\phi(-8-E)+\phi(-8+E))b_1b_2^3(b_1(z_2+w_2)+b_2(z_1+w_1)) \\ &+(\phi(4-E)+\phi(4+E))b_1z_2w_2(b_2(z_1+w_1)(z-2+w_2)+b_1z_2w_2) \\ &-(\phi(-4-E)+\phi(-4+E))b_2^3(b_1(z_1+w_1)(z_2+w_2)+b_2z_1w_1) \\ &+(\phi(-E)+\phi(E))b_2(z_2+w_2)(b_1^2z_2w_2-b_2^2z_1w_1)\Big] \quad , \end{aligned}$$

and $G_2^{(2)}$ is the contribution of the second cluster to $\frac{db_2}{dt}$:

$$\begin{aligned} G_2^{(2)} =& \frac{2b_2}{x^3y^3}\Big[\phi(12)z_1^2w_1^2z_2w_2 - \phi(-12)b_1^4b_2^2 \\ &+\phi(8)2b_1z_1w_1z_2w_2(z_1+w_1) - \phi(-8)2b_1^3b_2^2(z_1+w_1) \\ &+\phi(4)(b_1^2z_2w_2((z_1+w_1)^2+2z_1w_1) - b_2^2z_1^2w_1^2) \\ &-\phi(-4)b_1^2(b_2^2((z_1+w_1)^2+2z_1w_1) - b_1^2z_2w_2) \\ &+2b_1(z_1+w_1)(-b_2^2z_1w_1+b_1^2z_2w_2)\Big] \quad . \end{aligned}$$

The average current along the field is given by the following expression :

$$
\begin{aligned}
j = \frac{b_1}{x^3y^3}\Big[&(\phi(12-E)-\phi(12+E))z_1w_1z_2^2w_2^2+(\phi(-12-E)+\phi(-12+E))b_1^2b_2^4\\
&+(\phi(8-E)-\phi(8+E))z_2w_2(2z_1w_1b_2(z_2+w_2)+b_1z_2w_2(z_1+w_1))\\
&+(\phi(-8-E)-\phi(-8+E))b_1b_2^3(2b_1(z_2+w_2)+b_2(z_1+w_1))\\
&+(\phi(4-E)-\phi(4+E))(2b_1b_2z_2w_2(z_1+w_1)(z_2+w_2)\\
&\qquad\qquad+b_2^2z_1w_1(z_2+w_2)^2+2z_2w_2)+b_1^2z_2^2w_2^2)\\
&+(\phi(-4-E)-\phi(-4+E))b_2^2(2b_1b_2(z_1+w_1)(z_2+w_2)\\
&\qquad\qquad+b_1^2((z_2+w_2)^2+2z_2w_2)+b_2^2z_1w_1)\\
&+(\phi(-E)-\phi(E))b_2(b_1b_2(z_1+w_1)((z_2+w_2)^2+2z_2w_2)\\
&\qquad\qquad+2(z_2+w_2)(b_1^2z_2w_2+b_2^2z_2w_2+b_2^2z_1w_1))\Big] \quad .
\end{aligned}
$$

APPENDIX B
PROGRAM FEM

```
C
C
C     FINITE EL. FIELD WITH CURRENT; MINIMIZING THE FREE ENERGY f=F(M)
C     USING "DUVMIF"; COMPUTATION OF DU/DT AND DS/DU; FITTING OF F(M)
C     WITH EVEN POLYNOMIAL
C
      INTEGER ITMAX,N,K,NOUT,NOBS,NDEG,INTCEP,IWT,MAXFN
      PARAMETER (N=2,NOBS=100,NDEG=4,INTCEP=1,IWT=0)
      REAL*8 DT,E,DM,R,FE,FE1,G(3),DUDT,DSDU,FG(2),DMA,DUDTO,DFN
      COMMON DT,K,E,NOUT,R,DM,G
      REAL*8 FNORM,X(N),XGUESS(N),ERRREL
      REAL*8 WM,FK(3),FM(3)
      REAL*8 YGUESS(2),Y(2),S,S0,S1,DQDT,XK,wt,fup(3),fun(3)
      REAL*8 ST,DTU,V,RP,RN,R0,DMI,XA(2),XGN(2),wt2,wt2k,wtk
      REAL*8 B1,B2,Z1,W1,Z2,W2,FP12,FN12,FP8,FN8,FP4,FN4,F0,CE
      REAL*8 EPP(4),EPN(4),ENP(4),ENN(4),CP(4),CN(4)
      REAL*8 XDATA(NOBS),YDATA(NOBS),B(NDEG+1),SSE,WEIGHT,
     &XG(2),DM1,DM2,FA,F1,DMG,DMACC,STEP,BOUND,AB(3)
      COMMON /C1/EPP,EPN,ENP,ENN,CP,CN,AB
      COMMON /C2/ N1,ITMAX,ERRREL,XGUESS,X,FNORM,XG
      EXTERNAL FCN,DNEQNF,RF,DUVMIF,FE,FE1
      EXTERNAL UMACH,BF,DFNLSQ
C
      NP=0
      N1=N
      CALL UMACH(2,NOUT)
      OPEN (UNIT=NOUT,STATUS='UNKNOWN',FILE='FEMT.RES')
      WRITE (NOUT,101)
      DATA ERRREL/0.1D-08/,ITMAX/300/,R/1.D0/
      DATA DMI/0.1D-0/,XA/0.2029D0,0.2225D0/
      DATA DT/2.5d0/,ST/-0.5D-0/,DTU/5.0D0/,E/0.0D0/,K/2/
      DATA DMG/0.0D0/,XGN/0.2017d0,0.223D0/
      DATA STEP/0.1D-04/DMACC/0.1D-10/MAXFN/100/
      WRITE(NOUT,300) K,R
C
      DO 37 IT=0,6
C     DO 37 IP=0,10
C     E=DBLE(IP)
 10   DT=2.5D0+0.5D0*DBLE(IT)
      DK=1.D0/DT
      IF(E.EQ.0.D0.AND.K.EQ.1) XGN(2)=XGN(1)
      XGUESS(1)=XGN(1)
      XGUESS(2)=XGN(2)
      IF(IT.EQ.0)  WRITE(NOUT,555) XGUESS,DMG,ST,DT,E
C
C     COMPUTING THE RATES USING "RF"
C
```

```
  8   DO 9 J=1,4
      V=4.D0*DBLE(J-1)
      CALL RF(V,RP,RN,RO)
      EPP(J)=RP
      EPN(J)=RN
      CP(J)=RO
      CALL RF(-V,RP,RN,RO)
      ENP(J)=RP
      ENN(J)=RN
      CN(J)=RO
  9   CONTINUE
  501 FORMAT(2X,4(D13.6,3X))
C
C     DETERMINATION OF DM MINIMIZING THE FREE ENERGY - FE1,FE
C
      IF(DMG.GT.0.1D-04) GO TO 15
      DM=0.D0
      CALL DNEQNF(FCN,ERRREL,2,ITMAX,XGN,X,FNORM)
      GO TO 16
  15  BOUND=DMIN1(DMG,DABS(1.D0-DMG))
      CALL DUVMIF(FE,DMG,STEP,BOUND,DMACC,MAXFN,DM)
C
C     COMPUTATION OF THE EL. CURRENT - CE
      DMG=2.D0*DM-DMG
  16  XGN(1)=2.D0*X(1)-XGN(1)
      XGN(2)=2.D0*X(2)-XGN(2)
      IF(DMG.LE.0.D0) DMG=0.D0
      B1=X(1)
      B2=X(2)
      Z1=(1.D0+DM)/2.D0-B1
      W1=(1.D0-DM)/2.D0-B1
      Z2=(1.D0+DM)/2.D0-B2
      W2=(1.D0-DM)/2.D0-B2
      FP12=(EPN(4)-EPP(4))*Z1*W1*Z2**2*W2**2
      FUP(3)=-12.d0*(EPN(4)+EPP(4))*Z1*W1*Z2**2*W2**2
      FK(3)=-12.d0*CP(4)*Z2*W2*Z1**2*W1**2
      FN12=(ENN(4)-ENP(4))*B1**2*B2**4
      FUN(3)=12.d0*(ENN(4)+ENP(4))*B1**2*B2**4
