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KINETICS OF CLUSTERS IN A BINARY LINEAR SYSTEM

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Synopsis

We consider the stochastically time dependent behaviour of a finite linear chain of N units at temperature T and in an external field H. The kinetics is described in terms of cluster frequencies, of specified numbers of units in the ground state. A closed generating function for the cluster densities on the chain is derived by an approximation due to Kac. Method is applied to the relaxation time of fluctuations, and the zero-field frequency dependent susceptibility, as the fraction of units in a given state. Our results are compared to the phenomenology of linear irreversible thermodynamics.

1. *Introduction.* In this paper we consider a linear chain composed of N units, each of which may be in either of two states. Nature provides us with a great variety of such systems. Examples are long chain molecules in which each constituent may undergo a certain chemical reaction; polymer chains in which each unit may adsorb an extra molecule, and polypeptides in which each unity may be in an α-helix or in a random coil state[1]). Directly related to experimental observation are the fraction of units in a given state, and the fluctuations in that quantity, in equilibrium as well as during the course of a chemical reaction, a biological transformation, or a physical process.

In the case of polypeptides one has observed that below a certain temperature, T_{hc} the helical fraction is almost unity, whereas above T_{hc} it nearly vanishes. The transition region around T_{hc} is extremely narrow[1]). Moreover, the characteristic time in which the helix–coil equilibrium is reached shows a pronounced maximum near T_{hc}. Hence although there is no phase transition in the sense of statistical mechanics, the behaviour near T_{hc} shows many of the properties of a critical temperature[2–5]). Certain chemical reaction rates show the same peaked dependence on the composition of the solvent, *e.g.* on its pH. In magnetic spin systems one finds, at zero field, that the fluctuations in the magnetization (about its zero average), as well as their characteristic decay time, increase as the temperature is lowered, and finally diverge at the critical temperature[6]).

In chemical kinetics numerous attempts have been made to describe such time-

dependent phenomena and several models have been proposed. Detailed discussions of many of these were given by McQuarrie[7]). The existing models vary from a simple rate equation where the helical fraction is the only variable (speaking in terms of polypeptides) to models with several coupled variables corresponding to the numbers of certain kinds of specified sequences of helix and coil units, *e.g.* hhh, hch, hc[8-12]). Usually one obtains these equations by assuming certain elementary rate constants for h→c and c→h transitions of single units, dependent upon the states of their neighbouring units, and by then applying some truncating procedure to the infinite system of coupled correlations. In many cases[7]) one has considered *unidirectional* kinetics, *i.e.*, only h → c transitions are possible and the system ends in a complete random coil state. Evidently such kinetics precludes the study of time-dependent equilibrium correlations. In the physical literature the time-dependent Ising model was introduced by Glauber[1]) in 1963. This model describes a stochastically time-dependent Ising chain with nearest-neighbour interaction in zero magnetic field. Later authors[13,14]) showed that in this model, as well as in some interesting related models[15,16]) one can find the exact time dependence of arbitrary spin correlation functions. However, all these models are one-parameter models, depending only on temperature, and are too limited to describe more general situations.

In this chapter we aim at a compromise between the fully detailed description of Glauber's model, and the wider applicability of the equations of chemical kinetics. We present a two-parameter model of a binary system with bidirectional kinetics. For spin systems the two parameters can be related to temperature and magnetic field. The model is not exactly soluble, but, following a method recently introduced by Felderhof[17]) we reduce it to a soluble linear problem which still contains an infinite number of variables, thus giving a more refined treatment than usual in chemical kinetics.

We shall mostly use spin language and represent the units of the chain by N spin variables to be denoted by $\boldsymbol{s}_N \equiv (s_1, s_2, \ldots, s_N)$, each of which may take the values +1 or −1 according to the state of the corresponding unit. We denote by $\langle \cdots \rangle$ the average over some statistical ensemble which in general will be time dependent. The quantities of interest are then the average magnetization $\langle M \rangle$, where $M \equiv \sum_{j=1}^{N} s_j$, and the fluctuations defined by $\langle \delta M^2 \rangle \equiv \langle M^2 \rangle - \langle M \rangle^2$. The helical fraction in polypeptides corresponds to the quantity $\frac{1}{2}(1 - N^{-1}\langle M \rangle)$.

In section 2 we formulate the model, postulate the master equation for its time dependence, and expose the approximations which we shall make. In section 3 some equilibrium properties have been collected. A set of simplified kinetic equations is derived in section 4 and linearized in section 5. In section 6 these equations are solved and used to calculate the decay time for equilibrium fluctuations in the magnetization as a function of temperature and magnetic field. The result is discussed in section 7. In section 8 we finally calculate the frequency-dependent zero-field magnetic susceptibility. In section 9 we present our conclusions.

2. *The model.* We consider a system in which the configurational energy $\varepsilon(s_N)$ is determined by a nearest-neighbour interaction of strength J between the units of the chain, and an external force H acting on each unit individually. That is, we take

$$\varepsilon(s_N) = -J \sum_{j=1}^{N-1} s_j s_{j+1} - H \sum_{j=1}^{N} s_j + 2J \tag{2.1}$$

This is the configurational energy of a one-dimensional Ising model[18]. The constant $2J$ has been added for later convenience. In spin language J is the exchange energy and H the magnetic energy. In the case of polypeptides, J is the degree of cooperativity between neighbouring units, and H represents the temperature, favouring helix or coil states; the quantity $\varepsilon(s_N)$ is a free energy rather than an energy. In the case of a chemical reaction H is a parameter describing, e.g., the nature of the solvent.

Instead of using the spin variables s_N one can alternatively give a description of a binary linear system in terms of spin clusters. A detailed account of such a description was given by Helderhof[19]. An up cluster of length l (where $l = 1, 2, \ldots$) is defined as a sequence of l adjacent up-spins flanked by down-spins on both ends. The definition of a down-cluster of length l is analogous. For short we shall also refer to these two types of clusters as $(+l)$-clusters and $(-l)$-clusters, and indicate them by C_l and C_{-l}, respectively. Clearly up-clusters and down-clusters alternate on the chain. We shall denote by $n_k(s_N)$ the total number of k-clusters* in a chain of configuration s_N. Explicitly,

$$n_{\pm l}(s_N) = 2^{-l-2} \sum_{j=1}^{N-l+1} \left((1 \mp s_{j-1})(1 \mp s_{j+l}) \prod_{i=1}^{l-1} (1 \pm s_i) \right), \tag{2.2}$$

with $s_0 \equiv -s_1$ and $s_{N+1} \equiv -s_N$. Hence each microscopic configuration s_N implies uniquely a set of occupation numbers $\boldsymbol{n} \equiv (\ldots, n_{-2}, n_{-1}, n_1, n_2, \ldots)$. Inversely, a set $\boldsymbol{n}$ corresponds in general to a large number $\Omega(\boldsymbol{n})$ of configurations s_N. This number is a combinatorial factor,

$$\Omega(\boldsymbol{n}) = \sum_{s_N} \delta(\boldsymbol{n} - \boldsymbol{n}(s_N)) = [R(\boldsymbol{n})!]^2 \prod_k n_k! \tag{2.3}$$

Here and in the sequel we assume that the numbers of up-clusters and of down-clusters both equal $R(\boldsymbol{n}) \equiv \sum_{l=1}^{\infty} n_{+l}$, and that the first cluster on the chain is an up-cluster. Hence a set $\boldsymbol{n}$ does not give a fully detailed microscopic description of a configuration s_N.

It is possible to express the total energy and magnetization of a configuration in the variables $\boldsymbol{n}$. We ascribe to each $(\pm l)$-cluster an energy $\varepsilon_{\pm l}$ which is the sum

* We adopt the convention that l is always a positive number, whereas k may be either positive or negative.

of its internal exchange and magnetic energy, and half the binding energy with its neighbouring clusters. Explicitly,

$$\varepsilon_{\pm l} = -(l-2)J \mp lH. \tag{2.4}$$

The total energy (2.1) of a configuration s_N is obtained by summing over all its clusters.

$$\varepsilon(s_N) \equiv E(\boldsymbol{n}(s_N)) = \sum_{l=1}^{\infty} (n_l \varepsilon_l + n_{-l}\varepsilon_{-l}). \tag{2.5}$$

For the magnetization we have

$$M = \sum_{l=1}^{\infty} l(n_l - n_{-l}). \tag{2.6}$$

We shall adopt $\boldsymbol{n}$ as a set of coarse-grained variables, corresponding to a division of s_N space into cells.

The time dependence of the spin system is described by a master equation for the probability distribution $p(s_N; t)$ over the configurations,

$$\frac{\partial}{\partial t} p(s_N; t) \equiv \sum_{s_N} [w(s_N, s'_N)\, p(s'_N; t) - w(s'_N, s_N)\, p(s_N; t)]. \tag{2.7}$$

In vector notation we may write $\partial p(t)/\partial t = wp(t)$; the matrix elements of w are just $w(s_N, s'_N)$ if we agree to choose

$$w(s_N, s_N) = -\sum_{s'_N \neq s_N} w(s'_N, s_N). \tag{2.8}$$

The transition probabilities $w(s'_N, s_N)$ must be derived from physical considerations[20]) or have to be postulated, as we shall do. Our choice is described most easily in the cluster picture.

We shall admit only transitions in which clusters grow or decrease by one unit at the ends. That is, due to the change of state of a single spin, a neighbour pair of a C_l and a $C_{-l'}$ cluster* transforms into either a pair C_{l+1} and $C_{-(l'-1)}$ (provided $l \geqslant 2$) or into a pair C_{l-1} and $C_{-(l'+1)}$ (provided $l' \geqslant 2$). Thus the total number of clusters in the chain is conserved. We may think of such an elementary transition as a "reaction" between two species C_k in which two other species are produced. A specific reaction may be indicated by a pair r of integers. We shall write $r = (-l, l')$ to denote the reaction

$$r: \quad C_l + C_{-(l'+1)} \to C_{l+1} + C_{-l'}, \qquad l, l' = 1, 2, \ldots. \tag{2.9}$$

* We refer back to the beginning of this section for notation.

The reverse reaction will be denoted by $r = (-l', l)$. The kinetics of the spin system is due to the total effect of binary reactions r of the above type, so that

$$\frac{\partial}{\partial t} p(s_N; t) = \sum_r \sum_{s'_N} [w_r(s_N, s'_N) p(s'_N; t) - w_r(s'_N, s_N) p(s_N; t)], \tag{2.10}$$

with

$$w_r(s'_N, s_N) = w(s'_N, s_N) \delta_r(s_N, s'_N), \tag{2.11}$$

where $\delta_r(s'_N, s_N)$ is unity if s_N can transform into s'_N by a reaction of type r, and is zero otherwise.

