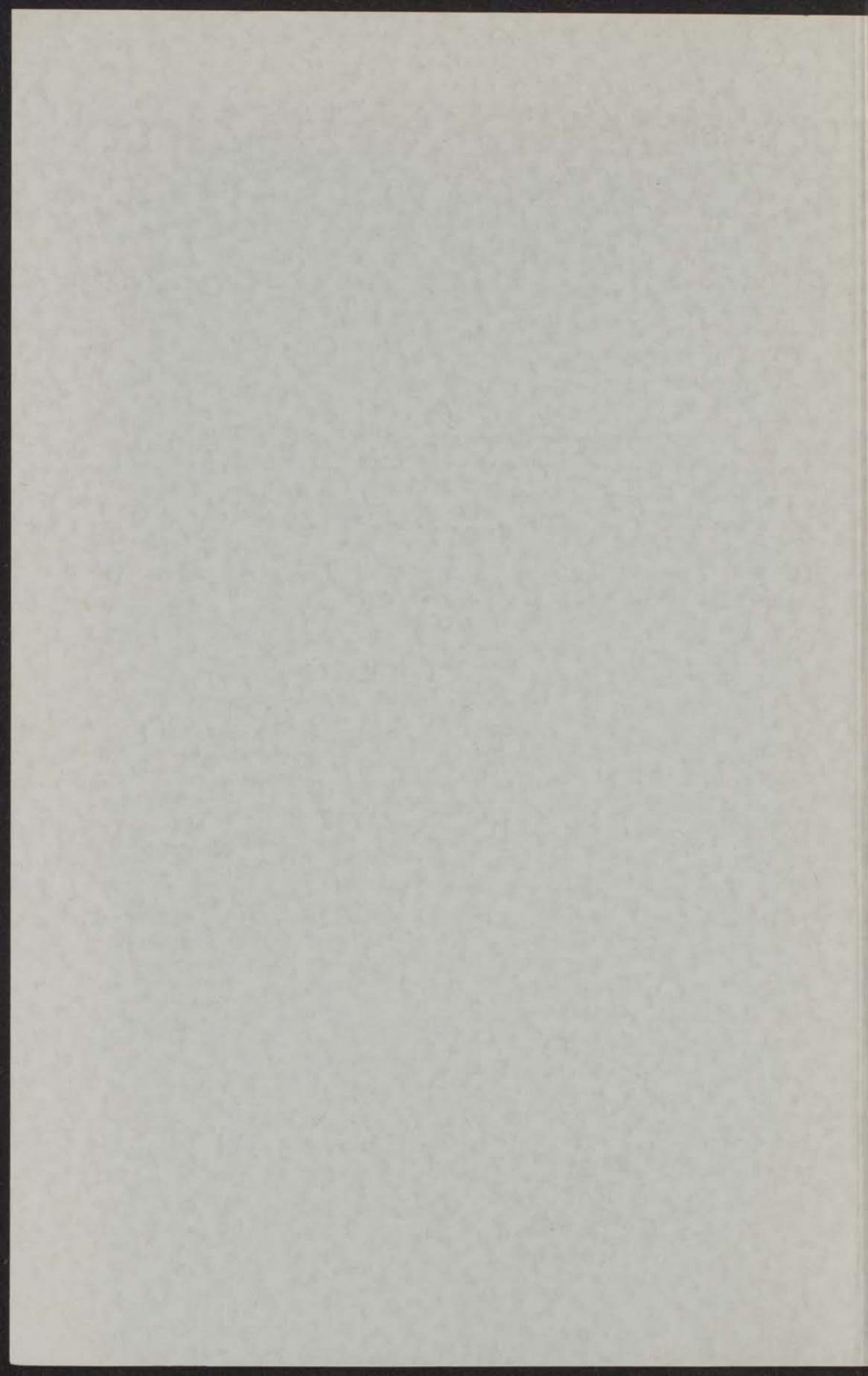


17 APR. 1977

ON THE THEORY OF DIAMAGNETIC RELAXATION
IN HARMONIC OSCILLATOR ASSEMBLIES

INSTITUUT-LORENTZ
voor theoretische natuurkunde
Houwsteeg 18-Leiden-Nederland

T. J. SISKENS



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PROEFSCHRIFT

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IN DE WISSENSCHAP EN NATUURWETENSCHAPPEN
VAN DE RIJSCHE UNIVERSITEIT TE LEIDEN, OP
BEZAAK VAN DE RECTOR MAGHINCOUS DE W. A. D.
ROLLIN-DE ROOGLERNAAF IN DE FACULTEIT DER
GEWISSENSCHAPPEN, VOORZIJT BESLUIT VAN HET
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GOSLINGS, HOOGLERAAR IN DE FACULTEIT DER
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ZALTBOMMEL

ON THE THEORY OF DIAMAGNETIC RELAXATION
BY HARMONIC OSCILLATOR ASSEMBLIES

PREFACE

The following work is a result of the author's researches in the field of diamagnetism, carried out in the Department of Physics, University of Toronto, during the years 1934-1935. It is a contribution to the theory of the magnetic susceptibility of solids, and is based on the assumption that the magnetic ions in a crystal lattice are represented by harmonic oscillators. The theory is developed in a series of chapters, and the results are compared with experimental data.

Promotor: PROF. DR. P. MAZUR

THEODORE JOHANNES SIEGERS

PH.D. DEGREE IN PHYSICS

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STELLINGEN

I

Voor de isotherme, adiabatiese en geïsoleerde susceptibiliteit, respectievelijk χ_T , χ_s en χ_{is} , van de in dit proefschrift beschreven diamagnetische systemen geldt de ongelijkheid $\chi_T \geq \chi_s \geq \chi_{is}$.

Hoofdstuk II van dit proefschrift.

II

Voor de in dit proefschrift beschreven diamagnetische systemen zijn de Kramers-Kronig relaties van toepassing op het reële en imaginaire gedeelte van $\chi(\omega) - \chi(\infty)$, waarin $\chi(\omega)$ de frequentie-afhankelijke susceptibiliteit is en $\chi(\infty) [\equiv \lim_{\omega \rightarrow \infty} \chi(\omega)]$ een reële, negatieve grootte is, die samenhangt met het optreden van een expliciet van de tijd afhankelijke component in de magnetisatie-operator. De Kramers-Kronig relaties zijn voor deze systemen derhalve niet incompatibel met $\text{Re } \chi(0) < 0$ en $\text{Im } \chi(\omega) \geq 0$ voor $\omega \geq 0$.

P. C. Martin, Phys. Rev. **161** (1967) 143.

Hoofdstuk II van dit proefschrift.

III

De door White gegeven definitie van diamagnetische systemen is te restrictief.

R. White, Quantum theory of magnetism, McGraw Hill (1970).

IV

De bewering van Kubo, dat voor een fasefunctie $A(p, q)$ de asymptotische waarde van de autocorrelatiefunctie in het mikrokanoniek ensemble

$\langle AA(t) \rangle_m$ in de limiet $t \rightarrow \infty$ gelijk is aan $\langle A \rangle_m^2$, indien de ergodiciteitsconditie voor $A(p, q)$ uniform geldt, is onjuist.

R. Kubo, J. Phys. Soc. of Japan **12** (1957) 570.

V

Papadopoulos wekt ten onrechte de indruk, dat de isotherme magnetische susceptibiliteit van een met de Einstein-theorie beschreven ionenrooster slechts voor zwakke magneetvelden negatief is.

G. J. Papadopoulos, J. Phys. A: Gen. Phys. **4** (1971) 773.

VI

De door Niemeijer afgeleide uitdrukkingen voor de spin-spin-correlatiefuncties en de autocorrelatiefunctie van de totale magnetisatie in het XY-model kunnen eenvoudiger worden verkregen, zonder gebruik te maken van een bepaalde representatie, door over te gaan op operatoren α_j en β_j ($j = 1, \dots, N$), gedefinieerd als $\alpha_j = (1/\sqrt{2})(c_j + c_j^*)$ en $\beta_j = (-i/\sqrt{2}) \cdot (c_j - c_j^*)$ ($j = 1, \dots, N$).