      FM(3)=12.d0*cn(4)*B2**2*B1**4
      FP8=(EPN(3)-EPP(3))*Z2*W2*(2.D0*Z1*W1*B2*(Z2+W2)+Z2*W2*B1*(Z1+W1))
      FUP(2)=Z2*W2*(2.D0*Z1*W1*B2*(Z2+W2)+Z2*W2*B1*(Z1+W1))
      FUP(2)=-8.d0*(EPN(3)+EPP(3))*fup(2)
      FK(2)=-8.d0*cp(3)*Z1*W1*(2.D0*Z2*W2*B1*(Z1+W1)+Z1*W1*B2*(Z2+W2))
      FN8=(ENN(3)-ENP(3))*B1*B2**3*(2.D0*B1*(Z2+W2)+B2*(Z1+W1))
      FUN(2)=8.d0*(ENN(3)+ENP(3))*B1*B2**3*(2.D0*B1*(Z2+W2)+B2*(Z1+W1))
      FM(2)=8.d0*cn(3)*B2*B1**3*(B1*(Z2+W2)+2.d0*B2*(Z1+W1))
      FP4=(EPN(2)-EPP(2))*(2.D0*B1*B2*Z2*W2*(Z1+W1)*(Z2+W2)+B1**2*Z2**2*
     &W2**2+B2**2*Z1*W1*((Z2+W2)**2+2.D0*Z2*W2))
      FUP(1)=(EPN(2)+EPP(2))*(2.D0*B1*B2*Z2*W2*(Z1+W1)*(Z2+W2)+B1**2*Z2*
```

```
     &*2*W2**2+B2**2*Z1*W1*((Z2+W2)**2+2.DO*Z2*W2))*(-4.d0)
      FK(1)=-4.d0*cp(2)*(2.DO*B1*B2*Z1*W1*(Z1+W1)*(Z2+W2)+B2**2*Z1*
     &*2*W1**2+B1**2*Z2*W2*((Z1+W1)**2+2.DO*Z1*w1))
      FN4=(ENN(2)-ENP(2))*B2**2*(2.DO*B1*B2*(Z1+W1)*(Z2+W2)+Z1*W1*B2**2+
     &B1**2*((Z2+W2)**2+2.DO*Z2*W2))
      FUN(1)=(ENN(2)+ENP(2))*B2**2*(2.DO*B1*B2*(Z1+W1)*(Z2+W2)+Z1*W1*B2*
     &*2+B1**2*((Z2+W2)**2+2.DO*Z2*W2))*4.d0
      FM(1)=4.d0*cn(2)*B1**2*(2.DO*B1*B2*(Z2+W2)*(Z1+W1)+Z2*W2*B1*
     &*2+B2**2*((Z1+W1)**2+2.DO*z1*W1))
      FO=(EPN(1)-EPP(1))*B2*(B1*B2*(Z1+W1)*((Z2+W2)**2+2.DO*Z2*W2)+2.DO*
     &(Z2+W2)*(B1**2*Z2*W2+B2**2*Z1*W1))
      CE=64.DO*B1*(FP12+FN12+FP8+FN8+FP4+FN4+FO)
      CE=CE/((1.DO+DM)*(1.DO-DM))**3
      WT=(FUP(1)+FUP(2)+FUP(3))+(FUN(1)+FUN(2)+FUN(3))
      WT=64.DO*B1*Wt/((1.DO+DM)*(1.DO-DM))**3
      WTK=WT/DT
      WM=(FK(3)+FK(2)+FK(1))+(FM(3)+FM(2)+FM(1))
      WM=128.DO*B2*WM/((1.DO+DM)*(1.DO-DM))**3
      WM=WM/DT
C                                                                     E
C     COMPUTATION OF THE THERMODYNAMIC THEMPERATURE - DU/DS OF THE SYSTEM
C     AND THE FREE ENERGY F1=FE1(B1,B2)
C
      DSDU=DLOG((Z1*W1*Z2*W2)/(B1**2*B2**2))/8.DO
      DSDU=1.DO/DSDU
      F1=FE1(B1,B2)
    5 WRITE(NOUT,777) DT,B1,B2,DM,F1,CE,FNORM
      DM1=DM
      DFN=(G(1)**2+G(2)**2)
      WT2=CE*E
      WT2K=WT2/DT
      WRITE(NOUT,403) WTK,WM,WTK+WM,WT2K
      DM2=AB(3)
      XGUESS(1)=AB(1)
      XGUESS(2)=AB(2)
C
C     COMPUTING DATA FOR FITTING THE FREE ENERGY F1 AS A FUNCTION OF DM
C     AROUND DM=0
C
      IF(NP.EQ.0) GO TO 87
      IF(DM1.GT.0.3DO) GO TO 87
      IF(DM1.GT.0.1DO) DMI=0.5DO
      IF(DM1.GT.0.05DO.AND.DM1.LE.0.1DO) DMI=0.1DO
      IF(DM1.LT.0.05DO) DMI=0.05DO
      XG(1)=XA(1)
      XG(2)=XA(2)
      DO 4 J2=1,NOBS
      DM=(DMI*DBLE(J2-1))/DBLE(NOBS)
      XDATA(J2)=DM
```

```
      CALL DNEQNF(FCN,ERRREL,2,ITMAX,XG,Y,FNORM)
      F1=FE1(Y(1),Y(2))
      IF(J2.NE.1) GO TO 77
      XA(1)=Y(1)
      XA(2)=Y(2)
 77   YDATA(J2)=F1
      XG(1)=Y(1)
      XG(2)=Y(2)
  4   CONTINUE
      CALL DFNLSQ(BF,INTCEP,NDEG,NOBS,XDATA,YDATA,IWT,WEIGHT,B,SSE)
      DM=DM1
      FA=B(1)+B(2)*(DM**2)+B(3)*(DM**4)+B(4)*(DM**6)+B(5)*(DM**8)
      DMA=0.D0
      DMG=DMA
      XK=DK/(2.D0*DABS(B(2)))
      IF(B(2).LT.0.D0) XK=XK/2.D0
      IF((-B(2)/B(3)).LT.0.D0) GO TO 55
      DMA=DSQRT(-B(2)/(2.D0*B(3)))
      DMG=DMA
C
  55  WRITE(NOUT,102) DSDU,DUDT,DUDT0
      WRITE(NOUT,106) S1,DQDT
      IF(NP.EQ.0) GO TO 66
      IF(DM1.GT.0.3D0) GO TO 66
      WRITE(NOUT,401)
      WRITE(NOUT,403) B
      WRITE(NOUT,404)
      WRITE(NOUT,403) FA,SSE,DMA,XK
 66   CONTINUE
 37   CONTINUE
101   FORMAT(2X,'FEM.FOR PROGRAM   FEM.RES   '/)
102   FORMAT(/2X,'     ',D13.6,3X,'       ',D13.6,3X,'       ',D13.6)
103   FORMAT(2X,'FG1=',D13.6,3X,'FG2=',D13.6,3X,'       ',D13.6)
105   FORMAT(2X,'ABI-BI ',3(D13.6,2X),'FNORM1=',D13.6)
106   FORMAT(2X,'   ',D13.6,2X,'      ',D13.6)
222   FORMAT(2X,I2,5(1X,D12.5))
300   FORMAT(2X,'k=',I2,2X,'r=',F7.3/)
333   FORMAT(/8X,'k=1  mETROPOLIS RATES'
     &/8X,'k=2  iNFINITE EL. FIELD '/8X,'k=3  fI=2/(1+E¬X) RATE FCN'
     &/8X,'k=4  fI=E¬(-X/2) RATE FCN'/8X,'r IS THE RATIO COEFFICIENT')
400   FORMAT(F9.6,1X,3(D13.6,1X))
401   FORMAT(//7X,'A0',13X,'A2',13X,'A4',13X,'A6',13X,'A8')
403   FORMAT(5(2X,D13.6))
404   FORMAT(/7X,'FA',13X,'SSE',13X,'MA',13X,'XK')
555   FORMAT(//4X,'B1G',9X,'B2G',9X,'MG',10X,'ST',10X,'DT',9X,'E'
     &/6(1X,D10.4,1X)/)
666   FORMAT(/5X,'t',8X,'B1',9X,'B2',8X,'M',9X,'f',9X,'i',9X,'FNOR