From (2.1) it is clear that in each transition the total exchange energy is conserved, whereas the magnetic energy changes by an amount $+2H$ or $-2H$. Hence it follows from detailed balancing that the ratio of the probabilities for a reaction $(l, -l')$ and the reverse reaction $(-l', l)$ is η^2, where $\eta \equiv e^{\beta H}$. Choosing an overall rate constant λ, equal for all transitions, we can write

$$\begin{aligned} w_{(l,-l')}(s'_N, s_N) &= \lambda \delta_{(l,-l')}(s'_N, s_N), \\ w_{(-l',l)}(s'_N, s_N) &= \lambda \eta^{-1} \delta_{(-l',l)}(s'_N, s_N) \end{aligned} \tag{2.12}$$

Equivalently and more explicitly we have entirely in terms of the microscopic variables s_N

$$\begin{aligned} w(s'_N, s_N) = \lambda \sum_{j=2}^{N-1} \Big\{ &[\eta \delta(s_j - s'_j - 2) + \eta^{-1} \delta(s_j - s'_j + 2)] \\ &\times \delta(s_{j-1} + s_{j+1}) \prod_{\substack{i=1 \\ i \neq j}}^{N} \delta(s_i - s'_i) \Big\}, \end{aligned} \tag{2.13}$$

where δ is the Kronecker delta. Substitution of (2.13) into (2.7) or of (2.12) into (2.10) then determines the master equation at the microscopic level. This master equation defines the kinetics of the system and will be the starting point for further analysis. For comparison with previous work[14-16]) we give the corresponding master operator in terms of Pauli spin operators,

$$w = \tfrac{1}{4}\lambda \sum_{j=2}^{N-1} (\sigma_j^z - 1)(1 - \sigma_{j-1}^z \sigma_{j+1}^z)(\cosh \beta H - \sigma_j^x \sinh \beta H). \tag{2.14}$$

One point needs some attention. The master equation conserves the total number of clusters, or, equivalently, the total exchange $-J \sum_{j=1}^{N-1} s_j s_{j+1}$. Hence the space of configurations s_N decomposes kinetically into subspaces characterized by their total cluster number, which we shall denote by $2R$. Within a given sub-

space each initial distribution $p(s_N; 0)$ tends to a uniquely determined equilibrium distribution, which is canonical with respect to the magnetic energy, but microcanonical with respect to the exchange energy, which by (2.5) equals $(N - 4R)J$. The relation between the temperature T, the magnetic field H, and the cluster density ϱ is given by (3.6). We shall henceforth consider a subspace with fixed R and N, and refer to it as the density ensemble. The notations $\langle\cdots\rangle_{NR}$ and $\langle\cdots\rangle_t$ will indicate equilibrium and time-dependent averages, respectively, in this ensemble. The thermodynamic limit will be denoted by "$\lim_{N,R\to\infty}$", where it is implied that the ratio $R/N \equiv \varrho$ remains fixed.

Since the master equation (2.10), (2.12) cannot be solved exactly, one has to look for approximations. In a recent paper[16] Felderhof has shown that for certain linear chains the master equation (2.7) can, in an approximate way, be reduced to a coarse-grained master equation for the cluster occupation numbers,

$$\frac{\partial P(\boldsymbol{n}; t)}{\partial t} = \sum_{\boldsymbol{n}'} [W(\boldsymbol{n}, \boldsymbol{n}') P(\boldsymbol{n}'; t) - W(\boldsymbol{n}', \boldsymbol{n}) P(\boldsymbol{n}; t)], \tag{2.15}$$

or, in vector notation, $\partial P/\partial t = WP$. Felderhof's derivation of (2.15) is based on a "stosszahlansatz" for the different types of clusters. It is general and requires only that the kinetics of a binary system can be expressed in terms of "reactions" between clusters. The coarse-grained transition probabilities $W(\boldsymbol{n}', \boldsymbol{n})$ are obtained by averaging $w(s'_N, s_N)$ over all possible configurations s_N in the initial state $\boldsymbol{n}$, and summing over all possible configurations s'_N in the final state $\boldsymbol{n}'$. We shall again indicate the type of reaction and write $W(\boldsymbol{n}', \boldsymbol{n}) = \sum_r W_r(\boldsymbol{n}', \boldsymbol{n})$. The actual calculation[17]) of $W_{(k,k')}(n', n)$ involves only simple combinatorics, such as counting the number of ways in which an adjacent pair of a k-cluster and a k'-cluster can occur in a configuration characterized by the occupation numbers $\boldsymbol{n}$. We immediately give the result.

$$\begin{aligned} W_{(l,-l')}(\boldsymbol{n}', \boldsymbol{n}) &= v n_l n_{-(l'+1)} R^{-1} \delta_{(l,-l')}(\boldsymbol{n}', \boldsymbol{n}), \\ W_{(-l',l)}(\boldsymbol{n}', \boldsymbol{n}) &= v^{-1} n_{-l'} n_{l'+1} R^{-1} \delta_{(-l',l)}(\boldsymbol{n}', \boldsymbol{n}), \end{aligned} \tag{2.16}$$

in which $\delta_r(\boldsymbol{n}', \boldsymbol{n})$ is unity if $\boldsymbol{n}$ can transform into $\boldsymbol{n}'$ by a reaction of type r, and is zero otherwise. Eqs. (2.15) and (2.16) define our new approximate master equation. The analysis of this equation is continued in section 4.

3. *Some equilibrium properties.* In this section we collect some equilibrium properties of the spin chain that will be needed in the sequel. For the canonical partition function we find by the transfer-matrix method

$$Z_N = \sum_{s_N} e^{-\beta\varepsilon(s_N)} = C_0 z_0^{-N} + C_1 z_1^{-N}, \tag{3.1}$$

in which C_0 and C_1 are independent of N, and

$$z_{0,1} = \tfrac{1}{2}\{u^2 - u^{-2})^{-1} \times \{u(v + v^{-1}) \mp [u^2(v + v^{-1})^2 - 4(u^2 - u^{-2})]^{\frac{1}{2}}\}, \tag{3.2}$$

with $u \equiv e^{\beta J}$ and $v \equiv e^{\beta H}$. Hence one finds for the free energy ϕ per unit length in the thermodynamical limit

$$\phi \equiv -\beta^{-1} \lim_{N\to\infty} N^{-1} \ln Z_N = \beta^{-1} \ln z_0 \tag{3.3}$$

The Boltzmann factors for clusters of length l are

$$e^{-\beta\varepsilon_l} = u^{-2}(uv)^l, \qquad e^{-\beta\varepsilon_{-l}} = u^{-2}(ut^{-1})^l. \tag{3.4}$$

Using these expressions in the cluster-generating function method[21]) one can derive[19]) the average equilibrium number densities of clusters of a given type and length. Denoting the canonical average by $\langle \cdots \rangle_N$ we find in the thermodynamical limit

$$\begin{aligned} \varrho_l^{eq} &\equiv \lim_{N\to\infty} N^{-1} \langle n_l \rangle_N = \varrho^{eq}(1 - yv)(yv)^{l-1}, \\ \varrho_{-l}^{eq} &\equiv \lim_{N\to\infty} N^{-1} \langle n_{-l} \rangle_N = \varrho^{eq}(1 - yv^{-1})(yv^{-1})^{l-1}, \end{aligned} \tag{3.5}$$

in which $y \equiv uz_0$ and where the average total equilibrium cluster density ϱ^{eq} is given by

$$\varrho^{eq} \equiv \sum_{l=1}^{\infty} \varrho_l^{eq} = \sum_{l=1}^{\infty} \varrho_{-l}^{eq} = [(1 - yv)^{-1} + (1 - yv^{-1})^{-1}]^{-1} \tag{3.6}$$

In the special case of $H = 0$ this reduces to

$$\varrho^{eq} = \tfrac{1}{2}(1 + u^2)^{-1}. \tag{3.7}$$

The expressions (3.5)–(3.7) are also valid in the density ensemble $\langle \cdots \rangle_{NR}$ if one takes $\lim_{N,R\to\infty}(N/R) \equiv \varrho = \varrho^{eq}$. We define average cluster fractions $f_k^{eq} \equiv \varrho_k^{eq}/\varrho^{eq}$ and obtain from (3.5) and (3.6) the average length of the up- and down-clusters,

$$l_\pm \equiv \sum_{l=1}^{\infty} l f_{\pm l}^{eq} = (1 - yv^{\pm 1})^{-1} \tag{3.8}$$

and the fluctuations in these quantities,

$$(\Delta l_\pm)^2 \equiv \sum_{l=1}^{\infty} (l - l_\pm)^2 f_{\pm l}^{eq} = yv^{\pm 1}(1 - yv^{\pm 1})^{-2}. \tag{3.9}$$

We shall also be interested in correlations between cluster occupation numbers. In the density ensemble these are different from those in the canonical ensemble. We define

$$G^{\mathrm{eq}}_{kk'} = \lim_{N\to\infty} N^{-1} \langle \Delta n_k \, \Delta n_{k'} \rangle_{NR}, \tag{3.10}$$

$$\Delta n_k = n_k - \langle n_k \rangle_{NR}. \tag{3.11}$$

The partition function in the density ensemble is

$$Z_{NR} = \sum_{\boldsymbol{n}}{}' \, \Omega(\boldsymbol{n}) \, \mathrm{e}^{-\beta E(\boldsymbol{n})}, \tag{3.12}$$

with $E(\boldsymbol{n})$ given by (2.5) and $\Omega(\boldsymbol{n})$ by (2.3). The prime on the summation sign indicates that all sets $\boldsymbol{n}$ in the sum should satisfy the three constraints

$$\sum_{l=1}^{\infty} n_l = \sum_{l=1}^{\infty} n_{-l} = R, \qquad \sum_{l=1}^{\infty} l\,(n_l - n_{-l}) = N. \tag{3.13}$$

For short we shall write these relations as $\boldsymbol{C}_1 \cdot \boldsymbol{n} = \boldsymbol{C}_2 \cdot \boldsymbol{n} = R$ and $\boldsymbol{C}_3 \cdot \boldsymbol{n} = N$, respectively. Putting $\boldsymbol{r} \equiv N^{-1}(\boldsymbol{n} - \langle \boldsymbol{n} \rangle_{NR})$ we find from (3.12)

$$Z_{NR} = \sum_{\boldsymbol{r}}{}' \, \mathrm{e}^{-\beta\Phi(N\boldsymbol{r})}, \tag{3.14}$$

$$G^{\mathrm{eq}}_{kk'} = \lim_{N,\,R\to\infty} Z_{NR}^{-1} N \sum_{\boldsymbol{r}} r_k r_{k'} \, \mathrm{e}^{-\beta\Phi(N\boldsymbol{r})}, \tag{3.15}$$

with the free energy $\Phi(N\boldsymbol{r})$ given by

$$-\beta\Phi(N\boldsymbol{r}) = -\beta E(N\boldsymbol{r}) + \ln \Omega(N\boldsymbol{r}). \tag{3.16}$$