Th. Niemeijer, Physica **36** (1967) 377.

VII

Uit hun experimenten omtrent het gedrag van atomaire waterstof op koude oppervlakken concluderen Brackmann en Fite, dat bij 80 K van de opvallende waterstofatomen 22% recombineert tot moleculen. Deze conclusie is aanvechtbaar.

R. T. Brackmann en W. L. Fite, J. chem. Phys. **34** (1961) 1572.

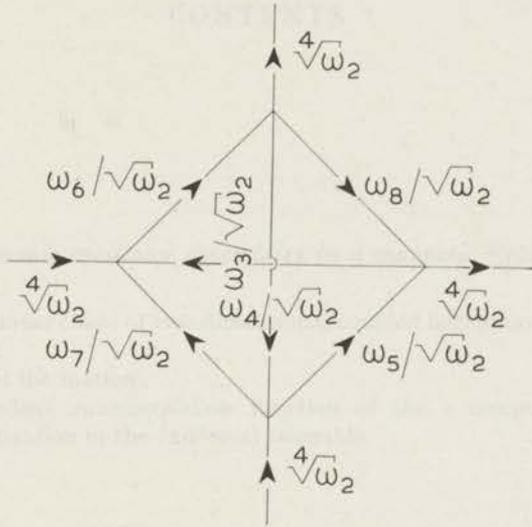
VIII

De door Balescu voor een systeem met hamiltoniaan $H = H_0 + \lambda V$ (waarin $H_0 = \sum_{k=1}^N \omega_k J_k$ de hamiltoniaan is van N onafhankelijke harmonische oscillatoren) gegeven afleiding van condities, die het bestaan uitsluiten van bewegingsconstanten die analytisch zijn in λ , is niet geheel bevredigend.

R. Balescu, Bull. Acad. Roy. Belgique Cl. Sci. (5e série) **XLII** (1956) 622.

IX

De door Fan en Wu met de dimerenmethode gegeven afleiding van een gesloten uitdrukking voor de vrije energie per vertex van "free-fermion" modellen kan vereenvoudigd worden door gebruik te maken van de hieronder afgebeelde "dimer-city".



C. Fan en F. Y. Wu, Phys. Rev. B 2 (1970) 723.

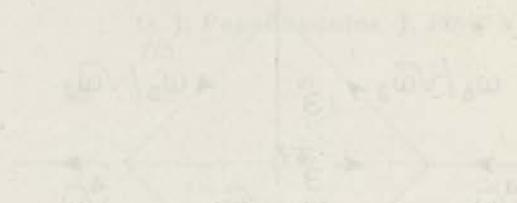
X

Het is te betreuren, dat de niet-confessionele partijen, wanneer zij regeeringsverantwoordelijkheid dragen, keer op keer toegeven aan de confessionele partijen in zaken betreffende de persoonlijke vrijheid van de Nederlandse burger.

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CONTENTS

| | |
|---|----|
| INTRODUCTION | 1 |
| CHAPTER I. <i>Harmonic oscillator assemblies in a magnetic field</i> | 3 |
| 1. Introduction | 3 |
| 2. Dynamics of a linear chain of two-dimensional coupled harmonic oscillators in a magnetic field | 5 |
| 3. The constants of the motion | 9 |
| 4. The time-dependent autocorrelation function of the z component of the external magnetization in the canonical ensemble | 10 |
| 5. Conclusions | 18 |
| Appendix I | 20 |
| Appendix II | 21 |
| Appendix III | 21 |
| CHAPTER II. <i>Theory of diamagnetic relaxation in harmonic oscillator assemblies</i> | 25 |
| 1. Introduction | 25 |
| 2. Linear response theory for simple diamagnetic systems in a time-dependent external magnetic field | 26 |
| 3. The relaxation function | 31 |
| 4. Isothermal, adiabatic, isolated and frequency-dependent susceptibilities for diamagnetic systems | 33 |
| 5. Diamagnetic relaxation in harmonic oscillator assemblies | 37 |
| 6. Conclusions | 46 |
| Appendix I | 47 |
| Appendix II | 52 |
| Appendix III | 53 |
| CHAPTER III. <i>Ergodic properties of the magnetization in harmonic oscillator assemblies</i> | 56 |
| 1. Introduction | 56 |
| 2. Microcanonical joint and conditional distribution functions for the magnetization in a linear chain of two-dimensional oscillators | 57 |

| | |
|---|--------|
| 3. The long-time behaviour of the conditional distribution function $P_m(X, t X_0)$ and the conditional average $\overline{X(t)}^{X_0}$ in connection with the ergodic properties of $X(t)$ | 62 |
| 4. An equality connecting microcanonical and canonical autocorrelation functions of sumvariables | 64 |
| Appendix | 67 |
| SAMENVATTING | 74 |
| STUDIEGEGEVENS | 76 |

CONTENTS

| | |
|----|---|
| 1 | INTRODUCTION |
| 2 | CHAPTER I. Fluctuations of the number of particles in a system |
| 3 | 1. Introduction |
| 4 | 2. Derivation of a linear chain of two-dimensional coupled harmonic oscillators |
| 5 | 3. Canonical ensemble |
| 6 | 4. The microcanonical ensemble |
| 7 | 5. The microcanonical ensemble |
| 8 | 6. The microcanonical ensemble |
| 9 | 7. Appendix I |
| 10 | 8. Appendix II |
| 11 | 9. Appendix III |
| 12 | CHAPTER II. Fluctuations of the number of particles in a system |
| 13 | 1. Introduction |
| 14 | 2. Derivation of a linear chain of two-dimensional coupled harmonic oscillators |
| 15 | 3. The microcanonical ensemble |
| 16 | 4. The microcanonical ensemble |
| 17 | 5. The microcanonical ensemble |
| 18 | 6. The microcanonical ensemble |
| 19 | 7. Appendix I |
| 20 | 8. Appendix II |
| 21 | 9. Appendix III |
| 22 | CHAPTER III. Fluctuations of the number of particles in a system |
| 23 | 1. Introduction |
| 24 | 2. Derivation of a linear chain of two-dimensional coupled harmonic oscillators |
| 25 | 3. The microcanonical ensemble |
| 26 | 4. The microcanonical ensemble |
| 27 | 5. The microcanonical ensemble |
| 28 | 6. The microcanonical ensemble |
| 29 | 7. Appendix I |
| 30 | 8. Appendix II |
| 31 | 9. Appendix III |

INTRODUCTION

The time-dependent statistical-mechanical behaviour of harmonic oscillator assemblies has been studied extensively, also in recent years. In particular these investigations have dealt with the stochastic types of motion of one single particle^{1, 2, 3, 4, 5, 6, 7}). Though *e.g.* Fourier's macroscopic law of heat conduction is violated in such assemblies⁸), it has been shown that harmonic oscillator assemblies exhibit some remarkable properties characteristic of the behaviour of systems with more realistic interactions.

The studies referred to above, have dealt with essentially local properties. In this thesis, however, we shall discuss a property of the system as a whole, *viz.* the total magnetization of a harmonic oscillator assembly in a magnetic field. In a time-dependent magnetic field such an assembly may then serve as a model for diamagnetic relaxation, *i.e.* may be expected to exhibit, in a qualitative way, the behaviour of real diamagnetic systems. In the theory of diamagnetic relaxation, which will be presented in this thesis, the time behaviour of the autocorrelation function of the magnetization in the canonical ensemble plays a central role. Mazur⁹) has pointed out recently that the time average of such an autocorrelation function is intimately connected with the ergodic properties of the phase function (or operator) involved. In this light considerable attention will be given to the ergodic behaviour of the total magnetization in harmonic oscillator assemblies.