     &M'/)
777   FORMAT(3(1X,F9.6),1X,D13.6,1X,2(F9.6,1X),D13.6)
```

```
      STOP
      END
C
C
C
      DOUBLE PRECISION FUNCTION FE1(B1,B2)
C     COMPUTES THE FREE ENERGY FOR GIVEN DM,B1,B2
      INTEGER K,NOUT
      REAL*8 C,D,DM,B1,B2,Z1,Z2,W1,W2,U,S,R,DT,E
      COMMON DT,K,E,NOUT,R,DM
      C=(1.0D0+DM)/2.0D0
      D=(1.0D0-DM)/2.0D0
      Z1=C-B1
      W1=D-B1
      Z2=C-B2
      W2=D-B2
C
      U=((4.D0*B1-1.D0)+R*(4.D0*B2-1.D0))/DT
      S=3.D0*(C*DLOG(C)+D*DLOG(D))
     &-(Z1*DLOG(Z1)+W1*DLOG(W1)+2.D0*B1*DLOG(B1))
     &-R*(Z2*DLOG(Z2)+W2*DLOG(W2)+2.D0*B2*DLOG(B2))
      FE1=U-S
      RETURN
      END
C
C
C
      DOUBLE PRECISION FUNCTION FE(DM)
C     COMPUTES B1,B2 FOR GIVEN DM AND CALLS "FE1" TO COMPUTE THE FREE ENERGY
      INTEGER N,ITMAX
      REAL*8 DM,FCN,ERRREL,XGUESS(2),X(2),FNORM,DT,E,R,FE1,DM1,XG(2)
      COMMON DT,K,E,NOUT,R,DM1
      COMMON /C2/ N,ITMAX,ERRREL,XGUESS,X,FNORM,XG
      EXTERNAL FCN,FE1
      DM1=DM
      XG(1)=XGUESS(1)
      XG(2)=XGUESS(2)
      CALL DNEQNF(FCN,ERRREL,N,ITMAX,XGUESS,X,FNORM)
      XGUESS(1)=X(1)
      XGUESS(2)=X(2)
      FE=FE1(X(1),X(2))
      RETURN
      END
C
C
C
      DOUBLE PRECISION FUNCTION BF(K,X)
C     FITTING POLYNOMIALS
      INTEGER K
```

```
      REAL*8 X
      BF=X**(2*K)
      RETURN
      END
C
C
C
      SUBROUTINE FCN (X,FG,N)
C     COMPUTES G1=DB1/DT & G2=DB2/DT FOR GIVEN B1,B2,DM
      INTEGER N,K,NOUT
      REAL*8 X(N),FG(N),G(3),R,DM,E
      REAL*8 C,D,B1,B2,Z1,W1,Z2,W2,G11,G12,G21,G22,DT
      REAL*8 FP12,FN12,FP8,FN8,FP4,FN4,F0
      REAL*8 EPP(4),EPN(4),ENP(4),ENN(4),CP(4),CN(4)
      REAL*8 DLOG,DM1
      INTRINSIC DLOG
C
      COMMON DT,K,E,NOUT,R,DM,G
      COMMON /C1/EPP,EPN,ENP,ENN,CP,CN,B1,B2,DM1
    9 IF (DM.GT.0.999999D-0.OR.DM.LT.-0.1D-06) GO TO 501
      IF (X(1).GT.0.249999D0.OR.X(1).LT.0.1D-05) GO TO 501
      IF (X(2).GT.0.249999D0.OR.X(2).LT.0.1D-05) GO TO 501
      IF (2.D0*X(1).GE.(1.D0-DM)) GO TO 501
      IF (2.D0*X(2).GE.(1.D0-DM)) GO TO 501
C
      DM1=DM
      C=(1.0D0+DM)/2.0D0
      D=(1.0D0-DM)/2.0D0
      B1=X(1)
      B2=X(2)
      Z1=C-B1
      W1=D-B1
      Z2=C-B2
      W2=D-B2
C
      FP12=Z1*W1*Z2**2*W2**2
      FP12=(EPP(4)+EPN(4))*FP12
      FN12=-B1**2*B2**4
      FN12=(ENP(4)+ENN(4))*FN12
      FP8=2.D0*Z1*W1*Z2*W2*B2*(Z2+W2)
      FP8=(EPP(3)+EPN(3))*FP8
      FN8=-2.D0*B1**2*B2**3*(Z2+W2)
      FN8=(ENP(3)+ENN(3))*FN8
      FP4=B2**2*Z1*W1*(Z2**2+W2**2+4.D0*Z2*W2)-B1**2*Z2**2*W2**2
      FP4=(EPP(2)+EPN(2))*FP4
      FN4=-B2**2*(B1**2*(Z2**2+W2**2+4.D0*Z2*W2)-B2**2*Z1*W1)
      FN4=(ENP(2)+ENN(2))*FN4
      F0=2.D0*B2*(Z2+W2)*(-B1**2*Z2*W2+B2**2*Z1*W1)
      F0=(EPP(1)+EPN(1))*F0
```

```
      G11=(FN12+FN8+FN4)
      G11=B1*(G11+F0+FP4+FP8+FP12)
C
      FP12=Z1**2*W1**2*Z2*W2
      FP12=CP(4)*FP12
      FN12=-B1**4*B2**2
      FN12=CN(4)*FN12
      FP8=Z1*W1*(B1*Z2*W2*(Z1+W1)+B2*Z1*W1*(Z2+W2))
      FP8=CP(3)*FP8
      FN8=-B2*B1**3*(B2*(Z1+W1)+B1*(Z2+W2))
      FN8=CN(3)*FN8
      FP4=B2*Z1*W1*(B1*(Z2+W2)*(Z1+W1)+B2*Z1*W1)
      FP4=CP(2)*FP4
      FN4=-B1**3*(B2*(Z2+W2)*(Z1+W1)+B1*Z2*W2)
      FN4=CN(2)*FN4
      F0=B1*(Z1+W1)*(B2**2*Z1*W1-B1**2*Z2*W2)
      G12=FN12+FN8+FN4
      G12=4.D0*B2*(G12+F0+FP4+FP8+FP12)
      G(1)=(G11+R*G12)
C
      FP12=Z1*W1*Z2**2*W2**2
      FP12=(EPP(4)+EPN(4))*FP12
      FN12=-B1**2*B2**4
      FN12=(ENP(4)+ENN(4))*FN12
      FP8=Z2*W2*(Z1*W1*B2*(Z2+W2)+B1*Z2*W2*(Z1+W1))
      FP8=(EPP(3)+EPN(3))*FP8
      FN8=-B1*B2**3*(B1*(Z2+W2)+B2*(Z1+W1))
      FN8=(ENP(3)+ENN(3))*FN8
      FP4=B1*Z2*W2*(B2*(Z1+W1)*(Z2+W2)+B1*Z2*W2)
      FP4=(EPP(2)+EPN(2))*FP4
      FN4=-B2**3*(B1*(Z1+W1)*(Z2+W2)+B2*Z1*W1)
      FN4=(ENP(2)+ENN(2))*FN4
      F0=B2*(Z2+W2)*(B1**2*Z2*W2-B2**2*Z1*W1)
      F0=(EPP(1)+EPN(1))*F0
      G21=FN12+FN8+FN4
      G21=2.D0*B1*(G21+F0+FP4+FP8+FP12)
C
      FP12=Z1**2*W1**2*Z2*W2
      FP12=CP(4)*FP12
      FN12=-B1**4*B2**2
      FN12=CN(4)*FN12
      FP8=2.D0*B1*Z1*W1*Z2*W2*(Z1+W1)
      FP8=CP(3)*FP8
      FN8=-2.D0*B2**2*B1**3*(Z1+W1)
      FN8=CN(3)*FN8
      FP4=B1**2*Z2*W2*(Z1**2+W1**2+4.D0*Z1*W1)-B2**2*Z1**2*W1**2
      FP4=CP(2)*FP4
      FN4=-B1**2*(B2**2*(Z1**2+W1**2+4.D0*Z1*W1)-B1**2*Z2*W2)
      FN4=CN(2)*FN4