Using (2.3) and (2.5) we can expand the free energy in powers of N. Keeping only the highest power and making $\boldsymbol{r}$ a continuous variable we obtain

$$G^{\mathrm{eq}}_{kk'} = \lim_{N,\,R\to\infty} \left[N \int r_k r_{k'} \exp\left(-\tfrac{1}{2} N\beta \boldsymbol{r}\boldsymbol{r} : \frac{\partial^2 \Phi}{\partial \boldsymbol{r}\,\partial \boldsymbol{r}} \right) \prod_{j=1}^{3} \delta(\boldsymbol{C}_j \cdot \boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \right.$$
$$\left. \times \left(\int \exp\left(-\tfrac{1}{2} N\beta \boldsymbol{r}\boldsymbol{r} : \frac{\partial^2 \Phi}{\partial \boldsymbol{r}\,\partial \boldsymbol{r}} \right) \prod_{j=1}^{3} \delta(\boldsymbol{C}_j \cdot \boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \right)^{-1} \right], \tag{3.17}$$

in which

$$\partial^2\Phi/\partial r_k \, \partial r_{k'} = \delta_{kk'} N \beta^{-1} \varrho_k^{\mathrm{eq}}. \tag{3.18}$$

The integrals in (3.17) may be carried out with the aid of the Fourier representation of the delta function, and one obtains

$$G^{eq}_{kk'} = \varrho^{eq}_k \delta_{kk'} - \varrho^{eq}_k \varrho^{eq}_{k'} \sum_{j=1}^{3} C_j^{-2} C_{jk} C_{jk'}, \tag{3.19}$$

$$C_j^2 = \sum_k \varrho^{eq}_k C^2_{jk}. \tag{3.20}$$

Relation (3.19) shows that the off-diagonal elements in the correlation matrix G^{eq} are entirely due to the three constraints C_j on the ensemble of statistically independent clusters.

It is now easy to find the expression for the fluctuations of the total magnetization in the density ensemble. Using (3.19), (3.5) and (3.9) we obtain readily

$$\lim_{N,R\to\infty} N^{-1} \langle \delta M^2 \rangle_{NR} = \sum_{k,k'} kk' G_{kk'} = 4\varrho_0 M_1^2 M^2 (M_2^2 + M^2)^{-1}$$

$$= \frac{4y(1-yt)(1-vt^{-1})}{[(1-vt)+(1-yt^{-1})][v^{-1}(1-vy)^2 + t(1-yv^{-1})^2]}. \tag{3.21}$$

An entirely different way leading to (3.19) is to use Felderhof's general expressions for the correlations between clusters in a canonical ensemble[16]), and to perform an inverse Laplace transformation with respect to the variable βH. The partition function Z_{NR} can similarly be obtained by Laplace-inverting the canonical partition function Z_N. Finally, we note that the fluctuations in the magnetization may also be obtained thermodynamically. We have

$$N^{-1} \langle M \rangle_{NR} = \beta^{-1} N^{-1} \left(\frac{\partial \ln Z_{NR}}{\partial H} \right)_\varrho, \tag{3.22}$$

whence

$$\chi_\varrho \equiv \lim_{N,R\to\infty} N^{-1} \left(\frac{\partial \langle M \rangle_{NR}}{\partial H} \right)_\varrho = \beta^{-1} \lim_{N,R\to\infty} N^{-1} \left(\frac{\partial^2 \ln Z_{NR}}{\partial H^2} \right)_\varrho$$

$$= \beta \lim_{N,R\to\infty} N^{-1} \langle \delta M^2 \rangle_{NR}. \tag{3.23}$$

Here χ_ϱ is the magnetic susceptibility at constant cluster density.

4. *The moment equations.* We turn again to the coarse-grained master equation (2.15) with transition probabilities (2.16). We shall not try to solve this equation, but rather study the equations for the first moments $N^{-1} \langle n_k \rangle_t$ which may be derived from it. With the aid of Van Kampen's parameter expansion[22, 23]) a closed set of moment equations may be obtained[19]), valid for distributions $P(\boldsymbol{n}, t)$ which

become infinitely sharp in the variables $N^{-1}\boldsymbol{n}$ as $N \to \infty$. In this limit the moments are just the time-dependent cluster densities ϱ_k, defined as

$$\varrho_k = \lim_{N\to\infty} N^{-1} \langle n_k \rangle_t, \qquad k = \pm 1, \pm 2, \ldots . \tag{4.1}$$

Since the total cluster density is conserved we must at all times have

$$\sum_{l=1}^{\infty} \varrho_l = \sum_{l=1}^{\infty} \varrho_{-l} = \varrho, \tag{4.2}$$

where ϱ is a time-independent parameter.

Following Van Kampen's procedure we multiply (2.15) by n_k, take the ensemble average, use (2.16), and expand in powers of N^{-1}, thus obtaining to lowest order in N^{-1} the equations for the time-dependent cluster fractions $f_k \equiv \varrho_k/\varrho$. The calculation is straightforward and we find

$$\begin{aligned} \frac{\partial f_l}{\partial t} &= \sum_{l'=1}^{\infty} [v f_{-(l'+1)}(f_{l-1} - f_l) - v^{-1} f_{-l'}(f_l - f_{l+1})], \\ \frac{\partial f_{-l}}{\partial t} &= \sum_{l'=1}^{\infty} [v^{-1} f_{l'+1}(f_{-(l-1)} - f_{-l}) - v f_{l'}(f_{-l} - f_{-(l+1)})], \\ & \qquad\qquad l = 2, 3, \ldots \end{aligned} \tag{4.3}$$

and for $l = 1$,

$$\begin{aligned} \frac{\partial f_1}{\partial t} &= \sum_{l'=1}^{\infty} (-v f_{-(l'+1)} f_1 + v^{-1} f_{-l'} f_2), \\ \frac{\partial f_{-1}}{\partial t} &= \sum_{l'=1}^{\infty} (-v^{-1} f_{l'+1} f_{-1} + v f_{l'} f_{-2}). \end{aligned} \tag{4.4}$$

These equations resemble the rate equations which one encounters in chemical kinetics for reacting species of molecules. The reactions corresponding to the individual terms on the right-hand side are easily identified.

It will be convenient to consider a finite system of equations rather than the infinite system (4.3)–(4.4). Therefore we shall limit ourselves to initial states in which no clusters occur with lengths greater than a large cutoff length L, and exclude in (4.3) all reactions involving clusters of length exceeding L. This yields the modified rate equations

$$\begin{aligned} \frac{\partial f_l}{\partial t} &= \sum_{l'=1}^{L-1} [v f_{-(l'+1)}(f_{l-1} - f_l) - v^{-1} f_{-l'}(f_l - f_{l+1})], \\ \frac{\partial f_{-l}}{\partial t} &= \sum_{l'=1}^{L-1} [v^{-1} f_{l'+1}(f_{-(l-1)} - f_{-l}) - v f_{l'}(f_{-l} - f_{-(l+1)})], \\ & \qquad\qquad l = 2, 3, \ldots, L-1 \end{aligned} \tag{4.5}$$

and the special cases

$$\frac{\partial f_1}{\partial t} = \sum_{l'=1}^{L-1} (-v f_{-(l'+1)} f_1 + v^{-1} f_{-l'} f_2),$$
$$\frac{\partial f_{-1}}{\partial t} = \sum_{l'=1}^{L-1} (-v^{-1} f_{l'+1} f_{-1} + v f_{l'} f_{-2}). \tag{4.6}$$

$$\frac{\partial f_L}{\partial t} = \sum_{l'=1}^{L-1} (v f_{-(l'+1)} f_{L-1} - v^{-1} f_{-l'} f_l),$$
$$\frac{\partial f_{-L}}{\partial t} = \sum_{l'=1}^{L-1} (v^{-1} f_{l'+1} f_{-(L-1)} - v f_{l'} f_{-L}). \tag{4.7}$$

We shall write $\boldsymbol{f} = (f_{-L}, f_{-(L-1)}, \ldots, f_{-1}, f_1, \ldots, f_L)$. It is easily verified that the rate equations (4.5)–(4.7) have the following properties. Let $\boldsymbol{f}(0)$ be an initial state satisfying the three conditions for being physical, *i.e.*

$$0 \leqslant f_k(0) \leqslant 1, \qquad k = \pm 1, \ldots, \pm L. \tag{4.8a}$$

$$\sum_{l=1}^{L} f_l(0) = \sum_{l=1}^{L} f_{-l}(0) = 1, \tag{4.8b}$$

$$\sum_{l=1}^{L} [f_l(0) + f_{-l}(0)] = 1/\varrho, \qquad 0 < \varrho \leqslant \tfrac{1}{2}. \tag{4.8c}$$

Then these conditions hold for all later times. Furthermore, as $t \to \infty$, $\bar{\boldsymbol{f}}(t)$ tends to an equilibrium value $\bar{\boldsymbol{f}}^{\mathrm{eq}}$ which is such that $\lim_{L\to\infty} \bar{\boldsymbol{f}}^{\mathrm{eq}} = \boldsymbol{f}^{\mathrm{eq}}$. By putting the right-hand sides of (4.5)–(4.7) equal to zero we find explicitly after some algebra

$$\bar{f}_l^{\mathrm{eq}} = (1 - \bar{y}_+)\, y_+^{l-1} \qquad l = 1, \ldots, L;$$
$$\bar{f}_{-l}^{\mathrm{eq}} = (1 - \bar{y}_-)\, y_-^{l-1}, \qquad l = 1, \ldots, L. \tag{4.9}$$

Here the four parameters $\bar{y}_\pm$ and $y_\pm$ satisfy the three relations

$$y_+ = v^2 y_- \tag{4.10}$$

and

$$\bar{y}_\pm = y_\pm (1 - y_\pm^{L-1})(1 - y_\pm^{L})^{-1}. \tag{4.11}$$

They are related to ϱ by

$$\frac{1}{\varrho} = \frac{1}{1 - y_+} + \frac{1}{1 - y_-} - L\left(\frac{y_+^L}{1 - y_+^L} + \frac{y_-^L}{1 - y_-^L}\right). \tag{4.12}$$

in which the last term vanishes for $L \to \infty$. Hence the equilibrium solution can be written entirely in terms of the two parameters v and ϱ.