In chapter I the dynamical problem of a linear chain of charged anisotropically coupled two-dimensional harmonic oscillators in a magnetic field B will be solved. We shall derive an explicit expression for the autocorrelation function $R(t)$ of the magnetization in the canonical ensemble. In the limit of an infinite system the asymptotic time behaviour of $R(t)$ will be discussed in connection with the ergodic properties of the magnetization for varying values of B and the anisotropy parameter γ . It will be shown that the magnetization is ergodic only in the case $\gamma \neq 0$ and $B \rightarrow 0$.

In chapter II a linear response theory for simple diamagnetic systems in a time-dependent magnetic field will be presented. We shall give expressions

for the isothermal, adiabatic, isolated and frequency-dependent susceptibilities per particle for diamagnetic systems. Inequalities between the various susceptibilities will be derived. The theory will be applied to the system discussed in Chapter I.

In chapter III the stochastic behaviour of the normalized total magnetization $X(t)$ of the system studied in chapter I, will be investigated in the classical limit. We shall, in the limit of an infinite system, derive expressions for the joint and conditional distribution functions of $X(t)$ in the microcanonical ensemble. The process $X(t)$ will be found to be a stationary, gaussian, non-markoffian process. We shall discuss the asymptotic time behaviour of the conditional distribution function and the conditional average of $X(t)$ in connection with the ergodic properties of $X(t)$ for varying values of γ and B . It will be found that, if $\gamma \neq 0$ and $B \rightarrow 0$, the process $X(t)$ is an ergodic process. Finally we shall establish an equality connecting microcanonical and canonical autocorrelation functions of sumvariables.

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- 9) Mazur, P., *Physica* **43** (1969) 533.

CHAPTER I

HARMONIC OSCILLATOR ASSEMBLIES IN A MAGNETIC FIELD

Synopsis

The dynamical problem of a linear chain of charged anisotropically coupled two-dimensional harmonic oscillators in a magnetic field B is solved. The constants of the motion of the system are analyzed for varying values of B and anisotropy parameter γ . It is shown that the invariants have an essentially different nature for $\gamma=0$ and for $\gamma \neq 0$, if B tends to zero. The autocorrelation function $R(t)$ of the magnetization in the canonical ensemble is explicitly derived. The asymptotic behaviour of $R(t)$ for long times is studied in the limit of an infinite system, with very general assumptions with respect to the interactions. It is shown that the magnetization is in general not an ergodic property of the system. Only in the case $B \rightarrow 0$ and $\gamma \neq 0$ is the magnetization found to be ergodic. There is, as expected, a close relation between the ergodic behaviour of the magnetization and the non-analytic nature in γ of the constants of the motion in the limit $B \rightarrow 0$.

1. *Introduction.* Considerable attention has been given, also in recent years, to the time-dependent statistical mechanical behaviour of harmonic oscillator assemblies. In particular the stochastic types of motion of a single particle in such assemblies were studied in great detail¹). Much of the relevant information for this case is contained in the momentum autocorrelation function of the specific particle considered. A number of significant results have been established by studying this single particle momentum autocorrelation function²). Thus it was found that a given particle in the limit of an infinite assembly will exhibit an irreversible behaviour in the following sense. In an ensemble in which all degrees of freedom of the assembly, except the specified momentum of the particle considered, are initially canonically distributed (at temperature T), this particle will perform a stochastic type of motion such that its momentum distribution function will for long times reach its equilibrium form and become Maxwellian. For a very heavy particle harmonically bound to a linear chain of harmonic oscillators of equal but light mass, this approach to equilibrium follows the stochastic equations of Brownian motion^{1,3}). Brownian motion can also be simulated by a particle having the same mass as the other particles in the

assembly provided a specific and unique choice is made for the interaction matrix of the chain⁴). A harmonic oscillator assembly may therefore act as a "heat bath" with respect to a specific particle of the assembly. However, the energy flow within such a "heat bath" does not obey the macroscopic law of Fourier. A number of papers have in particular dealt with the heat flow in linear chains of harmonic oscillators⁵).

In all the investigations referred to above, the properties studied were essentially local properties. In this chapter we discuss a model of coupled harmonic oscillators which enables us to study a property of the assembly as a whole. The model consists of a linear chain of N two-dimensional coupled charged harmonic oscillators in a magnetic field B , perpendicular to the plane of motion. Furthermore we introduce a uniform anisotropy in the interaction. The property studied is the total magnetization of the chain.

In section 2 we study the dynamics of the model. By means of canonical transformations the Hamiltonian is written as a sum of $2N$ independent linear harmonic oscillators whose frequencies are expressed in terms of the normal mode frequencies of the chain in the absence of an external field and of anisotropic coupling, and in terms of the field and the anisotropy parameter γ . The discussion of the dynamics is then reduced to solving the (operator) equations of motion for the independent oscillators.

In section 3 we discuss the behaviour of the constants of the motion expressed in the original coordinate and momentum operators of the chain, with varying magnetic field B and anisotropy for the "coupling" parameter γ .

It is shown that at finite value of the magnetic field the constants of the motion are analytic functions of γ (for sufficiently small γ). However, in the limit as B tends to zero, these invariants of the motion are non-analytic functions of γ : they reduce to different operator functions if γ is equal to zero, and if γ tends to zero.

In section 4 we study the time autocorrelation function of the total magnetization in a canonical ensemble. We first express a total magnetization operator in terms of the operators pertaining to the $2N$ independent modes of oscillation of the system. The autocorrelation function of the magnetization can then be evaluated in a straightforward way. In order to investigate the behaviour of the function in an infinite chain, some very general assumptions are made concerning the interaction matrix characterizing the chain. For the infinite chain the autocorrelation function is then written as an integral whose asymptotic value, as time tends to infinity, exists. It is shown that for finite magnetic field B this asymptotic value is not equal, but is larger than the value to be expected for thermodynamic behaviour, *i.e.* to be expected if the magnetization were an ergodic property of the system. However, in the limit as B , the magnetic field, tends to zero, the asymptotic value of the autocorrelation function is zero for finite γ , and

equal to the value to be expected in this case if the magnetization were an ergodic property of the system.

Therefore, according to a well known theorem on correlation functions, ergodicity of the magnetization is thus implied by the asymptotic value of the autocorrelation function in the latter case ($B \rightarrow 0$, $\gamma \neq 0$). It should be stressed here that ergodic behaviour of the magnetization in a limiting case for our model is in no way meant to imply that the system as such is then "an ergodic system". On the other hand we note that ergodicity in the above restricted sense, *viz.* ergodicity of the system with respect to a specific property of the system as a whole, in casu the magnetization, appears to be related, as we show, to the non-analyticity in the "coupling" constant γ of the constants of the motion of the system.

2. *Dynamics of a linear chain of two-dimensional coupled harmonic oscillators in a magnetic field.* We consider a linear chain of N identical charged particles, whose motions are restricted to the xy plane. The particles interact through harmonic forces and are subjected to a homogeneous external magnetic field \mathbf{B} along the z axis.