```

```
      F0=2.D0*B1*(Z1+W1)*(-B2**2*Z1*W1+B1**2*Z2*W2)
      G22=FN12+FN8+FN4
      G22=2.D0*B2*(G22+F0+FP4+FP8+FP12)
      G(2)=(G21+R*G22)
      G(3)=0.D0
C
      GO TO 502
  501 G(1)=111.D0
      G(2)=222.D0
      G(3)=333.D0
      WRITE(NOUT,600) G
      WRITE(NOUT,601) X,DM
  600 FORMAT(2X,'NONPHYS. SOLN.',3(D13.6,1X))
  601 FORMAT(2X,'B1 B2 M',4(1X,D13.6))
  502 DO 503 I=1,N
      FG(I)=G(I)
  503 CONTINUE
      RETURN
      END
C
C
C
      SUBROUTINE RF(V,RP,RN,R0)
C     k=1 -- mETROPOLIS RATE FUNCTION
      REAL*8 V,RP,RN,R0,DT,E ,CN
      INTEGER K
      COMMON DT,K,E
C
      IF (K.NE.1) GO TO 2
  1   RP=(V+E)/DT
      RP=DMIN1(1.D0,DEXP(-RP))
      RN=(V-E)/DT
      RN=DMIN1(1.D0,DEXP(-RN))
      R0=V/DT
      R0=DMIN1(1.D0,DEXP(-R0))
      RETURN
  2   IF (K.NE.2) GO TO 3
      RP=0.D0
      RN=1.D0
      R0=V/DT
      R0=DMIN1(1.D0,DEXP(-R0))
      RETURN
  3   IF(K.NE.3) GO TO 31
      RP=(V+E)/DT
      RP=1.D0/(1.D0+DEXP(RP))
      RN=(V-E)/DT
      RN=1.D0/(1.D0+DEXP(RN))
      R0=V/DT
      R0=1.D0/(1.D0+DEXP(R0))
```

```
      RETURN
 31   IF(K.NE.31) GO TO 4
      RP=0.D0
      RN=1.D0
      R0=V/DT
      R0=1.D0/(1.D0+DEXP(R0))
      RETURN
 4    IF(K.NE.4) GO TO 41
      CN=(12.D0+DABS(E))/DT
      CN=DEXP(CN/2.D0)
      RP=(V+E)/DT
      RP=DEXP(-RP/2.D0)/CN
      RN=(V-E)/DT
      RN=DEXP(-RN/2.D0)/CN
      R0=V/DT
      R0=DEXP(-R0/2.D0)/CN
 41   IF(K.NE.41) GO TO 5
      RP=0.D0
      RN=(V+12.D0)/DT
      RN=DEXP(-RN/2.D0)
      R0=0.D0
  5   CONTINUE
      RETURN
      END
```

```
                         PROGRAM AF1
C
C
C     AF1 IS DESIGNED TO CONSTRUCT THE PHASE DIAGRAM FOR THE DDIM
C     ( AF&FM CASE)
C
      PARAMETER (N=2,NOBS=100,NF=1)
      REAL*8 FP(4,64),FC(4,64),DHX(4,6,64),DE(64),DGM
      REAL*8 PM,GM,TI,ST,T,EI,SE,E(2),XG(6),XGM(N),X(N)
      REAL*8 EL,F,FE,FE1,STEP,DMACC,ERRREL,SM,B1,B2,R,EPB,EPB0
      REAL*8 XGS(3),XS(3),DJ,SSM,Z1,Z2,X3(3),XG3(3),X0(2),XG0(2)
      REAL*8 FNORM,FNORM1,FNORM2,FNORM3,GMS,EL0,FPM
      COMMON NOUT,K,J,T,E,R,PM,NP,SM
      COMMON /C0/FP,FC,DHX
      COMMON /C3/ITMAX,ERRREL,XGM,X,FNORM
      EXTERNAL EQM,DNEQNF,DUVMIF,FE,FE1,RF,CRT,DELTA,CONV,ELJ
      EXTERNAL PROB,PR,COMPX,FIT,BF
C
      NP=N
      CALL UMACH (2,NOUT)
      OPEN (UNIT=NOUT,STATUS='UNKNOWN',FILE='AF1T.RES')
      WRITE(NOUT,100)
      DATA XG0/0.208165D0,0.226238D0/,FPM/0.D0/
      DATA GM/0.92858D0/,XGM/0.029044D0,0.029044D0/
      DATA IE/10/,IT/0/,EI/0.0D0/,TI/2.D0/,SE/0.1D0/,ST/0.01D0/
      DATA ERRREL/0.1D-9/,ITMAX/300/,R/1.D0/,K/1/,E(2)/0.0D0/
      DATA STEP/0.1D-04/,DMACC/0.1D-12/,MAXFN/200/,J/1/
      WRITE(NOUT,101) K,J,R
      WRITE(NOUT,102)
      WRITE(NOUT,103)
C
      IF(J.EQ.1) SM=FPM
      IF(J.EQ.(-1)) PM=FPM
      WRITE(NOUT,109) GM,XGM
      DJ=DSIGN(1.D0,DBLE(J))
      XGM(1)=DJ*(1.D0-4.D0*XGM(1))
      XGM(2)=DJ*(1.D0-4.D0*XGM(2))
      XG0(1)=DJ*(1.D0-4.D0*XG0(1))
      XG0(2)=DJ*(1.D0-4.D0*XG0(2))
      WRITE(NOUT,109) GM,XGM
      CALL DELTA (DE,DHX)
C      WRITE(NOUT,104) (DE(M3),M3=1,64)
C      DO 11 M1=1,4
C      DO 11 M2=1,6
C      WRITE(NOUT,104) (DHX(M1,M2,M3),M3=1,64)
C   11 CONTINUE
```

```
      DO 10 I1=1,IE+1
      E(1)=EI+DBLE(I1-1)*SE
      DO 9 I2=1,IT+1
      T=TI+DBLE(I2-1)*ST
      CALL CRT (DE,FP,FC)
      WRITE(NOUT,112) K,NP,T,E
  112 FORMAT (2X,'K=',I2,'NP=',I2,3(D12.5,1X)/)
C      DO 20 L1=1,4
C      WRITE(NOUT,110) (FP(L1,L2),L2=1,64)
C      WRITE(NOUT,110) (FC(L1,L2),L2=1,64)
C   20 CONTINUE
      IF(J.EQ.(-1)) SM=GM
      IF(J.EQ.1) PM=GM
      IF(J.EQ.1) SM=FPM
      IF(J.EQ.(-1)) PM=FPM
      IF(J) 1,7,1
    1 IF(DABS(GM).GT.0.1D-04) GO TO 2
      IF(J.EQ.(-1)) SM=0.D0
      IF(J.EQ.1) PM=0.D0
      CALL DNEQNF (EQM,ERRREL,NP,ITMAX,XGM,X,FNORM)
      GO TO 3
    2 DGM=DABS(GM)
      BOUND=DMIN1(DGM,DABS(1.D0-DGM))
      CALL DUVMIF(FE,GM,STEP,BOUND,DMACC,MAXFN,GMS)
      GM=GMS
      IF(J.EQ.(-1)) SM=GMS
      IF(J.EQ.1) PM=GMS
      IF(J.EQ.1) SM=FPM
      IF(J.EQ.(-1)) PM=FPM
      CALL CONV (NP,X,XG)
      F=FE1(XG)/T
      CALL ELJ (XG,DE,EL,EPB)
      WRITE(NOUT,111)
      WRITE (NOUT,105) E,EPB,F,EL,FNORM
      WRITE (NOUT,106) XG
      SSM=0.5D0*(XG(1)+DJ*XG(2))