In the sequel we shall make use of the three quantities e_+, e_- and y_0 defined by

$$e_\pm = \bar{y}_\pm / y_\pm = 1 - (1 - \bar{y}_\pm) y_\pm^L, \qquad y_0 = (y_+ y_-)^{\frac{1}{2}}. \tag{4.13}$$

Note that

$$\lim_{L\to\infty} \bar{y}_\pm = \lim_{L\to\infty} y_\pm = y v^{\pm 1}; \qquad \lim_{L\to\infty} e_\pm = 1, \qquad \lim_{L\to\infty} y_0 = y. \tag{4.14}$$

5. *The linearized moment equations.* We are still unable to solve the nonlinear equations (4.5) (4.7). However, close to equilibrium they may be linearized and the solution of these linearized equations is sufficient for the calculation of equilibrium time correlation functions[22, 23])

We define $\boldsymbol{g} = \bar{\boldsymbol{f}} - \bar{\boldsymbol{f}}^{\mathrm{eq}}$ and obtain

$$\frac{\partial \boldsymbol{g}}{\partial t} = A\boldsymbol{g}, \tag{5.1}$$

where A is a $2L \times 2L$ matrix. The indices k and k' of the matrix elements $A_{kk'}$ take the values $-L, -(L-1), \ldots, -1, 1, \ldots, L$. The relation between $\boldsymbol{g}$ and the cluster occupation numbers is easily found *via* the definitions of $\bar{\boldsymbol{f}}$ and $\boldsymbol{\rho}$. It reads

$$\lim_{L\to\infty} g_k = \lim_{N\to\infty} R^{-1} \langle \Delta n_k \rangle_t. \tag{5.2}$$

Using the relations (4.9) for $\bar{f}_k^{\mathrm{eq}}$ we find the following expressions for these matrix elements,

$$\begin{aligned} A_{l',l} = {} & \delta_{l,l'-1}(1 - \delta_{l',1}) v\bar{y}_- \\ & - \delta_{l,l'}[(1 - \delta_{l',1}) v^{-1} e_- + (1 - \delta_{l',L}) v\bar{y}_-] \\ & + \delta_{l,l'+1}(1 - \delta_{l',L}) v^{-1} e_-, \end{aligned} \tag{5.3a}$$

$$\begin{aligned} A_{-l',-l} = {} & \delta_{l,l'-1}(1 - \delta_{l',1}) v^{-1}\bar{y}_+ \\ & - \delta_{l,l'}[(1 - \delta_{l',1}) v e_+ + (1 - \delta_{l',L}) v^{-1} \bar{y}_+] \\ & + \delta_{l,l'+1}(1 - \delta_{l',L}) v e_+, \end{aligned} \tag{5.3b}$$

$$A_{l,-l'} = y_0 a_l a_{-l'} \bar{f}_l^{\mathrm{eq}}, \qquad A_{-l',l} = y_0 a_{-l'} a_l \bar{f}_{-l'}^{\mathrm{eq}}. \tag{5.4}$$

with

$$a_{\pm l} = y_\pm^{-1}(1 - \delta_{l,1}) - (1 - \delta_{l,L}). \tag{5.5}$$

In the next section we shall analyze the linear problem (5.1) in detail and calculate the relaxation time of the magnetization. In this section we mention only some general properties of A. First of all, its matrix elements satisfy the symmetry relation

$$A_{kk'} f_{k'}^{eq} = A_{k'k} f_k^{eq}. \tag{5.6}$$

This relation may be verified explicitly with the aid of (5.3)–(5.5). Within the framework of Felderhof's general treatment[17]) it may be shown to result directly from the detailed balance between forward and backward reactions in the original master equation. From (5.6) it follows that A can be symmetrized and hence that all its eigenvalues are real. We define the symmetrized operator A^s by

$$A^s = F^{-\frac{1}{2}} A F^{\frac{1}{2}}, \qquad F_{kk'} = \delta_{kk'} f_k^{eq} \tag{5.7}$$

A second property which may be verified directly and traced back to the master-equation properties of W is

$$\sum_k A_{kk'} = 0 \tag{5.8}$$

Combining (5.6) and (5.8) we can derive that all eigenvalues of A are non-positive[24]).

The conditions (4.8b) and (4.8c) imply that physical states $\boldsymbol{g}$ should always lie in the $(2L-3)$-dimensional subspace of $\boldsymbol{g}$ space determined by the relations

$$\sum_{l=1}^{L} g_l = \sum_{l=1}^{L} g_{-l} = 0, \qquad \sum_{l=1}^{L} l(g_l + g_{-l}) = 0. \tag{5.9a, b}$$

Using the vectors $\boldsymbol{C}_i$ of section 3 we have

$$\boldsymbol{C}_i \cdot \boldsymbol{g} = 0, \qquad i = 1, 2, 3, \tag{5.10}$$

where $g_k \equiv 0$ for $|k| \geqslant L+1$. These relations result from conservation of total number of up-clusters, total number of down-clusters, and total number of units in the chain, respectively. Hence A must have the three eigenvalues $\lambda_1 = \lambda_2 = \lambda_3 = 0$. It is easily verified that the corresponding orthonormalized right hand eigenvectors $\boldsymbol{g}^1$, $\boldsymbol{g}^2$, and $\boldsymbol{g}^3$ of A may be chosen as

$$\begin{aligned} g_l^1 &= f_l^{eq}, \qquad g_l^2 = 0, \qquad g_l^3 = C(l - l_+) f_l^{eq}, \\ g_{-l}^1 &= 0, \qquad g_{-l}^2 = f_{-l}^{eq}, \qquad g_{-l}^3 = C(l - l_-) f_{-l}^{eq}, \end{aligned} \tag{5.11}$$

where $C \equiv (\Delta l_+)^2 + (\Delta l_-)^2$ and $l_\pm$ and $\Delta l_\pm$ are defined by (3.8) and (3.9) with f_k^{eq} instead of f_k^{eq}, and the summations running from 1 to L.

Let g^i for $i = 4, 5, \ldots, 2L$, denote the remaining eigenvectors of A, and $-\lambda_i$ their eigenvalues. Then the time evolution of an arbitrary initial state $g(0)$ in the physical subspace is in linear approximation given by

$$g(t) = \sum_{i=4}^{2L} [g^i \cdot F^{-1} \cdot g(0)]\, g^i\, e^{-\lambda_i t}. \tag{5.12}$$

The equilibrium time correlation for the cluster occupation numbers is defined as

$$\mathsf{G}(t) \equiv \lim_{N,\, R\to\infty} N^{-1} \langle \Delta \boldsymbol{n}(0)\, \Delta \boldsymbol{n}(t)\rangle_{NR} \equiv \lim_{N,\, R\to\infty} N^{-1} \langle \Delta \boldsymbol{n}\, \langle \Delta \boldsymbol{n}\rangle_t\rangle_{NR}, \tag{5.13}$$

in which $\langle \Delta \boldsymbol{n}\rangle_t$ denotes the average at time t for an initial state with occupation numbers $\langle \boldsymbol{n}\rangle_{NR} + \Delta \boldsymbol{n}$. We find from (5.12) with the use of (5.2)

$$\lim_{N\to\infty} R^{-1} \langle \Delta \boldsymbol{n}\rangle_t = \lim_{L\to\infty} \lim_{N\to\infty} R^{-1} \sum_{i=4}^{2L} (g^i \cdot F^{-1} \cdot \Delta \boldsymbol{n})\, g^i\, e^{-\lambda_i t}. \tag{5.14}$$

It follows from Van Kampen's general theory[22, 23]) that in equilibrium time correlation functions the use of the linear approximation in (5.12) is strictly justified. Inserting (5.14) in (5.13) yields

$$G_{kk'}(t) = \varrho \lim_{L\to\infty} \sum_{i=4}^{2L} \left(\sum_{k''} g^i_{k''} (f^{eq}_{k''})^{-1}\, G^{eq}_{k''k}\right) g^i_{k'}\, e^{-\lambda_i t}. \tag{5.15}$$

Substituting expression (3.19) for $G^{eq}_{k''k}$ and using (5.10) we obtain

$$G_{kk}(t) = \varrho \lim_{L\to\infty} \sum_{i=4}^{2L} g^i_k g^i_{k'}\, e^{-\lambda_i t}. \tag{5.16}$$

For the equilibrium time correlation function of the total magnetization we have by (2.6) and (5.16), and using (5.9b)

$$\lim_{N,\, R\to\infty} N^{-1} \langle \delta M(t)\, \delta M\rangle_{NR}$$
$$= 2\varrho \lim_{L\to\infty} \sum_{i=4}^{2L} \left[\left(\sum_{l=1}^{L} l g^i_l\right)^2 + \left(\sum_{l=1}^{L} l g^i_{-l}\right)^2\right] e^{-\lambda_i t}. \tag{5.17}$$

A characteristic time τ for the decay of fluctuations in the magnetization may be defined by

$$\tau = \lim_{N,\, R\to\infty} \langle \delta M^2\rangle^{-1}_{NR} \int_0^\infty \langle \delta M(t)\, \delta M\rangle_{NR}\, dt. \tag{5.18}$$

In the next section we shall calculate this quantity as a function of the two independent parameters of the model.

6. *Calculation of the relaxation time of the magnetization.* The purpose of this section is to calculate the relaxation time τ as defined by (5.18) and (5.17). To this end we study the symmetrized matrix $A^s = F^{-\frac{1}{2}} A F^{\frac{1}{2}}$ in greater detail.

First we define four $L \times L$ submatrices by

$$A^s = \begin{pmatrix} A^- & A^{+-} \\ A^{-+} & A^+ \end{pmatrix} \tag{6.1}$$

We shall denote the matrix elements of the submatrices by the same indices as the corresponding matrix elements of A^s; thus $A^s_{-L,-L'} = A^-_{-L,-L'}$, $A^s_{L,-L'} = A^{+-}_{L,-L'}$, *etc.* Combining (5.3), (5.4), (5.7) and (3.5) we find

$$A^- = \begin{bmatrix} -c_{-L} & d_- & & & & & \\ d_- & -c_- & d & & & 0 & \\ & d_- & -c_- & d_- & & & \\ & & & \ddots & \ddots & & \\ & & & d_- & -c_- & d_- & \\ & 0 & & & d_- & -c_- & d_- \\ & & & & & d_- & -c_{-L} \end{bmatrix}, \tag{6.2}$$

$$A^+ = \begin{bmatrix} -c_L & d_+ & & & & & \\ d & -c_+ & d_- & & & 0 & \\ & d_+ & -c_- & d_+ & & & \\ & & & & & & \\ & & & d_+ & -c_- & d_+ & \\ & 0 & & & d_- & -c_+ & d_+ \\ & & & & & d_+ & -c_L \end{bmatrix}, \tag{6.3}$$

$$A^{+-}_{L,-L'} = A^{-+}_{-L',L} = y_0 a_L a_{L'} (f^{eq}_L f^{eq}_{-L'})^{\frac{1}{2}}, \tag{6.4}$$

in which

$$d_{\pm} = e_{\mp} v^{\mp 1} y_{\pm}^{\frac{1}{2}}, \qquad c_{\pm 1} = e_{\pm} v^{\pm 1} y_{\pm},$$
$$c_{\pm} = e_{\mp} v^{\mp 1} (y_{\pm} + 1), \qquad c_{\pm M} = c_{\pm} - c_{\pm 1}, \tag{6.5}$$

and a_l and $f_{\pm}^{eq}$ are given by (5.5) and (4.9), respectively. With the aid of (6.5) and the appropriate formulas of the foregoing sections all matrix elements can be expressed in terms of two independent parameters, *e.g.*, in y_+ and y_-, in y_0 (or ϱ) and v, or in T and H.