The Hamiltonian is given by

$$H = \sum_{i=1}^N \frac{1}{2} (\mathbf{p}_i - \mathbf{A}(\mathbf{r}_i))^2 + \frac{1}{2} \sum_{\substack{i,j=1,\dots,N \\ \alpha,\beta=x,y}} r_i^\alpha \Omega_{ij} (1 + \gamma \sigma^z)^{\alpha\beta} r_j^\beta. \quad (1)$$

Here \mathbf{r}_i and \mathbf{p}_i are the two-dimensional displacement vector and momentum vector of the i th particle. The quantities Ω_{ij} are the elements of a symmetric $N \times N$ matrix Ω characterizing the interaction between the particles; $\mathbf{1}$ is the 2×2 unit matrix and σ^z the 2×2 matrix

$$\sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2)$$

The parameter γ^* is therefore a measure for the anisotropy of the interaction in the x and y direction. It is seen that in this model the anisotropy of the forces is independent of i and j . Finally $\mathbf{A}(\mathbf{r}_i)$ denotes the vector potential of the homogeneous magnetic field \mathbf{B} , which is given by

$$\mathbf{A}(\mathbf{r}_i) = \frac{1}{2} \mathbf{B} \wedge \mathbf{r}_i. \quad (3)$$

For reasons of convenience we have assumed both the mass and the charge of a particle to be equal to unity. We have also taken c to be unity. ($c =$ velocity of light). With eq. (3) the Hamiltonian (1) may be rewritten in the form

$$H = \sum_{i=1}^N \frac{1}{2} \mathbf{p}_i^2 - \frac{1}{2} i B (\mathbf{r}_i \cdot \sigma^y \cdot \mathbf{p}_i) + \frac{1}{8} B^2 (\mathbf{r}_i \cdot \mathbf{r}_i) + \frac{1}{2} \sum_{\substack{i,j=1,\dots,N \\ \alpha,\beta=x,y}} r_i^\alpha \Omega_{ij} (1 + \gamma \sigma^z)^{\alpha\beta} r_j^\beta. \quad (4)$$

* Without loss of generality we assume $\gamma \geq 0$.

where the 2×2 matrix σ^y is given by

$$\sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \quad (5)$$

The symmetric matrix Ω can be diagonalized by an orthogonal transformation:

$$\sum_{j,k=1}^N O_{ij} \Omega_{jk} O_{kl}^{-1} = \omega_i^2 \delta_{il}; \quad \sum_{i=1}^N O_{ij} O_{ik} = \delta_{jk}, \quad (6)$$

where the quantities $\omega_i^2 (i = 1, \dots, N)$ are the eigenvalues of Ω . Introducing new coordinates and momenta

$$\begin{aligned} (r_i^\alpha)' &= \sum_j O_{ij} r_j^\alpha, \\ (p_i^\alpha)' &= \sum_j O_{ij} p_j^\alpha \quad (\alpha = x, y) \end{aligned} \quad (7)$$

the Hamiltonian then becomes (dropping the primes denoting the new variables)

$$H = \sum_{i=1}^N \frac{1}{2} \mathbf{p}_i^2 - \frac{1}{2} i B (\mathbf{r}_i \cdot \sigma^y \cdot \mathbf{p}_i) + \frac{1}{2} \mathbf{r}_i \cdot \{ (\omega_i^2 + \frac{1}{4} B^2) \mathbf{1} + \gamma \omega_i^2 \sigma^z \} \cdot \mathbf{r}_i. \quad (8)$$

The Hamiltonian H is thus the sum of N uncoupled quasiparticle Hamiltonians H_i

$$H_i = \frac{1}{2} \mathbf{p}_i^2 - \frac{1}{2} i B (\mathbf{r}_i \cdot \sigma^y \cdot \mathbf{p}_i) + \frac{1}{2} \mathbf{r}_i \cdot \{ (\omega_i^2 + \frac{1}{4} B^2) \mathbf{1} + \gamma \omega_i^2 \sigma^z \} \cdot \mathbf{r}_i. \quad (9)$$

Each quasiparticle is thus an anisotropic two-dimensional oscillator acted upon by a magnetic field \mathbf{B} . In order to solve the dynamical problem for each quasiparticle we shall now perform an additional canonical transformation by which the Hamiltonian H_i becomes a sum of two independent Hamiltonians H_i^+ and H_i^- each describing a one dimensional oscillator. To this end we introduce new coordinates \mathbf{R}_i and momenta \mathbf{P}_i related to \mathbf{r}_i and \mathbf{p}_i by

$$\begin{aligned} \mathbf{r}_i &= \mathbf{R}_i - c_i \sigma^x \cdot \mathbf{P}_i, \\ \mathbf{p}_i &= a_i \sigma^x \cdot \mathbf{R}_i + (1 - a_i c_i) \mathbf{P}_i \quad (i = 1, \dots, N), \end{aligned} \quad (10)$$

where σ^x is the 2×2 matrix

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (11)$$

and where a_i and c_i are arbitrary constants. It can easily be checked that the transformation (10) is indeed a canonical transformation for all values of a_i and c_i .

With a_i and c_i given by

$$a_i = \frac{\gamma\omega_i^2 - (\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2))^{\frac{1}{2}}}{B}, \quad (12)$$

$$c_i = -\frac{B}{2(\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2))^{\frac{1}{2}}}, \quad (13)$$

the Hamiltonian H_i given by (9) assumes the form $H_i = H_i^+ + H_i^-$ with:

$$H_i^+ = \frac{1}{2}A_i^+ P_{x,i}^2 + \frac{1}{2}B_i^+ X_i^2, \quad (14)$$

$$H_i^- = \frac{1}{2}A_i^- P_{y,i}^2 + \frac{1}{2}B_i^- Y_i^2, \quad (15)$$

where A_i^\pm and B_i^\pm are defined by

$$A_i^\pm = \frac{2(\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2))^{\frac{1}{2}} + 2\gamma\omega_i^2 \pm B^2}{4(\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2))^{\frac{1}{2}}}, \quad (16)$$

$$B_i^\pm = \frac{1}{B^2} \{2\gamma^2\omega_i^4 + 2B^2(\omega_i^2 + \frac{1}{4}B^2) - (2\gamma\omega_i^2 \mp B^2)(\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2))^{\frac{1}{2}}\}. \quad (17)$$

We refer to appendix I for details of this calculation. By suitably rescaling the coordinates and momenta according to

$$X'_i = \frac{1}{(A_i^+)^{\frac{1}{2}}} X_i, \quad P'_{x,i} = (A_i^+)^{\frac{1}{2}} P_{x,i}, \quad (18)$$

$$Y'_i = \frac{1}{(A_i^-)^{\frac{1}{2}}} Y_i, \quad P'_{y,i} = (A_i^-)^{\frac{1}{2}} P_{y,i},$$

we finally obtain (dropping the primes once again)

$$H_i^+ = \frac{1}{2}P_{x,i}^2 + \frac{1}{2}\omega_{+,i}^2 X_i^2, \quad (19)$$

$$H_i^- = \frac{1}{2}P_{y,i}^2 + \frac{1}{2}\omega_{-,i}^2 Y_i^2, \quad (20)$$

where $\omega_{\pm,i}^2$ and $\omega_{-,i}^2$ ($i = 1, \dots, N$), defined as

$$\omega_{\pm,i}^2 = A_i^\pm B_i^\pm = \frac{1}{2}\{B^2 + 2\omega_i^2 \pm 2(\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2))^{\frac{1}{2}}\} \quad (21)$$

are the squares of the frequencies of the $2N$ uncoupled one-dimensional harmonic oscillators.

We note that

$$\lim_{B \rightarrow 0} \omega_{\pm,i} = \omega_i(1 \pm \gamma)^{\frac{1}{2}} \quad (22)$$

as it should be, according to (8).

Furthermore

$$\lim_{\gamma \rightarrow 0} \omega_{\pm, i} = (\omega_i^2 + \frac{1}{4}B^2)^{\frac{1}{2}} \pm \frac{1}{2}B, \quad (23)$$

which is the well-known result for an isotropic oscillator in a magnetic field.