      B1=0.25D0*(1.D0+(XG(1)-XG(2))-XG(3))
      B2=0.25D0*(1.D0+(XG(1)-XG(2))-XG(4))
      Z1=0.25D0*(1.D0+(XG(1)+XG(2))+XG(3))
      Z2=0.25D0*(1.D0+(XG(1)+XG(2))+XG(4))
      WRITE (NOUT,106) T,SSM,B1,B2,Z1,Z2
    3 XGS(1)=PM+SM
      XGS(2)=X(1)
      XGS(3)=X(2)
      CALL DNEQNF (EQM,ERRREL,NP+1,ITMAX,XGS,XS,FNORM1)
      DO 4 I3=1,NP+1
    4 XGS(I3)=XS(I3)
      WRITE (NOUT,113)
      WRITE(NOUT,104) XS,FNORM1
```

```
      IF(DGM.LT.0.1D-04) GO TO 9
      IF(J.EQ.(-1)) GO TO 5
      PM=0.D0
      GO TO 6
    5 SM=0.D0
    6 CALL DNEQNF (EQM,ERRREL,NP,ITMAX,XG0,X0,FNORM2)
      XG0(1)=X0(1)
      XG0(2)=X0(2)
      XG3(1)=PM+SM
      XG3(2)=X0(1)
      XG3(3)=X0(2)
      WRITE(NOUT,114)
      WRITE(NOUT,104 ) XG3(1),X0,FNORM2
      CALL DNEQNF (EQM,ERRREL,NP+1,ITMAX,XG3,X3,FNORM3)
      GO TO 8
    7 GO TO 12
    8 CALL CONV (NP+1,XG3,XG)
      F0=FE1(XG)/T
      CALL ELJ (XG,DE,EL0,EPB0)
      WRITE(NOUT,106) T,F-F0,F0,EL0,FNORM2
      WRITE(NOUT,115)
      WRITE(NOUT,104) X3,FNORM3
      SSM=0.5D0*(XG(1)+DJ*XG(2))
      B1=0.25D0*(1.D0+(XG(1)-XG(2))-XG(3))
      B2=0.25D0*(1.D0+(XG(1)-XG(2))-XG(4))
      Z1=0.25D0*(1.D0+(XG(1)+XG(2))+XG(3))
      Z2=0.25D0*(1.D0+(XG(1)+XG(2))+XG(4))
      WRITE (NOUT,106) T,SSM,B1,B2,Z1,Z2
      IF(NF.NE.1) GO TO 9
      IF(DGM.GT.0.2D0) GO TO 9
      CALL FIT (NOBS,DGM,X0)
    9 CONTINUE
   10 CONTINUE
      GO TO 13
   12 WRITE(NOUT,107) J,NP
   13 CONTINUE
  100 FORMAT (2X,'AF1.FOR PROGRAM    AF1T.RES     '/)
  101 FORMAT (2X,'K=',I2,2X,'J=',I2,2X,'R=',F7.3/)
  102 FORMAT (8X,'K=1   METROPOLIS RATES'
     &/8X,'K=2   IEF (M.R.)'/8X,'K=3   KAWASAKI RATES'/8X,'K=31
     &  IEF (K.R.)'/8X,'R IS THE RATIO COEFFICIENT'/)
  103 FORMAT (2X,' E       EP      PM       F       EL       FNORM'
     &/2X,' HX1     HX2     HX3      HX4     HX5      HX6'/
     &2X,' T       SM      B1      B2'/)
  104 FORMAT (4(1X,D15.8))
  105 FORMAT(/2(F7.3,2X),4(D13.6,2X))
  106 FORMAT(1X,F6.3,1X,5(D13.6,1X))
  107 FORMAT (2X,'M.P.  J=',I2,2X,'AND N=',I2/)
  109 FORMAT (2X,'M.P.',4(D12.5,1X))
```

```
  110 FORMAT (6(D10.3,1X))
  111 FORMAT (/4X,'A  1. MINIMIZING THE FREE ENERGY')
  113 FORMAT (/4X,'A  2. SOLVING 3 EQ. OF MOTION')
  114 FORMAT (/4X,'B  1. SOLVING 2 EQ. OF MOTION')
  115 FORMAT (/4X,'B  2. SOLVING 3 EQ. OF MOTION')
      STOP
      END
C
C
C
C
      DOUBLE PRECISION FUNCTION BF(K,X)
      INTEGER K
      REAL*8 X
      BF=X**(2*K)
      RETURN
      END
C
C
C
C
      SUBROUTINE FIT (NOBS,GM,X0)
C    "FIT" FITS FREE ENERGY WITH EVEN POLYNOMIAL IN GM AROUND GM=0
      PARAMETER (NDEG=4,INTCEP=1,IWT=0)
      REAL*8 GM,X0(2),GMI,TGM
      REAL*8 XDATA(100),YDATA(100),B(NDEG+1),AMG,FT
      REAL*8 ERRREL,XGI(2),Y(2),FNORM,SSE,WEIGHT
      COMMON NOUT,K,J,T
      COMMON /C3/ITMAX,ERRREL,XGI,Y,FNORM
      EXTERNAL BF,FE,DFNLSQ
C
      IF(GM.GE.0.1D0) GMI=0.05D0
      IF(GM.LT.0.1D0.AND.GM.GE.0.05D0) GMI=0.1D0
      IF(GM.LT.0.05D0.AND.GM.GE.0.01D0) GMI=0.05D0
      IF(GM.LT.0.01D0) GMI=0.01D0
      XGI(1)=X0(1)
      XGI(2)=X0(2)
      DO 1 I=1,NOBS
      TGM=(GMI*DBLE(I-1))/DBLE(NOBS)
      XDATA(I)=TGM
      YDATA(I)=FE(TGM)/T
    1 CONTINUE
      CALL DFNLSQ(BF,INTCEP,NDEG,100,XDATA,YDATA,IWT,WEIGHT,B,SSE)
      FT=B(1)+B(2)*(GM**2)+B(3)*(GM**4)+B(4)*(GM**6)
      IF(NDEG.EQ.4) FT=FT+B(5)*(GM**8)
      AGM=0.D0
      IF((-B(2)/B(3)).LT.0.D0) GO TO 2
      AGM=DSQRT(-B(2)/(2.D0*B(3)))
    2 WRITE(NOUT,100)
```

```
      WRITE(NOUT,101) B
      WRITE(NOUT,102) FT,AGM,SSE,GMI
  100 FORMAT(//7X,'A0',13X,'A2',13X,'A4',13X,'A6',13X,'A8')
  101 FORMAT(5(2X,D13.6))
  102 FORMAT(/2X,'FA ',D13.6,' GMA ',D13.6,' SSE ',D13.6,' GMI ',
     &D13.6/)
      RETURN
      END
C
C
C
C
      DOUBLE PRECISION FUNCTION FE(GM)
C    "FE" IS USED HERE FOR J=+1,-1; "FE" CALLS "DNEQNF" TO FIND
C     HX(3) AND HX(4) FOR GIVEN GM AND THEN CALLS "FE1" TO CALCULATE
C     THE FREE ENERGY F(GM)
      REAL*8 GM,T,E(2),R,PM,FE1,ERRREL,FNORM,HX(6),SM
      COMMON NOUT,K,J,T,E,R,PM,N,SM
      REAL*8 XGI(2),X(2)
      COMMON /C3/ITMAX,ERRREL,XGI,X,FNORM
      EXTERNAL DNEQNF,EQM,CONV,FE1
C
      IF(J.EQ.1) PM=GM
      IF(J.EQ.(-1)) SM=GM
C      WRITE(NOUT,100) GM,XGI,N
C      WRITE(NOUT,100) T,E,J,K