The matrix A^+ is tridiagonal. In a mechanical picture it describes the problem of a chain of L particles, each bound in a harmonic potential of strength $c_+ - 2d_+$, and bound to its two nearest neighbours by another harmonic force of strength d_+. The end particles behave slightly differently. A^- describes a second such chain with force constants $c_- - 2d_-$ and d_-, respectively. In the case $H = 0$ we have the symmetry property $A^+_{l,l'} = A^-_{-l,-l'}$. The symmetrically conjugate matrices A^{+-} and A^{-+} represent an interaction between any two particles not in the same chain. The factorization of the matrix elements $A^{\mp\pm}_{kk'}$ into a row- and a column-dependent part will be of use in the sequel.

We shall denote the normalized eigenvectors of A^+ and A^- by $X^r = (X_1^r, X_2^r, \ldots, X_L^r)$ and $X^{-r} = (X_{-1}^{-r}, X_{-2}^{-r}, \ldots, X_{-L}^{-r})$, respectively, where $r = 1, 2, \ldots, L$, and the corresponding eigenvalues by $-\varkappa_{\pm r}$. One finds easily

$$X_{\pm l}^{\pm r} = (2e_{\mp}^{-1} v^{\pm 1} \varkappa_{\pm r} L)^{\frac{1}{2}} [\sin q_r \cos lq_r + (y_{\pm}^{\frac{1}{2}} - \cos q_r) \sin lq_r],$$
$$r = 2, 3, \ldots, L, \tag{6.6}$$

where $q_r = \pi (r - 1)/L$ and $\varkappa_{\pm r} = c_{\pm} - 2d_{\pm} \cos q_r$. For $r = 1$ we have

$$X_{\pm l}^{\pm 1} = (f_{\pm}^{eq})^{\frac{1}{2}}, \qquad \varkappa_{\pm 1} = 0. \tag{6.7}$$

Hence A^+ and A^- each have a nondegenerate spectrum which, apart from the isolated eigenvalue zero, forms a quasicontinuum on the negative real axis. The two quasicontinua coincide for $H = 0$, for small H they overlap and for larger H they become completely separated.

We can transform A^+ and A^- to diagonal form,

$$(X^{\pm})^{-1} A^{\pm} X^{\pm} = K^{\pm}, \tag{6.8}$$

where X^+ and X^- are the matrices with column vectors X^{+r} and X^{-r}, respectively, and $K^{\pm}_{\pm l, \pm l'} = -\varkappa_{\pm l} \delta_{ll'}$. Defining

$$X = \begin{pmatrix} X^- & 0 \\ 0 & X^+ \end{pmatrix}, \qquad K = \begin{pmatrix} K^- & 0 \\ 0 & K^+ \end{pmatrix}, \qquad V = \begin{pmatrix} 0 & V^{-+} \\ V^{+-} & 0 \end{pmatrix}, \tag{6.9}$$

we obtain

$$X^{-1}A^{s}X = K + V. \tag{6.10}$$

Using (6.4) one finds easily

$$V_{r}^{+-}{}_{-r'} = V_{-r',r}^{-+} = \lambda_{r}V_{r}\delta_{-r'}, \tag{6.11}$$

$$V_{\pm r} = \sum_{l=1}^{\infty} a_{\pm l}(f_{\pm l}^{eq})^{\frac{1}{2}} X_{\pm l}^{\pm r}, \qquad r = 1, \ldots, L. \tag{6.12}$$

Hence the matrix elements of V^{+-} and V^{-+} have the same factorization property as those of A^{+-} and A^{-+}. Explicit calculation with the aid of (6.12), (6.7), (5.5) and the orthogonality property $X^{\pm l} \cdot X^{\pm l'} = \delta_{ll'}$, shows that

$$V_{\pm 1} = 0, \tag{6.13a}$$

$$V_{-r} = -\gamma_{2}^{-1}(f_{-1}^{eq})^{\frac{1}{2}} X_{-1}^{-r} + (f_{2L}^{eq})^{\frac{1}{2}} X_{2L}^{-r} \tag{6.13b}$$

Let $F^{\frac{1}{2}}g^{l}$ be an eigenvector of A^{s} with eigenvalue $-\lambda_{l}$, normalized such that

$$g^{l} \cdot F \cdot g^{l} = \sum_{k} f_{k}^{eq}(g_{k}^{l})^{2} = 1, \qquad l = 1, \ldots, 2L \tag{6.14}$$

We find from (6.10) that the transformed eigenvector

$$\xi^{l} \equiv X^{-1}F^{-\frac{1}{2}}g^{l}, \tag{6.15}$$

is a solution of the eigenvalue equation

$$(K + V)\xi = -\lambda\xi, \tag{6.16}$$

for $\lambda = \lambda_{l}$. We analyze this equation by somewhat generalizing a method used by Van Kampen[25]. From (6.16) we find the equations for the rth and $-r$th components,

$$\begin{aligned} -\varkappa_{r}\xi_{r} + \nu_{0}V_{r}\sum_{r'=2}^{L} V_{-r'}\xi_{-r'} &= -\lambda\xi_{r}, \\ -\varkappa_{-r}\xi_{-r} + \nu_{0}V_{-r}\sum_{r'=2}^{L} V_{r'}\xi_{r'} &= -\lambda\xi_{-r}, \end{aligned} \tag{6.17}$$

where we have used that $V_{\pm 1} = 0$. We shall abbreviate

$$\lambda_{\pm r} = \sum_{r'=2}^{L} V_{\pm r'}\xi_{\pm r'}. \tag{6.18a, b}$$

Putting $r = 1$ in (6.17) and using $V_{\pm 1} = \varkappa_{\pm 1} = 0$ shows that $\xi^i_{+1} = \xi^i_{-1} = 0$ for all eigenvectors unless $\lambda_i = 0$. This confirms the existence of at least two zero eigenvalues. From (6.17) we have for $r = 2, \ldots, L$,

$$\xi_r = -\frac{y_0 V_r \eta_-}{\lambda - \varkappa_r}, \tag{6.19a}$$

$$\xi_{-r} = -\frac{y_0 V_{-r} \eta_+}{\lambda - \varkappa_{-r}}. \tag{6.19b}$$

Multiplying (6.19a) by V_r and (6.19b) by V_{-r}, summing both equations over $r = 2, \ldots, L$, and using (6.18) we obtain

$$\eta_+ + \eta_- F_+(\lambda) = 0, \qquad \eta_- + \eta_+ F_-(\lambda) = 0, \tag{6.20}$$

with

$$F_+(\lambda) = y_0 \sum_{r=2}^{L} \frac{V_r^2}{\lambda - \varkappa_r}, \qquad F_-(\lambda) = y_0 \sum_{r=2}^{L} \frac{V_{-r}^2}{\lambda - \varkappa_{-r}}. \tag{6.21}$$

In order that (6.20) have nonzero solutions η_+ and η_- we must require

$$D(\lambda) \equiv 1 - F_+(\lambda) F_-(\lambda) = 0, \tag{6.22}$$

which is the secular equation for the matrix A^s.

The qualitative behaviour of $D(\lambda)$ as a function of λ can be derived from the expressions (6.21) for $F_+(\lambda)$ and $F_-(\lambda)$. It is quite easy to sketch $D(\lambda) - 1$ for the two cases: (i) $H = 0$; (ii) $|H| \neq 0$ and large enough that $c_- - 2d_- > c_+ + 2d_+$. For $c_- - 2d_- < c_+ + 2d_+$ the graph depends sensitively on the precise value of H. In each case careful inspection shows that there are $2L - 2$ solutions $\lambda_3, \lambda_4, \ldots, \lambda_{2L}$, which are all different. Since we know that A^s has three eigenvalues 0, the lowest solution of $D(\lambda) = 0$ must be $\lambda = \lambda_3 > 0$. The bulk of the eigenvalues of A^s is distributed over two quasi-continua, *viz.*, $c_+ - 2d_+ < \lambda < c_+ + 2d_+$ and $c_- - 2d_- < \lambda < c_- + 2d_-$. In the limit $L \to \infty$ the zeros in these regions become dense and $D(\lambda)$ develops branch cuts. The quasicontinua coincide for $H = 0$, overlap for small $|H|$ and are completely separated for larger $|H|$. The condition for separation is $c_+ - 2d_+ > c_- + 2d_-$ which by (6.5) and the definitions of v and y reduces to $|H| > k_B T \ln 3$. When $|H|$ is larger than this value, there is a clear distinction between long and short relaxation times. If one calculates the decay modes $F^{\frac{1}{2}} g^i$ in the way indicated below, one finds that the short relaxation times correspond to decay amplitudes $(f_k^{eq})^{-\frac{1}{2}} g_k^i$ with a wave-like k dependence, oscillating for $k < 0$ and damped as k grows in the positive direction. The decay modes with the long relaxation times have an oscillating

part for $k > 0$ and a damped part for $k < 0$. Hence for $|H| > k_B T$ in 3 the systems of up-clusters and of down-clusters decay to equilibrium on different time scales. For small $|H|$ there are decay modes with amplitudes oscillating in both k directions. Finally, there is a region of the TH plane where the maximum eigenvalue λ_{2L} is isolated from the continuum; it then corresponds to a "bound state" with very short relaxation time and amplitude $(\bar{h}_k^{eq})^{-1} g_k^+$ decaying in both k directions.

Let λ_i be a solution of (6.22) and let η_i^l be defined by (6.18) with $\xi_{\pm r} = \xi_{\pm r}^l$. Then in view of (6.20)

$$\eta_{\pm}^l = -F_{\pm}(\lambda_l)\,\xi_{\pm}^l \tag{6.23}$$

The normalization (6.14) and the unitarity of Λ imply for ξ^l the normalization

$$\sum_{r=1}^{L} \xi_r^{l\,2} + \sum_{r=1}^{L} |\xi_{-r}^l|^2 = 1. \tag{6.24}$$

Substituting in (6.24) the expressions (6.19a), (6.19b) for ξ_r^l and ξ_{-r}^l, and using (6.21), (6.22) and (6.23) we find expressions for $\eta_{\pm}^l$ in terms of $F_{\pm}(\lambda)$ namely

$$(\eta_{\pm}^l)^2 = \frac{F_{\pm}(\lambda_l)}{\lambda_l D'(\lambda_l)}, \tag{6.25}$$

where the prime denotes differentiation with respect to λ. From (6.19a), (6.19b) and (6.25) we finally have

$$(\xi_r^l)^2 = \frac{\lambda_l F_{\pm}'(\lambda_l)}{(\lambda_l + 1)^r} \frac{F_{\pm}(\lambda_l)}{D'(\lambda_l)}. \tag{6.26}$$

This relation will be needed in the sequel. Moreover, by inserting it into (6.15) and applying the operator Λ on both sides one obtains an expression for the decay modes $F^{\pm} g^{\pm}$. It contains a summation over r which for $L \to \infty$ can be carried out explicitly by using (6.13b) and (6.6) and letting q_i become a continuous variable.