We are now in a position to solve in a simple way the dynamical problem involved. Indeed from (19) and (20) we obtain the following equations of motion

$$\begin{aligned} \dot{P}_{x, i} &= -\omega_{+, i}^2 X_i, & \dot{X}_i &= P_{x, i}, \\ \dot{P}_{y, i} &= -\omega_{-, i}^2 Y_i, & \dot{Y}_i &= P_{y, i} \end{aligned} \quad (i = 1, \dots, N), \quad (24)$$

with solutions:

$$\begin{aligned} P_{x, i}(t) &= P_{x, i} \cos \omega_{+, i} t - X_i \omega_{+, i} \sin \omega_{+, i} t, \\ X_i(t) &= X_i \cos \omega_{+, i} t + P_{x, i} \frac{1}{\omega_{+, i}} \sin \omega_{+, i} t, \\ P_{y, i}(t) &= P_{y, i} \cos \omega_{-, i} t - Y_i \omega_{-, i} \sin \omega_{-, i} t, \\ Y_i(t) &= Y_i \cos \omega_{-, i} t + P_{y, i} \frac{1}{\omega_{-, i}} \sin \omega_{-, i} t \end{aligned} \quad (i = 1, \dots, N), \quad (25)$$

where $P_{x, i}$, $P_{y, i}$ and X_i , Y_i are the initial (for $t = 0$) momenta and coordinates.

The treatment given above, holds both classically and quantum-mechanically, if one replaces in the latter case the classical momenta and coordinates by the corresponding quantum-mechanical operators. For the quantum-mechanical case, however, it is useful in view of the statistical analysis of section 4, to introduce boson creation- and annihilation-operators:

$$\begin{aligned} a_{+, i}^\dagger &= \frac{P_{x, i} + i\omega_{+, i} X_i}{(2\hbar\omega_{+, i})^{\frac{1}{2}}}, & a_{+, i} &= \frac{P_{x, i} - i\omega_{+, i} X_i}{(2\hbar\omega_{+, i})^{\frac{1}{2}}}, \\ a_{-, i}^\dagger &= \frac{P_{y, i} + i\omega_{-, i} Y_i}{(2\hbar\omega_{-, i})^{\frac{1}{2}}}, & a_{-, i} &= \frac{P_{y, i} - i\omega_{-, i} Y_i}{(2\hbar\omega_{-, i})^{\frac{1}{2}}}, \end{aligned} \quad (i = 1, \dots, N) \quad (26)$$

satisfying the commutation relations:

$$\begin{aligned} [a_{\pm, i}, a_{\pm, j}^\dagger] &= \delta_{ij}, \\ [a_{+, i}, a_{-, j}] &= [a_{+, i}^\dagger, a_{-, j}] = 0 \end{aligned} \quad \text{for all } i \text{ and } j. \quad (27)$$

In terms of these operators we may now write the Hamiltonian as

$$H_i = H_i^+ + H_i^-.$$

with

$$H_i^+ = (a_{+,i}^\dagger a_{+,i} + \frac{1}{2}) \hbar \omega_{+,i} \quad (28)$$

and

$$H_i^- = (a_{-,i}^\dagger a_{-,i} + \frac{1}{2}) \hbar \omega_{-,i}. \quad (29)$$

The equations of motion are:

$$\begin{aligned} \dot{a}_{+,i}^\dagger &= \frac{i}{\hbar} [H, a_{+,i}^\dagger] = i\omega_{+,i} a_{+,i}^\dagger, \\ \dot{a}_{+,i} &= \frac{i}{\hbar} [H, a_{+,i}] = -i\omega_{+,i} a_{+,i}, \\ \dot{a}_{-,i}^\dagger &= \frac{i}{\hbar} [H, a_{-,i}^\dagger] = i\omega_{-,i} a_{-,i}^\dagger, \\ \dot{a}_{-,i} &= \frac{i}{\hbar} [H, a_{-,i}] = -i\omega_{-,i} a_{-,i} \quad (i = 1, \dots, N), \end{aligned} \quad (30)$$

with solutions

$$\begin{aligned} a_{+,i}^\dagger(t) &= a_{+,i}^\dagger \exp i\omega_{+,i}t, \\ a_{+,i}(t) &= a_{+,i} \exp -i\omega_{+,i}t, \\ a_{-,i}^\dagger(t) &= a_{-,i}^\dagger \exp i\omega_{-,i}t, \\ a_{-,i}(t) &= a_{-,i} \exp -i\omega_{-,i}t. \end{aligned} \quad (31)$$

3. *The constants of the motion.* Let us now study in somewhat more detail the behaviour of the constants of the motion of the system, expressed in terms of the coordinate and momentum operators of the quasiparticles, with varying external magnetic field B and "coupling" constant γ .

In terms of the operators defined by (18) we had found $2N$ constants of the motion given by (19) and (20). Inverting the transformations (18) and (10) and expressing (19) and (20) in terms of the quasiparticle operators, we obtain

$$\begin{aligned} H_i^+ &= \frac{1}{2} A_i^+ p_{xi}^2 + \frac{1}{2} B_i^+ (1 - a_i c_i)^2 x_i^2 + \frac{1}{2} B_i^+ c_i^2 p_{yi}^2 + \frac{1}{2} A_i^+ a_i^2 y_i^2 + \\ &+ B_i^+ c_i (1 - a_i c_i) x_i p_{yi} - A_i^+ a_i y_i p_{xi} \quad (i = 1, \dots, N), \end{aligned} \quad (32)$$

$$\begin{aligned} H_i^- &= \frac{1}{2} B_i^- c_i^2 p_{xi}^2 + \frac{1}{2} A_i^- a_i^2 x_i^2 + \frac{1}{2} A_i^- p_{yi}^2 + \frac{1}{2} B_i^- (1 - a_i c_i)^2 y_i^2 - \\ &- A_i^- a_i x_i p_{yi} + B_i^- c_i (1 - a_i c_i) y_i p_{xi} \quad (i = 1, \dots, N), \end{aligned} \quad (33)$$

where a_i and c_i are given by (12) and (13) and A_i^\pm and B_i^\pm by (16) and (17). From inspection of these last four expressions it is seen that all constants, and therefore (32) and (33), for $B \neq 0$ may be expanded in a power series in

γ . However, the radii of convergence of these series depend on B and vanish for B tending to zero. Indeed, defining the function $I(\gamma)$ to be

$$I(\gamma) = \begin{cases} 1 & \gamma = 0 \\ 0 & \gamma \neq 0 \end{cases} \quad (34)$$

one obtains, by taking the limit $B \rightarrow 0$ of the coefficients in (32) and (33), for the constants of the motion the following expressions

$$H_i^+ = \frac{1}{2}\{p_{xi}^2 + \omega_i^2(1 + \gamma)x_i^2\} + \frac{1}{4}I(\gamma)\{(p_{yi}^2 + \omega_i^2y_i^2) - (p_{xi}^2 + \omega_i^2x_i^2)\} - \frac{1}{2}I(\gamma)\omega_iL_i \quad (i = 1, \dots, N), \quad (35)$$

$$H_i^- = \frac{1}{2}\{p_{yi}^2 + \omega_i^2(1 - \gamma)y_i^2\} + \frac{1}{4}I(\gamma)\{(p_{xi}^2 + \omega_i^2x_i^2) - (p_{yi}^2 + \omega_i^2y_i^2)\} + \frac{1}{2}I(\gamma)\omega_iL_i \quad (i = 1, \dots, N), \quad (36)$$

where

$$L_i = x_i p_{yi} - y_i p_{xi} \quad (37)$$

is the angular momentum of the i th quasiparticle. Thus in this limit these constants are not analytic in γ . In particular we then have for $\gamma \neq 0$:

$$H_i^+ = \frac{1}{2}\{p_{xi}^2 + \omega_i^2(1 + \gamma)x_i^2\} \quad (i = 1, \dots, N), \quad (38)$$

$$H_i^- = \frac{1}{2}\{p_{yi}^2 + \omega_i^2(1 - \gamma)y_i^2\} \quad (i = 1, \dots, N), \quad (39)$$

which are Hamiltonians for the two normal modes of an anisotropic two-dimensional oscillator in the absence of a magnetic field.