      CALL DNEQNF(EQM,ERRREL,N,ITMAX,XGI,X,FNORM)
C      WRITE(NOUT,100) GM,X
      XGI(1)=X(1)
      XGI(2)=X(2)
      CALL CONV (N,X,HX)
      FE=FE1(HX)
C      WRITE(NOUT,100) FE
  100 FORMAT(2X,'FE',3(D12.5,1X),2I2)
      RETURN
      END
C
C
C
C
      SUBROUTINE CONV (N1,XGI,XGF)
C
      REAL*8 XGI(N1),XGF(6),T,E(2),R,PM,SM
      COMMON NOUT,K,J,T,E,R,PM,NP,SM
C
      XGF(1)=PM+SM
      XGF(2)=PM-SM
      IF(J) 1,5,1
    1 IF(N1.EQ.2) GO TO 6
```

```
      XGF(1)=XGI(1)
      XGF(2)=2.D0*PM-XGF(1)
      IF (N1.NE.3) GO TO 3
      DO 2 I1=2,3
      XGF(I1+1)=XGI(I1)
    2 XGF(I1+3)=XGI(I1)
      RETURN
    3 IF (N1.NE.5) GO TO 5
      DO 4 I1=2,N1
      XGF(I1+1)=XGI(I1)
    4 CONTINUE
      RETURN
    5 WRITE(NOUT,100) J,N1
      RETURN
    6 XGF(3)=XGI(1)
      XGF(5)=XGI(1)
      XGF(4)=XGI(2)
      XGF(6)=XGI(2)
  100 FORMAT (2X,'CONV',2X,'J=',I3,'N1=',I3/)
      RETURN
      END
C
C
C
C
      SUBROUTINE EQM (HX1,GF,N)
C    "EQM" CALCULATES THE VALUES "GF" OF THE EQ. OF MOTION FOR THE CORRELA
C     TION FUNCTIONS HX(6)
C
      REAL*8 HX(6),HX1(N),GF(N),GX(6),P(4,64),C(4,64)
      REAL*8 FP(4,64),FC(4,64),DHX(4,6,64),GXT(6,4)
      REAL*8 X1(2),X2(2),X3(2,2),X4(2,2),X5(2,2),X6(2,2)
      REAL*8 T,E(2),R,SUT,DJ
      COMMON NOUT,K,J,T,E,R
      COMMON /C0/FP,FC,DHX
      COMMON /C1/X1,X2,X3,X4,X5,X6
      EXTERNAL PROB,COMPX,CONV
C
      DJ=DSIGN(1.D0,DBLE(J))
      CALL CONV (N,HX1,HX)
      IF(J.LE.0) GO TO 11
      DO 10 L=3,6
      IF(HX(L).LT.0.D0.OR.HX(L).GE.1.D0) GO TO 6
   10 CONTINUE
      GO TO 12
   11 IF(J.EQ.0) GO TO 6
      DO 12 L=3,6
      IF(HX(L).GT.0.D0.OR.HX(L).LE.(-1.D0)) GO TO 6
   12 CONTINUE
```

```
      CALL COMPX (HX,X1,X2,X3,X4,X5,X6)
C      IF(N.NE.3) GO TO 89
C      WRITE(NOUT,99)
      WRITE(NOUT,101) HX
C      WRITE(NOUT,101) HX1
      WRITE(NOUT,101) X1,X2
      WRITE(NOUT,101) X1(1)-DJ*X2(1),X1(2)+DJ*X2(1)
      WRITE(NOUT,101) X3(1,1),X4(1,1),X5(1,1),X6(1,1)
      WRITE(NOUT,101) X3(1,2),X4(1,2),X5(1,2),X6(1,2)
      WRITE(NOUT,101) X3(2,1),X4(2,1),X5(2,1),X6(2,1)
      WRITE(NOUT,101) X3(2,2),X4(2,2),X5(2,2),X6(2,2)
   89 CALL PROB (P,C)
C      DO 90 I1=1,4
C      WRITE(NOUT,101) (P(I1,I2),I2=1,64)
C      WRITE(NOUT,101) (C(I1,I2),I2=1,64)
C   90 CONTINUE
      DO 1 I=1,6
      GX(I)=0.D0
      DO 1 I1=1,4
      GXT(I,I1)=0.D0
    1 CONTINUE
      DO 22 L=2,6
      DO 21 M=1,4
      IF(L.EQ.3.AND.M.EQ.1) GO TO 20
      IF(L.EQ.4.AND.M.EQ.2) GO TO 20
      IF(L.EQ.5.AND.M.EQ.3) GO TO 20
      IF(L.EQ.6.AND.M.EQ.4) GO TO 20
      DO 2 I=1,64
      SUT=DHX(M,L,I)*(FP(M,I)*P(M,I)-FC(M,I)*C(M,I))
      GXT(L,M)=GXT(L,M)+SUT
C      IF(L.NE.2) GO TO 2
C      IF(M.EQ.1.OR.M.EQ.3) GO TO 9
C      GO TO 2
C  102 FORMAT(2X,3(I2,1X),D13.6,1X,2(D15.9,1X))
C    9 WRITE(NOUT,102) L,M,I,SUT,FP(M,I)*P(M,I),FC(M,I)*C(M,I)
C      WRITE(NOUT,101) DHX(M,L,I),FP(M,I),P(M,I),FC(M,I),C(M,I)
C      WRITE(NOUT,101) P(M,I)-C(M,I),FP(M,I)*P(M,I)-FC(M,I)*C(M,I)
    2 CONTINUE
      GO TO 25
   20 GXT(L,M)=0.D0
   25 GX(L)=GX(L)+GXT(L,M)
   21 CONTINUE
      GX(L)=0.25D0*GX(L)
   22 CONTINUE
      GX(1)=-GX(2)
C      IF(N.NE.3) GO TO 23
      WRITE(NOUT,101) (GXT(I1,1),I1=1,6)
      WRITE(NOUT,101) (GXT(I1,2),I1=1,6)
      WRITE(NOUT,101) (GXT(I1,3),I1=1,6)
```

```
      WRITE(NOUT,101) (GXT(I1,4),I1=1,6)
      WRITE(NOUT,101) GXT(2,1)+DJ*GXT(2,3),GXT(2,2)+DJ*GXT(2,4)
      WRITE(NOUT,101) GX
C      WRITE(NOUT,100) J,N
   23 IF (J) 3,6,7
    3 IF(N.EQ.2.OR.N.EQ.3) GO TO 7
    4 IF(N.NE.5) GO TO 6
      GF(1)=GX(1)
      DO 5 L=2,N
      GF(L)=GX(L+1)
    5 CONTINUE
C      WRITE(NOUT,101) GF
      RETURN
    6 WRITE(NOUT,100) J,N
      DO 60 L=1,N
   60 GF(L)=5.D0
      RETURN
    7 IF (N.NE.2) GO TO 8
      GF(1)=GX(3)+GX(5)
      GF(2)=GX(4)+GX(6)
      RETURN
    8 IF (N.NE.3) GO TO 6
      GF(1)=0.5D0*(GX(1)+DJ*GX(2))
      GF(2)=GX(3)+GX(5)
      GF(3)=GX(4)+GX(6)
C      WRITE(NOUT,101) GF
   99 FORMAT(2X,'EQM'/)
  100 FORMAT(2X,'EQM','J=',I2,2X,'N=',I2/)
  101 FORMAT(1X,6(D13.5))
      RETURN
      END
C
C
C
C
      SUBROUTINE COMPX (HX,X1,X2,X3,X4,X5,X6)
C     "COMPX" COMPUTES X1,...,X6 FOR GIVEN VALUES OF HX(I), I=1,...,6
      REAL*8 X1(2),X2(2),X3(2,2),X4(2,2),X5(2,2),X6(2,2),HX(6)