We now turn to the relaxation of the magnetization. From (5.17) we have for the unnormalized relaxation time τ

$$\tau = \lim_{N,R\to\infty} N^{-1} \int_0^\infty \langle M(t)\, M \rangle_k \, dt$$

$$= 2\mu \lim_{L\to\infty} \sum_{l=1}^{2L} \lambda_l^{-1} \left[\left(\sum_{r=1}^{L} \xi_r^l \right)^2 + \left(\sum_{r=1}^{L} \xi_{-r}^l \right)^2 \right], \tag{6.27}$$

Transformation (6.15) can be used to express the components of g^t in those of ξ^t, which can subsequently be eliminated by (6.26). We obtain

$$\bar{\tau} = 2\varrho \lim_{L\to\infty} \sum_{i=4}^{2L} \lambda_i^{-1} \left[\left(\sum_{r=1}^{L} M_r \xi_r^t\right)^2 + \left(\sum_{r=1}^{L} M_{-r} \xi_{-r}^t\right)^2\right]$$

$$= 2\varrho \lim_{L\to\infty} y_0 \sum_{i=4}^{2L} [\lambda_i D'(\lambda_i)]^{-1} [M_+^2(\lambda_i) F_-(\lambda_i) + M_-^2(\lambda_i) F_+(\lambda_i)], \tag{6.28}$$

where we have abbreviated

$$M_\pm(\lambda) = \sum_{r=2}^{L} M_{\pm r} V_{\pm r}/(\lambda - \varkappa_{\pm r}), \tag{6.29}$$

$$M_{\pm r} = \sum_{l=1}^{L} l(f_{\pm l}^{\mathrm{eq}})^{\frac{1}{2}} X_{\pm l}^{\pm r}. \tag{6.30}$$

Hence (6.28), together with (6.29), (6.30), (6.22) and (6.21) express $\bar{\tau}$ entirely in terms of the known matrix elements of X and V. Substituting the explicit expressions (6.6) for $X_{\pm l}^{\pm r}$ in (6.13b) and (6.30) we find

$$V_{\pm r} = -(2B_\pm e_\mp/y_\pm v^{\pm 1} \varkappa_{\pm r} L)^{\frac{1}{2}} [1 - (-1)^{r-1} y_\pm^{L/2}] \sin q_r \tag{6.31}$$

$$B_\pm = (1 - y_\pm)(1 - y_\pm^L)^{-1}, \tag{6.32}$$

$$M_{\pm r} = y_\pm e_\mp (v^{\pm 1} \varkappa_{\pm r})^{-1} V_{\pm r} \tag{6.33}$$

and by combining (6.33), (6.29) and (6.21),

$$M_\pm(\lambda) = (e_\mp/\lambda) [F_\pm(\lambda) - F_\pm(0)] \tag{6.34}$$

Relation (5.9b), which expresses conservation of total number of spins, may be subjected to the same transformations which produced (6.28) from (6.27). We find

$$M_+^2(\lambda_i) F_-(\lambda_i) = M_-^2(\lambda_i) F_+(\lambda_i). \tag{6.35}$$

Combining this with (6.34) and eliminating $F_-(\lambda_i)$ by (6.22) yields a quadratic equation for $F_+(\lambda_i)$ which can be satisfied only if all its coefficients vanish. This condition gives

$$F_\pm(0) = -e_\pm/e_\mp. \tag{6.36}$$

Upon inserting (6.34) in (6.28) and using (6.22), (6.25), and (6.36) we arrive at an expression for $\bar{\tau}$ entirely in terms of the functions $F_\pm(\lambda)$.

$$\bar{\tau} = 4\varrho \lim_{L\to\infty} y_0 \sum_{i=4}^{2L} \frac{e_+^2 F_+(\lambda_i) + 2e_+e_- + e_-^2 F_-(\lambda_i)}{\lambda^3 D'(\lambda)}. \tag{6.37}$$

The next step is to eliminate the summation in (6.37). We define

$$P(\lambda) = [e_+^2 F_+(\lambda) + 2e_+e_- + e_-^2 F_-(\lambda)]\,[\lambda^3 D(\lambda)]^{-1} \tag{6.38}$$

From the properties of $F_+(\lambda)$ and $F_-(\lambda)$ it is clear that owing to $D(\lambda_i) \equiv 1 - F_+(\lambda_i) \times F_-(\lambda_i) = 0$ the function $P(\lambda)$ has simple poles for $\lambda = \lambda_i$, $i = 4, 5, \ldots, 2L$. The terms in the summation (6.37) are easily seen to correspond to the residues for $\lambda_4, \lambda_5, \ldots, \lambda_{2L}$. For $\lambda = \lambda_3 = 0$ both $e_+^2 F_+(\lambda) + 2e_+e_- + e_-^2 F_-(\lambda)$ and $D(\lambda)$ have simple zeros and hence $P(\lambda)$ has a third-order pole due to the factor λ^{-3}. The poles in $F_+(\lambda)$ and $F_-(\lambda)$ for $\lambda = \varkappa_2, \varkappa_3, \ldots, \varkappa_L$ and $\lambda = \varkappa_{-2}, \varkappa_{-3}, \ldots, \varkappa_{-L}$, respectively, occur in the numerator as well as in the denominator; hence they cancel. Expression (6.37) can therefore be written as a contour integration around the poles $\lambda = \lambda_i$, $i = 4, 5, \ldots, 2L$, and the contour can subsequently be shifted to form a circle $\bigcirc$ around the only other pole, viz. the isolated one at $\lambda = \lambda_3 = 0$. We obtain

$$\bar{\tau} = (2\pi i)\,\varrho \lim_{L\to\infty} y_0 \oint_{\bigcirc} P(\lambda)\,d\lambda. \tag{6.39}$$

The normalization $\lim_{\lambda\to\infty} \langle \delta M^2 \rangle_{\lambda,P}$, given by (3.20), may alternatively be obtained by putting $t = 0$ in (5.17). Hence it can be expressed in $P(\lambda)$ in a similar way, and writing $\mathcal{P}(\lambda) = \lim_{L\to\infty} P(\lambda)$ we find

$$\tau = \bar{\tau} \lim_{\lambda\to\infty} \lambda^2 \langle \delta M^2 \rangle_{\lambda,P} = \oint \mathcal{P}(\lambda)\,d\lambda \Big/ \oint \mathcal{P}(\lambda)\,d\lambda. \tag{6.40}$$

Since $P(\lambda)$ is analytic in a region around the origin which remains finite as $L \to \infty$, we can expand

$$\mathcal{P}(\lambda) = p_{-3}\lambda^{-3} + p_{-2}\lambda^{-2} + p_{-1}\lambda^{-1} + \cdots. \tag{6.41}$$

Finally we obtain the simple expression

$$\tau = p_{-1}/p_{-2}, \tag{6.42}$$

by substituting (6.41) in (6.40) and performing the contour integrations.

In order to find the coefficients p_j, $j = -3, -2, -1, \ldots$, in (6.41) we have to evaluate $P(\lambda)$ in the limit of large L. In this limit we may pass from the discrete variable $\varkappa_r$

in (6.21) to a continuous variable $\varkappa$, and from summation to integration. We shall write $\mathscr{F}_{\pm}(\lambda) = \lim_{L\to\infty} F_{\pm}(\lambda)$ Using (6.31) and defining $\varkappa_0 = v^{-1}[1-(yv)^{\frac{1}{2}}]^2$ and $\varkappa_m = v^{-1}[1+(yv)^{\frac{1}{2}}]^2$ we find

$$\mathscr{F}_{+}(\lambda) = \frac{1-yv}{2\pi i v}\int_{\varkappa_0}^{\varkappa_m} \frac{[(\varkappa-\varkappa_0)(\varkappa_m-\varkappa)]^{\frac{1}{2}}}{\varkappa(\lambda-\varkappa)}\,d\varkappa$$

$$= \frac{1-yv}{2iv}\left(-\frac{(1-yv)}{v\lambda} + 1 + \frac{1}{\lambda}[(\lambda-\varkappa_0)(\lambda-\varkappa_m)]^{\frac{1}{2}}\right)$$

$$= -\left(1 + \frac{v\lambda}{(1-yv)^2} + \frac{(1+yv)\,v^2\lambda^2}{(1-yv)^4} + \frac{(1+3yv+y^2v^2)\,v^3\lambda^3}{(1-yv)^6} + \cdots\right). \tag{6.43}$$

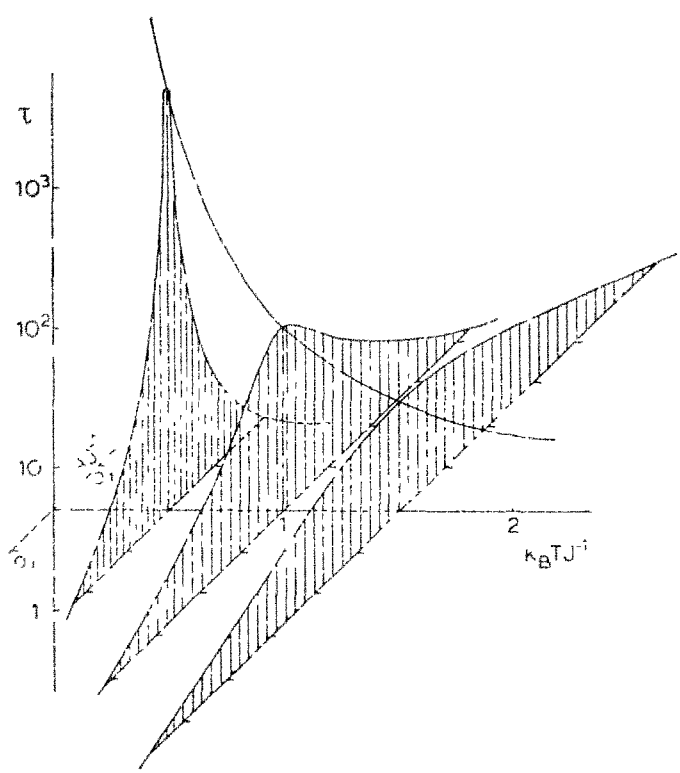

Fig. 1. Relaxation time τ of the magnetization as a function of temperature T and magnetic field H

The expression for $\mathscr{F}_-(\lambda)$ is obtained from (6.43) by changing v into v^{-1}. The series expansions about $\lambda = 0$ can then be inserted, for $L \to \infty$, into expression (6.38) for $P(\lambda)$. Using $\lim_{L\to\infty} e_\pm = 1$ we thus obtain the coefficients p_j in (6.41), hence the relaxation time (6.42). The calculation is straightforward and yields

$$\tau = \frac{1 + y(v + v^{-1})}{v^{-1}(1 - yv)^2 + v(1 - yv^{-1})^2}. \tag{6.44}$$

With the aid of the formulas of section 3 the relaxation time may be expressed entirely in terms of $u = e^{\beta J}$ and $v = e^{\beta H}$. Fig. 1 shows the relaxation time τ as a function of the magnetic field H at various temperatures T. With relation (6.44) we have achieved the purpose of this section. The next section will be devoted to a discussion of this result.