On the other hand, if $\gamma = 0$, we find

$$H_i^+ = \frac{1}{2}(H_i - \omega_i L_i) \quad (i = 1, \dots, N), \quad (40)$$

$$H_i^- = \frac{1}{2}(H_i + \omega_i L_i) \quad (i = 1, \dots, N), \quad (41)$$

where

$$H_i = \frac{1}{2}(p_{xi}^2 + \omega_i^2x_i^2) + \frac{1}{2}(p_{yi}^2 + \omega_i^2y_i^2) \quad (i = 1, \dots, N) \quad (42)$$

is the Hamiltonian of a two-dimensional isotropic oscillator in the absence of a magnetic field.

Thus for this value of γ and in the limit $B \rightarrow 0$, the constants of the motion (32) and (33) reduce to linear combinations of the Hamiltonian and the angular momentum of a quasiparticle.

This non-analytic behaviour in γ of the constants of the motion is directly related to the asymptotic behaviour for long times of the autocorrelation function of the magnetization in the limit $B \rightarrow 0$, as we shall show in the next section.

4. *The time-dependent autocorrelation function of the z component of the magnetization in the canonical ensemble.* In this section we shall investigate the time-dependent autocorrelation function $R(t)$ of the z component

of the magnetization in the canonical ensemble, defined by

$$R(t) = \frac{1}{N} \{ \langle \rho M M(t) \rangle - \langle \rho M \rangle^2 \}, \quad (43)$$

where $\langle \dots \rangle$ denotes the quantum-mechanical trace and where the density operator ρ is defined by

$$\rho = \frac{\exp -\beta H}{\langle \exp -\beta H \rangle}. \quad (44)$$

We shall restrict the discussion to the quantum-mechanical case. The classical results can be found trivially by taking the limit $\hbar \rightarrow 0$. In terms of the original coordinate and momentum operators the magnetization is given by

$$M = \frac{1}{2} \sum_{i=1}^N \{ \mathbf{r}_i \wedge \mathbf{p}_i - \frac{1}{2} B(\mathbf{r}_i \cdot \mathbf{r}_i) \}. \quad (45)$$

By performing the transformations given by (7), (10), (18) and (26) we may write M in terms of the boson creation and annihilation operators as

$$M = \sum_{i=1}^N m_i, \quad (46)$$

with

$$m_i = \frac{1}{2} c_i \left\{ 2(H_i^+ - H_i^-) - \frac{\hbar(2\gamma\omega_i^2 - B^2)(\omega_{+,i}\omega_{-,i})^{\frac{1}{2}}}{2iB\omega_i(1+\gamma)^{\frac{1}{2}}} (a_{+,i}^\dagger - a_{+,i})(a_{-,i}^\dagger + a_{-,i}) \right. \\ \left. + \frac{\hbar(2\gamma\omega_i^2 + B^2)(\omega_{+,i}\omega_{-,i})^{\frac{1}{2}}}{2iB\omega_i(1-\gamma)^{\frac{1}{2}}} (a_{-,i}^\dagger - a_{-,i})(a_{+,i}^\dagger + a_{+,i}) \right\} \\ (i = 1, \dots, N), \quad (47)$$

where H_i^+ and H_i^- are defined by (28) and (29) and where we have used the following relations:

$$A_i^\pm B_i^\pm = \omega_{\pm,i}^2 \quad (\text{by definition}) \quad (21)$$

$$A_i^+ B_i^- = \omega_i^2 (1 - \gamma) \quad (48)$$

$$A_i^- B_i^+ = \omega_i^2 (1 + \gamma) \quad (i = 1, \dots, N). \quad (49)$$

Using now the relation

$$\omega_{+,i}\omega_{-,i} = \omega_i^2 \sqrt{1 - \gamma^2} \quad (i = 1, \dots, N) \quad (50)$$

we may write m_i as follows

$$m_i = \frac{1}{2} c_i \left\{ 2(H_i^+ - H_i^-) + i\hbar \frac{2\gamma\omega_i^2 - B^2}{2B} \left(\frac{1-\gamma}{1+\gamma} \right)^{\frac{1}{2}} (a_{+,i}^\dagger - a_{+,i})(a_{-,i}^\dagger + a_{-,i}) \right. \\ \left. - i\hbar \frac{2\gamma\omega_i^2 + B^2}{2B} \left(\frac{1+\gamma}{1-\gamma} \right)^{\frac{1}{2}} (a_{-,i}^\dagger - a_{-,i})(a_{+,i}^\dagger + a_{+,i}) \right\} \\ (51)$$

or, using the commutation relations (27)

$$m_i = c_i(H_i^+ - H_i^-) + \frac{1}{2}i\hbar K_i(a_{+,i}^\dagger a_{-,i}^\dagger - a_{+,i} a_{-,i}) + \frac{1}{2}i\hbar L_i(a_{+,i}^\dagger a_{-,i} - a_{+,i} a_{-,i}^\dagger), \quad (52)$$

where the quantities K_i and L_i are defined by

$$K_i = c_i \left\{ \frac{2\gamma\omega_i^2 - B^2}{2B} \left(\frac{1-\gamma}{1+\gamma} \right)^{\frac{1}{2}} - \frac{2\gamma\omega_i^2 + B^2}{2B} \left(\frac{1+\gamma}{1-\gamma} \right)^{\frac{1}{2}} \right\}, \quad (53)$$

$$L_i = c_i \left\{ \frac{2\gamma\omega_i^2 - B^2}{2B} \left(\frac{1-\gamma}{1+\gamma} \right)^{\frac{1}{2}} + \frac{2\gamma\omega_i^2 + B^2}{2B} \left(\frac{1+\gamma}{1-\gamma} \right)^{\frac{1}{2}} \right\} \quad (i = 1, \dots, N). \quad (54)$$

Inserting the solutions of the equations of motion for the boson operators (31) into (47) we get for $M(t)$ the following expression

$$M(t) = \sum_{i=1}^N m_i(t), \quad (55)$$

with

$$m_i(t) = c_i(H_i^+ - H_i^-) + \frac{1}{2}i\hbar K_i \{ a_{+,i}^\dagger a_{-,i}^\dagger \exp i(\omega_{+,i} + \omega_{-,i})t - a_{+,i} a_{-,i} \exp -i(\omega_{+,i} + \omega_{-,i})t \} + \frac{1}{2}i\hbar L_i \{ a_{+,i}^\dagger a_{-,i} \exp i(\omega_{+,i} - \omega_{-,i})t - a_{+,i} a_{-,i}^\dagger \exp -i(\omega_{+,i} - \omega_{-,i})t \} \quad (i = 1, \dots, N). \quad (56)$$

On the other hand, substituting (55) into (43) we obtain for $R(t)$:

$$R(t) = \frac{1}{N} \sum_{i,j=1}^N \{ \langle \rho m_i m_j(t) \rangle - \langle \rho m_i \rangle \langle \rho m_j \rangle \}. \quad (57)$$

Since H_i commutes with m_j for $i \neq j$, we have

$$\begin{aligned} \langle \rho m_i m_j(t) \rangle &= \langle \rho m_i \exp(iH_j t) m_j \exp(-iH_j t) \rangle \\ &= \langle \rho m_i \rangle \langle \rho \exp(iH_j t) m_j \exp(-iH_j t) \rangle \\ &= \langle \rho m_i \rangle \langle \rho m_j \rangle \quad (i \neq j) \end{aligned} \quad (58)$$

so that $R(t)$ then assumes the following form:

$$R(t) = \frac{1}{N} \sum_{i=1}^N \{ \langle \rho m_i m_i(t) \rangle - \langle \rho m_i \rangle^2 \}. \quad (59)$$