      REAL*8 E1,E2,E3,XT,DJ,XT1
      COMMON NO,K,JP
C
      DJ=DSIGN(1.D0,DBLE(JP))
C      WRITE(NO,101) HX(1)-DJ*HX(2),HX(3)-HX(4),HX(4)-HX(5),HX(5)-HX(6)
      DO 2 I=1,2
      E1=DSIGN(1.D0,DBLE(3-2*I))
      X1(I)=0.5D0*(1.D0+E1*HX(1))
      X2(I)=0.5D0*(1.D0+E1*HX(2))
      DO 1 J=1,2
      E2=DSIGN(1.D0,DBLE(3-2*J))
```

```
      E3=DSIGN(1.D0,E1*E2)
      XT=1.D0+(E1*HX(1)+E2*HX(2))
      XT1=XT
      X3(I,J)=0.25D0*(XT+E3*HX(3))
      X4(I,J)=0.25D0*(XT+E3*HX(4))
      X5(I,J)=0.25D0*(XT1+E3*HX(5))
      X6(I,J)=0.25D0*(XT1+E3*HX(6))
C       WRITE(NO,100) I,J,E1,E2,E3,XT
    1 CONTINUE
    2 CONTINUE
C       WRITE(NO,101) X3(2,2)-X4(2,2),X4(2,2)-X5(2,2),X5(2,2)-X6(2,2)
C       WRITE(NO,101) X3(1,2)-X4(1,2),X4(1,2)-X5(1,2),X5(1,2)-X6(1,2)
C       WRITE(NO,101) X3(1,2)-DJ*X3(2,1),X4(1,2)-DJ*X4(2,1)
C       WRITE(NO,101) X3(1,2)-DJ*X5(2,1),X3(2,1)-X4(2,1)
C       WRITE(NO,101) X3(1,1)+DJ*X3(2,2),X3(1,1)+DJ*X4(2,2)
  100 FORMAT('X',1X,'I=',I2,'J=',I2,4(D13.6,1X))
  101 FORMAT('DX',4(D13.6,1X))
      RETURN
      END
C
C
C
C
      SUBROUTINE PROB (P,C)
C     "PROB" CHANGES THE VARIABLES Y1,...,Y6 ACCORDING TO THE TRANSFORMA-
C     TIONS: T1=E,T2(X->Y),T3(X->(-X)),T4(X->(-Y)) IN ORDER FOR "PR" TO
C     COMPUTE P(4,64)&C(4,64) -THE PROBABILITIES OF APPEARANCE OF DIFFERENT
C     CONFIGURATIONS ON THE 4 TYPES OF CLUSTERS
      REAL*8 P(4,64),C(4,64),PT(64),CT(64)
      REAL*8 X1(2),X2(2),X3(2,2),X4(2,2),X5(2,2),X6(2,2)
      REAL*8 Y1(2),Y2(2),Y3(2,2),Y4(2,2),Y5(2,2),Y6(2,2)
      COMMON /C1/X1,X2,X3,X4,X5,X6
      COMMON /C2/Y1,Y2,Y3,Y4,Y5,Y6
      COMMON NOUT
      EXTERNAL PR
C
      K=1
    1 DO 2 I=1,2
      Y1(I)=X1(I)
      Y2(I)=X2(I)
      DO 2 J=1,2
      Y3(I,J)=X3(I,J)
      Y4(I,J)=X4(I,J)
      Y5(I,J)=X5(I,J)
      Y6(I,J)=X6(I,J)
    2 CONTINUE
      GO TO 5
    3 DO 4 I=1,2
      DO 4 J=1,2
```

```
      Y3(I,J)=X4(I,J)
      Y4(I,J)=X5(I,J)
      Y5(I,J)=X6(I,J)
      Y6(I,J)=X3(I,J)
    4 CONTINUE
    5 CALL PR(K,PT,CT)
      DO 6 I=1,64
      P(K,I)=PT(I)
      C(K,I)=CT(I)
    6 CONTINUE
C      WRITE(NOUT,100) K
C      DO 7 L=1,4
C      WRITE(NOUT,101) PT(L),CT(L),PT(L)-CT(L)
C    7 CONTINUE
      K=K+1
      IF(K.EQ.2.OR.K.EQ.4) GO TO 3
      IF(K.EQ.3) GO TO 1
  100 FORMAT(2X,'K=',I3)
  101 FORMAT(3(D15.8,1X))
      RETURN
      END
C
C
C
C
      SUBROUTINE PR(KC,PT,CT)
C     "PR" CALCULATES THE PROBABILITIES OF APPEARANCE OF A GIVEN CONFIGU-
C     RATION IN TERMS OF Y1,...,Y6 ( AND THEREFORE IN TERMS OF THE CORRE-
C     LATION FUNCTIONS HX(L) L=1,...,6)
      REAL*8 PT(64),CT(64)
      REAL*8 Y1(2),Y2(2),Y3(2,2),Y4(2,2),Y5(2,2),Y6(2,2)
      COMMON /C2/Y1,Y2,Y3,Y4,Y5,Y6
      COMMON NO
C
      I=0
      DO 2 I1=1,2
      DO 2 I2=1,2
      DO 2 I3=1,2
      DO 2 I4=1,2
      DO 2 I5=1,2
      DO 2 I6=1,2
      I=I+1
      IF(KC.EQ.3.OR.KC.EQ.4) GO TO 1
      PT(I)=Y4(1,I1)*Y5(1,I2)*Y6(1,I3)*Y4(I4,2)*Y5(I5,2)*Y6(I6,2)
      CT(I)=Y4(2,I1)*Y5(2,I2)*Y6(2,I3)*Y4(I4,1)*Y5(I5,1)*Y6(I6,1)
      GO TO 2
    1 PT(I)=Y6(I1,1)*Y3(I2,1)*Y4(I3,1)*Y6(2,I4)*Y3(2,I5)*Y4(2,I6)
      CT(I)=Y6(I1,2)*Y3(I2,2)*Y4(I3,2)*Y6(1,I4)*Y3(1,I5)*Y4(1,I6)
    2 CONTINUE
```

```
      DO 4 I=1,64
      IF(KC.EQ.3.OR.KC.EQ.4) GO TO 3
      PT(I)=PT(I)*Y3(1,2)/(Y1(1)*Y2(2))**3
      CT(I)=CT(I)*Y3(2,1)/(Y1(2)*Y2(1))**3
      GO TO 4
    3 PT(I)=PT(I)*Y5(2,1)/(Y2(1)*Y1(2))**3
      CT(I)=CT(I)*Y5(1,2)/(Y2(2)*Y1(1))**3
    4 CONTINUE
  100 FORMAT(2X,'I=',I3)
      RETURN
      END
C
C
C
C
      SUBROUTINE DELTA (DE,DH)
C     "DELTA" CALCULATES THE CHANGE IN ENERGY DE(I) AND THE CHANGES IN THE
C     CORRELATION FUNCTIONS DH(K,J,I) FOR ALL CONFIGURATIONS- I=1,...,64 ,
C     FOR THE FOUR TYPES OF CLUSTERS K=1,...,4 AND FOR 6 CORR. FCTNS-J=1,...,6
      REAL*8 DE(64),DH(4,6,64),DHT(6,64),DJ
      COMMON NOUT,K1,J
C
      DJ=DSIGN(1.D0,DBLE(J))
      I=0
      DO 1 I1=1,2
      DO 1 I2=1,2
      DO 1 I3=1,2
      DO 1 I4=1,2
      DO 1 I5=1,2
      DO 1 I6=1,2
      I=I+1
      DHT(1,I)=-2.D0
      DHT(2,I)=2.D0
      DHT(3,I)=0.D0
      DHT(4,I)=-2.D0*(DSIGN(1.D0,DBLE(3-2*I1))-DSIGN(1.D0,DBLE(3-2*I4)))
      DHT(5,I)=-2.D0*(DSIGN(1.D0,DBLE(3-2*I2))-DSIGN(1.D0,DBLE(3-2*I5)))
      DHT(6,I)=-2.D0*(DSIGN(1.D0,DBLE(3-2*I3))-DSIGN(1.D0,DBLE(3-2*I6)))