7. *Discussion of the relaxation time.* For the discussion of the relaxation time (6.44) two regions are of interest.

(i) $T > 0$ fixed and $H \approx 0$. For $H \approx 0$ the relaxation time τ exhibits a maximum which becomes more peaked as the temperature gets lower. This describes qualitatively the experimental findings mentioned in the introduction, and agrees with related theoretical results[4, 8]). At sufficiently low temperature the peak may become experimentally indistinguishable from a critical divergence, hence one is used to speaking of "critical slowing down" near $H = 0$. We shall also speak of "quasidivergence". Putting $\varepsilon = e^{-2\beta J}$ we may approximate the shape of the peak by

$$\tau \simeq \tfrac{3}{2}/[\varepsilon^2 + 2(\beta H)^2], \qquad |\beta H| \lesssim \varepsilon^{\frac{1}{2}} \ll 1. \tag{7.1}$$

In the same region of the TH plane we find the static susceptibility χ_0 in (3.23) with the aid of (3.21)

$$\chi_0 \simeq \frac{\beta\varepsilon^2}{[\varepsilon^2 + (\beta H)^2]^{\frac{1}{2}}\,[\varepsilon^2 + 2(\beta H)^2]}, \qquad |\beta H| \lesssim \varepsilon^{\frac{1}{2}} \ll 1. \tag{7.2}$$

Hence we have for the ratio χ_0/τ

$$\chi_0/\tau \simeq \tfrac{2}{3}\beta\varepsilon^2\,[\varepsilon^2 + (\beta H)^2]^{-\frac{1}{2}}, \qquad |\beta H| \lesssim \varepsilon^{\frac{1}{2}} \ll 1. \tag{7.3}$$

From this we see that at fixed temperature (fixed ε) the quantity χ_0/τ has a maximum for $H = 0$ and decreases rapidly for $|H| \gtrsim \beta^{-1}\varepsilon = 2J\varepsilon\,|\ln\varepsilon|^{-1}$.

(ii) $H = 0$ and $T \to 0$. At zero field the above formulas show that τ and χ_0 diverge as $\frac{3}{2}\varepsilon^{-2}$ and $(2J)^{-1}\varepsilon^{-1}\,|\ln\varepsilon|$, respectively, as T goes to zero, so that their ratio χ_0/τ vanishes as $\frac{1}{3}J^{-1}\varepsilon\,|\ln\varepsilon|$. This divergence in τ is the same as was found

in Glauber's model[1]) and its generalizations[15, 16]). For $H = 0$ Glauber's model reduces to ours if one imposes conservation of energy (or equivalently, of total number of clusters). Thus energy conservation appears not to affect the critical behaviour of the relaxation time along the line $H = 0$.

In both cases, (i) and (ii), the relaxation time τ exhibits a divergent (or quasidivergent) behaviour which is different from that of the static susceptibility, *i.e.*, τ behaves nonclassically. To illustrate this we write the phenomenological equation of motion for the magnetization in the form

$$\frac{\partial}{\partial t}(m_t - m_{eq}) = -L\left[\left(\frac{\partial g(m_t, \varrho)}{\partial m_t}\right)_\varrho - H\right]$$

$$\simeq -L\chi_\varrho^{-1}(m_t - m_{eq}) \qquad \text{near equilibrium.} \tag{7.4}$$

where m_t is the time-dependent magnetization, m_{eq} is its equilibrium value, $g(m, \varrho) \equiv -k_B T \lim_{N,R\to\infty} N^{-1} \ln Z_{NR} + mH$ is the Gibbs free energy, and L is an Onsager kinetic coefficient. Classically one assumes that the coefficient L is a constant independent of T and H, which implies that the relaxation time $\tau = \chi_\varrho L$ has the same singular behaviour as the thermodynamic quantity $\chi_\varrho = \beta \lim_{N,R\to\infty} N^{-1} \times \langle \delta M^2 \rangle_{NR}$. This assumption is evidently not valid here. The Onsager coefficient varies strongly as a function of both T and H. The effect of this on the relaxation time τ is termed "kinetic", as distinguished from the classical thermodynamic contribution. In case (ii) above, where $T \to 0$ at $H = 0$, the coefficient L vanishes, thus implying a kinetic critical slowing down. In case (i), where H varies at fixed low temperature L has a pronounced maximum for $H \approx 0$, which implies kinetic (quasicritical) speeding up. These kinetic contributions to the relaxation time τ are accompanied by their own characteristic modifications of the (quasi)-divergent behaviour, as shown by (7.1)–(7.3).

A general theory of critical slowing down, both for stochastic and hamiltonian systems, has been formulated by Suzuki[26]). The presence or absence of kinetic critical slowing down is shown to depend on a complicated expression which involves, in general, all moments of the master operator (or hamiltonian). Kinetic critical slowing down of the magnetization is known to occur in the Glauber model, as mentioned before, and in the zero-temperature XY model at the critical field[26]). The intriguing question of its presence in the two-dimensional generalization of Glauber's model has not yet been settled; it has recently been considered in connection with the dynamical scaling hypothesis[27-29]). Experimental support for the occurrence of kinetic critical slowing down comes from dielectric relaxation data on $NaNO_3$ [30]).

8 *The frequency-dependent susceptibility.* A second result which is easily found on the basis of the analysis of section 6 is the frequency-dependent zero-field

susceptibility $\chi(\omega)$. It is defined by[31]

$$\chi(\omega) = \beta \lim_{N,R\to\infty} \left(\langle \delta M^2 \rangle_{NR} - i\omega \int_0^\infty \langle \delta M(t)\, \delta M \rangle_{NR}\, e^{-i\omega t}\, dt \right). \tag{8.1}$$

The spectral density function $S(\omega)$, which gives the frequency distribution of the fluctuations in the total magnetization, can be related to $\chi(\omega)$ by

$$S(\omega) \equiv (2/\pi) \lim_{N,R\to\infty} \int_0^\infty \langle \delta M(t)\, \delta M \rangle_{NR} \cos \omega t\, dt$$

$$= -2(\pi\beta\omega)^{-1} \operatorname{Im} \chi(\omega). \tag{8.2}$$

Expression (8.1) can again be written as an integral involving $\mathcal{P}(\lambda)$. Following the same procedure as for $\bar{\tau}$ in section 6 we find

$$\chi(\omega) = \frac{2\beta\omega}{\pi} \oint_C \frac{\lambda^2 \mathcal{P}(\lambda)}{\lambda - i\omega}\, d\lambda, \tag{8.3}$$

where C encircles the two simple poles of the integrand at $\lambda = 0$ and $\lambda = -i\omega$. Putting $H = 0$ we find by straightforward calculation

$$\chi(\omega) = \frac{4\beta\omega}{\pi} \oint \frac{d\lambda}{\lambda(\lambda - i\omega)[\mathcal{F}_{-}(\lambda) - 1]}$$

$$= -\frac{2\beta(1-y)}{i\omega} \left(1 + \frac{1}{\mathcal{F}_{-}(-i\omega) - 1} \right), \tag{8.4}$$

where $\mathcal{F}_{-}(\lambda) = \mathcal{F}_{-}(\lambda)$ is given by (6.43) with $v = 1$. Hence the susceptibility exhibits a branch-cut singularity for $\omega = i\lambda$, $\varkappa_0 \leq \lambda \leq \varkappa_n$.

From (8.2), (8.4) and (6.43) we find for the spectral density

$$S(\omega) = \frac{4y(1-y)}{\pi\omega^2} \left(1 + \frac{4(1-y)S_1(\omega)}{S_1^2(\omega) + S_2^2(\omega)} \right), \tag{8.5}$$

with

$$S_1(\omega) = (1 - 3y)\,\omega - (1-y)\,[S_3(\omega) + S_4(\omega)]^{\frac{1}{2}},$$

$$S_2(\omega) = -(1-y)^2 + (1-y)\,[S_3(\omega) - S_4(\omega)]^{\frac{1}{2}},$$

$$S_3(\omega) = \tfrac{1}{2}\,[(1-y)^4 + 2(1 + 6y + y^2)\,\omega^2 + \omega^4]^{\frac{1}{2}},$$

$$S_4(\omega) = \tfrac{1}{2}\,[(1-y)^2 - \omega^2]. \tag{8.6}$$

Here the parameter y represents the temperature; by the formulas of section 3 we have $y = (1 + e^{-2\beta J})^{-1}$. It is suggested by expansion (6.43) for $\mathscr{F}_+(\lambda)$ that at low temperature, *i.e.* for $y \to 1$, the frequency ω scales as ω/ω_c with $\omega_c = (1-y)^2 \simeq \varepsilon^2$. In fig. 2 we have plotted for various temperatures the scaled *lineshape function* $F(\omega/\omega_c)$ defined[6]) by

$$F(\omega/\omega_c) \equiv \omega_c S(\omega) \Big/ \int_{-\infty}^{\infty} S(\omega)\, d\omega = [(1-y)^3/2y]\, S(\omega). \tag{8.7}$$

One easily verifies the normalization

$$\tfrac{1}{2} \int_{-\infty}^{\infty} F(x)\, dx = 1. \tag{8.8}$$

Comparison is made with the lorentzian lineshapes obtained from the exponential decay curves $e^{-t/\tau}$ and e^{-t/τ_i}, where τ is the relaxation time of the previous sections, and τ_i is the initial relaxation time. The latter is defined as the coefficient of the linear term in the initial time expansion.

$$\lim_{N,R\to\infty} \frac{\langle \delta M(t)\, \delta M\rangle_{NR}}{\langle \delta M^2\rangle_{NR}} = \lim_{N,R\to\infty} \frac{\langle \delta M\, e^{Wt}\, \delta M\rangle_{NR}}{\langle \delta M^2\rangle_{NR}}$$

$$= \lim_{N,R\to\infty} \left(1 + \frac{\langle \delta M\, W\, \delta M\rangle_{NR}}{\langle \delta M^2\rangle_{NR}}\, t + \frac{1}{2}\, \frac{\langle \delta M\, W^2\, \delta M\rangle_{NR}}{\langle \delta M^2\rangle_{NR}}\, t^2 + \cdots\right). \tag{8.9}$$

Here W is the coarse-grained operator of section 2. For τ_i we find, for general H,

$$\tau_i \equiv \lim_{N,R\to\infty} \langle \delta M\, W\, \delta M\rangle_{NR} / \langle \delta M^2\rangle_{NR} = \tau/[1 + y(v + v^{-1})]. \tag{8.10}$$

where the method of section 6 has again been used. Note that the inequality $\tau_i \geqslant \tau$ is satisfied, as it should for a stochastic process[29]). For $H = 0$ we find from (8.10) that $\tau_i = \tau/(1 + 2y) = \frac{1}{2}(1-y)^{-2}$. It can be shown that at zero field the moments $\lim_{N,R\to\infty} \langle \delta M\, W^n\, \delta M\rangle_{NR}$ in (8.9) are equal to the moments $\lim_{N,R\to\infty} \langle \delta M\, w^n\, \delta M\rangle_{NR}$ of the exact microscopic master operator (2.14), for $n = 1, 2, 3$. The equality for $n = 1$ implies[29]) that e^{-t/τ_i} is at all times a lower bound to the exact relaxation curve as well as to the curve in our approximation. Fig. 2 shows that our lineshape is much narrower than the lorentzian based on the initial-time behaviour, especially at low temperature (y close to 1). This indicates that for later times the logarithmic derivative of the relaxation curve decreases significantly below its initial value.