Inserting now the expressions (56) into (59) we get:

$$R(t) = \frac{1}{4N} \sum_{i=1}^N [4c_i^2 \{ \langle \rho (H_i^+)^2 \rangle - 2\langle \rho H_i^+ H_i^- \rangle + \langle \rho (H_i^-)^2 \rangle \} + \hbar^2 K_i^2 \{ \langle \rho a_{+,i}^\dagger a_{-,i}^\dagger a_{+,i} a_{-,i} \rangle \exp -i(\omega_{+,i} + \omega_{-,i})t +$$

$$\begin{aligned}
& + \langle \rho a_{+,i} a_{-,i} a_{+,i}^\dagger a_{-,i}^\dagger \rangle \exp i(\omega_{+,i} + \omega_{-,i}) t \} + \\
& + \hbar^2 L_i^2 \{ \langle \rho a_{+,i}^\dagger a_{-,i} a_{+,i} a_{-,i}^\dagger \rangle \exp -i(\omega_{+,i} - \omega_{-,i}) t + \\
& + \langle \rho a_{+,i} a_{-,i}^\dagger a_{+,i}^\dagger a_{-,i} \rangle \exp i(\omega_{+,i} - \omega_{-,i}) t \} - \\
& - 4c_i^2 \{ \langle \rho H_i^+ \rangle^2 - 2 \langle \rho H_i^+ \rangle \langle \rho H_i^- \rangle + \langle \rho H_i^- \rangle^2 \}, \quad (60)
\end{aligned}$$

where we have used the fact that the following traces vanish:

$$\langle \rho H_i^\pm a_{+,i}^\dagger a_{-,i}^\dagger \rangle = \langle \rho a_{+,i}^\dagger a_{-,i}^\dagger H_i^\pm \rangle = 0, \quad (61)$$

$$\langle \rho H_i^\pm a_{+,i}^\dagger a_{-,i} \rangle = \langle \rho a_{+,i}^\dagger a_{-,i} H_i^\pm \rangle = 0, \quad (62)$$

$$\langle \rho a_{+,i}^\dagger a_{-,i}^\dagger a_{+,i}^\dagger a_{-,i} \rangle = \langle \rho a_{+,i}^\dagger a_{-,i} a_{+,i}^\dagger a_{-,i}^\dagger \rangle = 0, \quad (63)$$

$$\langle \rho a_{+,i} a_{-,i} a_{+,i}^\dagger a_{-,i} \rangle = \langle \rho a_{+,i}^\dagger a_{-,i} a_{+,i} a_{-,i}^\dagger \rangle = 0, \quad (64)$$

$$\langle \rho a_{+,i}^\dagger a_{-,i}^\dagger \rangle = \langle \rho a_{+,i}^\dagger a_{-,i} \rangle = 0 \quad (i = 1, \dots, N). \quad (65)$$

Since furthermore

$$\langle \rho H_i^+ H_i^- \rangle = \langle \rho H_i^+ \rangle \langle \rho H_i^- \rangle \quad (i = 1, \dots, N), \quad (66)$$

we may write for $R(t)$

$$\begin{aligned}
R(t) = & \frac{1}{4N} \sum_{i=1}^N [4c_i^2 \{ \langle \rho (H_i^+)^2 \rangle - \langle \rho H_i^+ \rangle^2 + \langle \rho (H_i^-)^2 \rangle - \langle \rho H_i^- \rangle^2 \} + \\
& + \hbar^2 K_i^2 \{ \langle \rho a_{+,i}^\dagger a_{-,i}^\dagger a_{+,i} a_{-,i} \rangle \exp -i(\omega_{+,i} + \omega_{-,i}) t + \\
& + \langle \rho a_{+,i} a_{-,i} a_{+,i}^\dagger a_{-,i}^\dagger \rangle \exp i(\omega_{+,i} + \omega_{-,i}) t \} + \\
& + \hbar^2 L_i^2 \{ \langle \rho a_{+,i}^\dagger a_{-,i} a_{+,i} a_{-,i}^\dagger \rangle \exp -i(\omega_{+,i} - \omega_{-,i}) t + \\
& + \langle \rho a_{+,i} a_{-,i}^\dagger a_{+,i}^\dagger a_{-,i} \rangle \exp i(\omega_{+,i} - \omega_{-,i}) t \}]. \quad (67)
\end{aligned}$$

In order to evaluate the remaining traces in the expression (67) we make use of the following relations:

$$\langle \rho (a_{\pm,i}^\dagger a_{\pm,i} + \frac{1}{2}) \rangle = - \frac{\partial \ln Z}{\partial \beta \hbar \omega_{\pm,i}} = \frac{1}{2} \coth \frac{1}{2} \beta \hbar \omega_{\pm,i} \quad (i = 1, \dots, N), \quad (68)$$

$$\begin{aligned}
& \langle \rho (a_{\pm,i}^\dagger a_{\pm,i} + \frac{1}{2})^2 \rangle - \langle \rho (a_{\pm,i}^\dagger a_{\pm,i} + \frac{1}{2}) \rangle^2 = \\
& = \frac{\partial^2 \ln Z}{\partial (\beta \hbar \omega_{\pm,i})^2} = \frac{1}{4 \sinh^2 \frac{1}{2} \beta \hbar \omega_{\pm,i}} \quad (i = 1, \dots, N), \quad (69)
\end{aligned}$$

where the last members follow from the explicit form of the partition function Z for our system:

$$Z = \langle \exp -\beta H \rangle = \prod_{i=1}^N \frac{1}{4 \sinh \frac{1}{2} \beta \hbar \omega_{+,i} \sinh \frac{1}{2} \beta \hbar \omega_{-,i}}. \quad (70)$$

Indeed, also using the commutation relations (27), we obtain from (68):

$$\begin{aligned} \langle \rho a_{+,i}^\dagger, a_{-,i}^\dagger, a_{+,i}, a_{-,i} \rangle &= \langle \rho a_{+,i}^\dagger, a_{+,i}, a_{-,i}^\dagger, a_{-,i} \rangle = \\ &= \frac{1}{4} (\coth \frac{1}{2} \beta \hbar \omega_{+,i} - 1) (\coth \frac{1}{2} \beta \hbar \omega_{-,i} - 1), \end{aligned} \quad (71)$$

$$\begin{aligned} \langle \rho a_{+,i}, a_{-,i}, a_{+,i}^\dagger, a_{-,i}^\dagger \rangle &= \langle \rho (a_{+,i}^\dagger, a_{+,i} + 1) (a_{-,i}^\dagger, a_{-,i} + 1) \rangle = \\ &= \frac{1}{4} (\coth \frac{1}{2} \beta \hbar \omega_{+,i} + 1) (\coth \frac{1}{2} \beta \hbar \omega_{-,i} + 1), \end{aligned} \quad (72)$$

$$\begin{aligned} \langle \rho a_{+,i}^\dagger, a_{-,i}, a_{+,i}, a_{-,i}^\dagger \rangle &= \langle \rho a_{+,i}^\dagger, a_{+,i}, (a_{-,i}^\dagger, a_{-,i} + 1) \rangle = \\ &= \frac{1}{4} (\coth \frac{1}{2} \beta \hbar \omega_{+,i} - 1) (\coth \frac{1}{2} \beta \hbar \omega_{-,i} + 1), \end{aligned} \quad (73)$$

$$\begin{aligned} \langle \rho a_{+,i}, a_{-,i}^\dagger, a_{+,i}^\dagger, a_{-,i} \rangle &= \langle \rho (a_{+,i}^\dagger, a_{+,i} + 1) a_{-,i}^\dagger, a_{-,i} \rangle = \\ &= \frac{1}{4} (\coth \frac{1}{2} \beta \hbar \omega_{+,i} + 1) (\coth \frac{1}{2} \beta \hbar \omega_{-,i} - 1) \quad (i = 1, \dots, N) \end{aligned} \quad (74)$$

and from (69):

$$\langle \rho (H_i^\pm - \langle \rho H_i^\pm \rangle)^2 \rangle = \frac{\hbar^2 \omega_{\pm,i}^2}{4 \sinh^2 \frac{1}{2} \beta \hbar \omega_{\pm,i}} \quad (i = 1, \dots, N). \quad (75)$$