      DE(I)=-DJ*(DHT(4,I)+DHT(5,I)+DHT(6,I))
    1 CONTINUE
      K=1
      DO 2 I=1,64
      DH(K,1,I)=DHT(1,I)
      DH(K,2,I)=DHT(2,I)
      DH(K,3,I)=DHT(3,I)
      DH(K,4,I)=DHT(4,I)
      DH(K,5,I)=DHT(5,I)
      DH(K,6,I)=DHT(6,I)
    2 CONTINUE
      K=2
```

```
      DO 3 I=1,64
      DH(K,1,I)=DHT(1,I)
      DH(K,2,I)=DHT(2,I)
      DH(K,3,I)=DHT(6,I)
      DH(K,4,I)=DHT(3,I)
      DH(K,5,I)=DHT(4,I)
      DH(K,6,I)=DHT(5,I)
    3 CONTINUE
      K=3
      DO 4 I=1,64
      DH(K,1,I)=-DHT(1,I)
      DH(K,2,I)=-DHT(2,I)
      DH(K,3,I)=DHT(5,I)
      DH(K,4,I)=DHT(6,I)
      DH(K,5,I)=DHT(3,I)
      DH(K,6,I)=DHT(4,I)
    4 CONTINUE
      K=4
      DO 5 I=1,64
      DH(K,1,I)=-DHT(1,I)
      DH(K,2,I)=-DHT(2,I)
      DH(K,3,I)=DHT(4,I)
      DH(K,4,I)=DHT(5,I)
      DH(K,5,I)=DHT(6,I)
      DH(K,6,I)=DHT(3,I)
    5 CONTINUE
      RETURN
      END
C
C
C
C
      SUBROUTINE  CRT (DE,FP,FC)
C     "CRT" COMPUTES CLUSTER RATES FOR EVERY T FOR ALL THE
C     CONFIGURATIONS ON THE 4 TYPES OF CLUSTERS USING "RF"
      REAL*8 DE(64),FP(4,64),FC(4,64),R(4)
      EXTERNAL RF
C
      DO 1 L=1,64
      CALL RF (DE(L),R)
      DO 1 I=1,3,2
      FP(I,L)=R(1)
      FC(I,L)=R(2)
      FP(I+1,L)=R(3)
      FC(I+1,L)=R(4)
    1 CONTINUE
      RETURN
      END
C
```

```
C
C
C
      DOUBLE PRECISION FUNCTION FE1(XG)
C     "FE1" CALCULATES FREE ENERGY F FOR THE GIVEN VALUES OF THE
C     VARIABLES XG(I) - I=1,6
C
      REAL*8 T,R,XG(6),X1(2),X2(2),X3(2,2),X4(2,2),X5(2,2),X6(2,2)
      REAL*8 E(2),U,S,Z1,Z2,Z3,Z4,Z5,Z6,DJ
      COMMON NOUT,K,J,T,E,R
      EXTERNAL COMPX
C
      DJ=DSIGN(1.D0,DBLE(J))
      CALL COMPX (XG,X1,X2,X3,X4,X5,X6)
C      WRITE(NOUT,99)
C      WRITE(NOUT,100) XG
C      WRITE(NOUT,100) X3(1,1),X4(1,1),X5(1,1),X6(1,1)
C      WRITE(NOUT,100) X3(1,2),X4(1,2),X5(1,2),X6(1,2)
C      WRITE(NOUT,100) X3(2,1),X4(2,1),X5(2,1),X6(2,1)
C      WRITE(NOUT,100) X3(2,2),X4(2,2),X5(2,2),X6(2,2)
      U=-0.5D0*DJ*(XG(3)+XG(4)+XG(5)+XG(6))
      Z1=0.D0
      Z2=0.D0
      Z3=0.D0
      Z4=0.D0
      Z5=0.D0
      Z6=0.D0
      DO 1 I1=1,2
      Z1=Z1+X1(I1)*DLOG(X1(I1))
      Z2=Z2+X2(I1)*DLOG(X2(I1))
      DO 1 I2=1,2
      Z3=Z3+X3(I1,I2)*DLOG(X3(I1,I2))
      Z4=Z4+X4(I1,I2)*DLOG(X4(I1,I2))
      Z5=Z5+X5(I1,I2)*DLOG(X5(I1,I2))
      Z6=Z6+X6(I1,I2)*DLOG(X6(I1,I2))
    1 CONTINUE
      S=0.5D0*(3.0D0*(Z1+Z2)-(Z3+Z4+Z5+Z6))
      FE1=U-T*S
   99 FORMAT(2X,'FE1'/)
  100 FORMAT(1X,6(D13.5))
      RETURN
      END
C
C
C
C
      SUBROUTINE ELJ (XG,DE,EL,EPB)
C     "ELJ" COMPUTES EL. CURRENT EL FOR GIVEN T AND GIVEN VALUES OF THE
C     VARIABLES XG(I) - I=1,6
```

```
      REAL*8 X1(2),X2(2),X3(2,2),X4(2,2),X5(2,2),X6(2,2),DE(64)
      REAL*8 FP(4,64),FC(4,64),P(4,64),C(4,64),ELT,EL,XG(6),EPB
      COMMON /C0/FP,FC
      COMMON /C1/X1,X2,X3,X4,X5,X6
      EXTERNAL COMPX,PROB
C
      CALL COMPX (XG,X1,X2,X3,X4,X5,X6)
      CALL PROB(P,C)
      EPB=0.D0
      ELT=0.D0
      DO 1 I1=1,3,2
      DO 1 I2=1,64
      EL=(FP(I1,I2)*P(I1,I2)-FC(I1,I2)*C(I1,I2))
      ELT=ELT+EL
      EPB=EPB+DE(I2)*EL
    1 CONTINUE
      EL=0.5D0*ELT
      EPB=0.5D0*EPB
      RETURN
      END
C
C
C
C
      SUBROUTINE RF(V,R)
C     "RF" CALCULATES THE RATES
C
      REAL*8 V,R(4),T,E(2)
      COMMON NOUT,K,J,T,E
C
      DO 1 L=1,2
      R(L)=DSIGN(1.D0,DBLE(3-2*L))*(V-E(1))/T
  1   R(L+2)=DSIGN(1.D0,DBLE(3-2*L))*(V-E(2))/T
      IF (K.NE.1) GO TO 2
      DO 10 L=1,4
      R(L)=DMIN1(1.D0,DEXP(-R(L)))
  10  CONTINUE
      RETURN
  2   IF (K.NE.2) GO TO 3
      R(1)=1.D0
      R(2)=0.D0
      R(3)=DMIN1(1.D0,DEXP(-R(3)))
      R(4)=DMIN1(1.D0,DEXP(-R(4)))
      RETURN
  3   IF(K.NE.3) GO TO 31
      R(1)=2.D0/(1.D0+DEXP(R(1)))
      R(2)=2.D0/(1.D0+DEXP(R(2)))
      R(3)=2.D0/(1.D0+DEXP(R(3)))
      R(4)=2.D0/(1.D0+DEXP(R(4)))
```

```
      RETURN
31    IF(K.NE.31) GO TO 4
      R(1)=2.D0
      R(2)=0.D0
      R(3)=2.D0/(1.D0+DEXP(R(3)))
      R(4)=2.D0/(1.D0+DEXP(R(4)))
      RETURN
4     IF(K.NE.4) GO TO 5
      R(1)=DEXP(-R(1)/2.D0)
      R(2)=DEXP(-R(2)/2.D0)
      R(3)=DEXP(-R(3)/2.D0)
      R(4)=DEXP(-R(4)/2.D0)
5     CONTINUE
      RETURN
      END
```

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