Our results are based on the master equation (2.15), which was derived from the basic master equation (2.7) by means of a "stosszahlansatz". The question

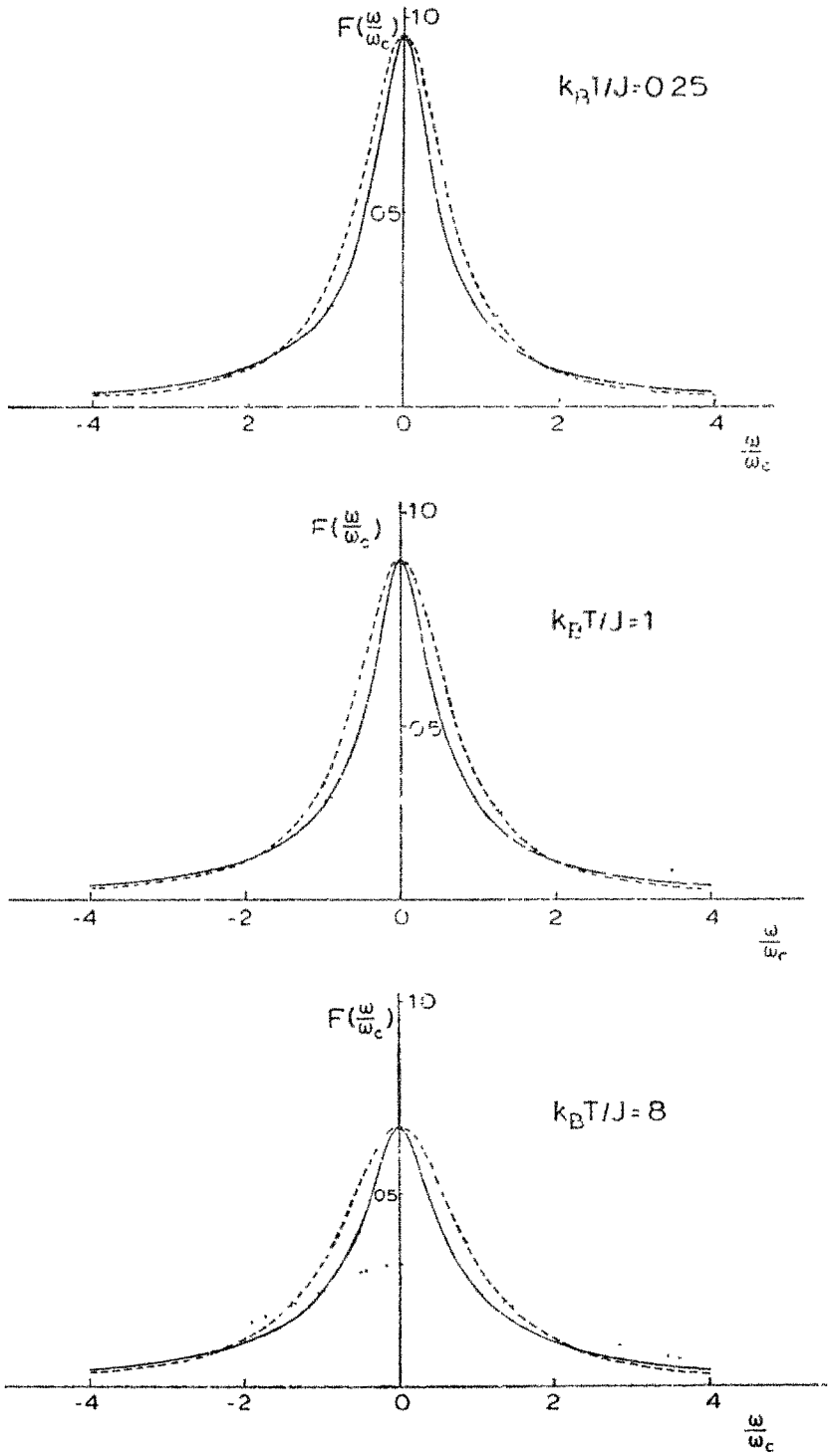

Fig. 2. Lineshape function $F(\omega/\omega_c)$ for zero field and several temperatures. Solid curves: the results of eqs (8.5)–(8.7). Dashed curves: lorentzians obtained from $e^{-t/\tau}$. Dotted curves: lorentzians obtained from e^{-t/τ_i}.

concerning the validity of this "stosszahlansatz" remains, and is difficult to answer, even though one can in principle calculate correction terms to our approximation[32]. A general scheme for computing time correlation functions has been proposed by Mori[33, 34]. It is a continued fraction expansion based on the knowledge of the lowest few moments of the time evolution operator (which determine the short-time behaviour), and it can also accommodate an assumed long-time behaviour. Mori's method has been employed in calculating the lineshape function of the Fourier components of the magnetization in the Heisenberg and the XY models[35-37] and the results are found to be in reasonable agreement with experimental data. Our "stosszahlansatz" rather approximates the master operator by a coarse-grained one, W, whose moment equations involve only the cluster fraction variables f_k. The approximation is exact for the lowest moments of the master operator and hence it has the same merits as Mori's method for the initial-time behaviour. For the long-time behaviour no further assumptions are needed. It is obtained by solving exactly the moment equations, thus taking into account the detailed coupling between all variables f_k. These variables are still infinite in number and give a refined description of the decay process. We therefore feel that our results are likely to be a good approximation to the true behaviour of the system.

9. *Conclusion.* The conclusions of this paper can be summarized as follows. We considered a stochastic Ising chain with nearest-neighbour interaction in magnetic field H and calculated the relaxation time $\tau(T, H)$ of the fluctuations in the magnetization. We wrote $\tau = \chi_\varrho/L$ with χ_ϱ the magnetic susceptibility and L an Onsager kinetic coefficient. It was shown that at fixed T the relaxation time τ exhibits a pronounced maximum for $H \simeq 0$, caused by a sharp peak in χ_ϱ (thermodynamical slowing down), but weakened by a peak in L (kinetic speeding up). At fixed low temperature the peak in τ becomes very sharp, which explains the quasicritical slowing down observed in many physical, chemical and biological relaxation processes. At fixed $H = 0$ we found that τ diverges as ε^{-2} when T goes to zero, due to divergences of both χ_ϱ and L (thermodynamical and kinetic critical slowing down). The same singularity $\approx \varepsilon^{-2}$ in τ was found in Glauber's model, so that it appears to be insensitive to conservation of energy. The peaked behaviour of the phenomenological "constant" L as a function of T and H is nonclassical.

Finally, the frequency-dependent susceptibility $\chi(\omega)$ and the related spectral density of fluctuations $S(\omega)$ were calculated for $H = 0$. The spectral lineshape was shown to be significantly narrower than the initial-time behaviour of the correlation function would suggest, which indicates that for later times the logarithmic derivative of the decay curve decreases well below its initial value. At low temperature $S(\omega)$ scales as $S(\omega) = (1-y)^{-3}\,\tilde{S}(\omega/(1-y)^2)$,

APPENDIX

Equivalence to other models. Recently so-called $\sigma\tau$ transformations[15, 38]) have been employed to demonstrate a number of interesting equivalences among spin hamiltonians and master operators for spin systems. Another such equivalence is obtained here by applying to the master operator (2.14) for $H = 0$ the following $\sigma\tau$ transformation[15]).

$$\tau_j^z = \sigma_{j-1}^z \sigma_j^z, \qquad \tau_j^x = \sigma_j^x \sigma_{j+1}^x \cdots \sigma_N^x \qquad j = 1, 2, \ldots, N, \qquad \sigma_0^z \equiv 1. \tag{A.1}$$

where it may be verified that the τ operators satisfy again spin-$\frac{1}{2}$ Pauli commutation relations. The inverse transformation reads

$$\sigma_j^z = \tau_1^z \tau_2^z \cdots \tau_j^z, \qquad \sigma_j^x = \tau_j \tau_{j+1}^x, \qquad j = 1, 2, \ldots, N, \qquad \tau_N^x \equiv 1. \tag{A.2}$$

Application of this transformation to the operator $\mathcal{L}$ in (2.14) for $H = 0$ yields

$$\mathcal{L} = \frac{1}{2} \sum_{j=2}^{N-1} (\tau_j^x \tau_{j+1}^x - 1)(1 - \tau_j^z \tau_{j+1}^z) = \frac{1}{2} \sum_{j=2}^{N-1} \boldsymbol{\tau}_j \cdot \boldsymbol{\tau}_{j+1} - \frac{1}{2}(N - 2), \tag{A.3}$$

which is precisely the isotropic Heisenberg hamiltonian for a chain of $N - 2$ spins τ. The first line of (A.1) shows that a down-spin in the τ picture corresponds to a break between two clusters of σ spins. Hence the Heisenberg chain with $2R - 1$ spin waves, whose solution is in principle given by Bethe's method[39]), corresponds to the subspace with $2R$ clusters in the σ picture.

It should be noted, however, that the above $\sigma\tau$ transformation does not transform the correlation function of the total magnetization in our model into an ordinary quantum-mechanical average. It may be verified that

$$\langle M(t)\, \delta M(0) \rangle_{\mathrm{eq}} = \sum_{\nu \neq 0} \langle \nu | M | R \rangle \langle R | M | \nu \rangle e^{-\lambda_\nu t}, \tag{A.4}$$

where ν runs through all Bethe eigenstates with $2R - 1$ spin waves, and the eigenvalues λ_ν enter as decay times rather than as frequencies of oscillation, and $|R\rangle$ is the equilibrium.

A second obvious interpretation is that we have a model of interacting random walkers, each random walker corresponding to a break between two clusters of σ spins, or to a deviating τ spin. For $H = 0$ the random walkers show a tendency to form pairs.

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