With these results the expression for $R(t)$ finally becomes:

$$\begin{aligned} R(t) &= \frac{\hbar^2}{4N} \sum_{i=1}^N \left\{ c_i^2 \left(\frac{\omega_{+,i}^2}{\sinh^2 \frac{1}{2} \beta \hbar \omega_{+,i}} + \frac{\omega_{-,i}^2}{\sinh^2 \frac{1}{2} \beta \hbar \omega_{-,i}} \right) \right. \\ &\quad + \frac{1}{2} K_i^2 (\coth \frac{1}{2} \beta \hbar \omega_{+,i} \coth \frac{1}{2} \beta \hbar \omega_{-,i} + 1) \cos(\omega_{+,i} + \omega_{-,i}) t \\ &\quad + \frac{1}{2} K_i^2 (\coth \frac{1}{2} \beta \hbar \omega_{+,i} + \coth \frac{1}{2} \beta \hbar \omega_{-,i}) i \sin(\omega_{+,i} + \omega_{-,i}) t \\ &\quad + \frac{1}{2} L_i^2 (\coth \frac{1}{2} \beta \hbar \omega_{+,i} \coth \frac{1}{2} \beta \hbar \omega_{-,i} - 1) \cos(\omega_{+,i} - \omega_{-,i}) t \\ &\quad \left. - \frac{1}{2} L_i^2 (\coth \frac{1}{2} \beta \hbar \omega_{+,i} - \coth \frac{1}{2} \beta \hbar \omega_{-,i}) i \sin(\omega_{+,i} - \omega_{-,i}) t \right\}. \end{aligned} \quad (76)$$

So far we have only required the interaction matrix Ω to be symmetric and to have positive eigenvalues. As we are going to investigate the behaviour of the system in the limit $N \rightarrow \infty$, we shall now make more specific assumptions concerning the matrix Ω . We suppose the elements Ω_{jk} of Ω to be given by

$$\Omega_{jk} = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta f(\theta) \exp i(j-k)\theta, \quad (77)$$

where $f(\theta)$ is an even positive function so that the elements of the matrix Ω are real and have the property that $\Omega_{jk} = \Omega_{|j-k|}$. Furthermore we require $f(\theta)$ to be piecewise strictly monotonic and differentiable for $-\pi \leq \theta \leq \pi$.

Let us define the following functions

$$\omega_{\pm}(\theta) = [\frac{1}{2} \{ B^2 + 2f(\theta) \pm 2(\gamma^2 \{ f(\theta) \}^2 + B^2 \{ f(\theta) + \frac{1}{4} B^2 \})^{\frac{1}{2}} \}]^{\frac{1}{2}}, \quad (78)$$

$$g_{\pm}(\theta) = \omega_{+}(\theta) \pm \omega_{-}(\theta), \quad (79)$$

$$\kappa(\theta) = - \frac{\{2\gamma f(\theta) - B^2\} \left(\frac{1-\gamma}{1+\gamma}\right)^{\frac{1}{2}} - \{2\gamma f(\theta) + B^2\} \left(\frac{1+\gamma}{1-\gamma}\right)^{\frac{1}{2}}}{4[\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\}]^{\frac{1}{2}}}, \quad (80)$$

$$\lambda(\theta) = - \frac{\{2\gamma f(\theta) - B^2\} \left(\frac{1-\gamma}{1+\gamma}\right)^{\frac{1}{2}} + \{2\gamma f(\theta) + B^2\} \left(\frac{1+\gamma}{1-\gamma}\right)^{\frac{1}{2}}}{4[\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\}]^{\frac{1}{2}}}. \quad (81)$$

With these definitions we may in the limit $N \rightarrow \infty$, using the theorem stated in appendix II, write $R(t)$ in the following form:

$$\begin{aligned} R(t) = & \frac{\hbar^2}{8\pi} \int_{-\pi}^{\pi} d\theta \frac{B^2}{4[\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\}]} \times \\ & \times \left[\frac{\{\omega_+(\theta)\}^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{\{\omega_-(\theta)\}^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right] + \\ & + \frac{\hbar^2}{16\pi} \int_{-\pi}^{\pi} d\theta \{\kappa(\theta)\}^2 \{\coth \frac{1}{2}\beta\hbar\omega_+(\theta) \cdot \coth \frac{1}{2}\beta\hbar\omega_-(\theta) + 1\} \cos g_+(\theta)t \\ & + \frac{\hbar^2}{16\pi} \int_{-\pi}^{\pi} d\theta \{\kappa(\theta)\}^2 \{\coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \coth \frac{1}{2}\beta\hbar\omega_-(\theta)\} i \sin g_+(\theta)t \\ & + \frac{\hbar^2}{16\pi} \int_{-\pi}^{\pi} d\theta \{\lambda(\theta)\}^2 \{\coth \frac{1}{2}\beta\hbar\omega_+(\theta) \cdot \coth \frac{1}{2}\beta\hbar\omega_-(\theta) - 1\} \cos g_-(\theta)t \\ & - \frac{\hbar^2}{16\pi} \int_{-\pi}^{\pi} d\theta \{\lambda(\theta)\}^2 \{\coth \frac{1}{2}\beta\hbar\omega_+(\theta) - \coth \frac{1}{2}\beta\hbar\omega_-(\theta)\} i \sin g_-(\theta)t. \end{aligned} \quad (82)$$

The behaviour of $R(t)$ is then completely determined by the choice of $f(\theta)$. Its asymptotic value for $t \rightarrow \infty$ can, for the general case, be found with the theorem of Riemann-Lebesgue:

$$\begin{aligned} \lim_{t \rightarrow \infty} R(t) = & \frac{\hbar^2}{8\pi} \int_{-\pi}^{\pi} d\theta \frac{B^2}{4[\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\}]} \times \\ & \times \left[\frac{\{\omega_+(\theta)\}^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{\{\omega_-(\theta)\}^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right]. \end{aligned} \quad (83)$$

In the classical limit this becomes

$$\lim_{t \rightarrow \infty} R(t) = \frac{1}{4\pi\beta^2} \int_{-\pi}^{\pi} d\theta \frac{B^2}{\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\}}. \quad (84)$$

Taking now the limit $B \rightarrow 0$ we find for the asymptotic value

$$\lim_{B \rightarrow 0} \lim_{t \rightarrow \infty} R(t) = I(\gamma) \frac{\hbar^2}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{1}{\sinh^2 \frac{1}{2} \beta \hbar \sqrt{f(\theta)}}, \quad (85)$$

where $I(\gamma)$ is the function defined by (34).

For the classical case we have

$$\lim_{B \rightarrow 0} \lim_{t \rightarrow \infty} R(t) = I(\gamma) \frac{1}{4\pi\beta^2} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)}. \quad (86)$$

We note that by taking first the limit $B \rightarrow 0$ in (82) and subsequently the limit $t \rightarrow \infty$, one finds again (85) and (86).

The asymptotic behaviour for long times of the correlation function $R(t)$ discussed above, is directly related to the ergodicity properties of the total magnetization $M(t)$. Indeed, ergodicity of $M(t)$ would imply that the time average of $R(t)$ is given by:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T R(t) dt = \frac{1}{N} \langle \rho(\bar{M}(E) - \langle \rho M \rangle)^2 \rangle, \quad (87)$$

where $\bar{M}(E)$ is the microcanonical average of M when the eigenvalue of the total Hamiltonian H is E . It can be shown that for the present model the following equality holds in the limit $N \rightarrow \infty$ (cf. appendix III):

$$\frac{1}{N} \langle \rho(\bar{M}(E) - \langle \rho M \rangle)^2 \rangle = \frac{1}{N} \frac{\langle \rho(M - \langle \rho M \rangle)(H - \langle \rho H \rangle) \rangle^2}{\langle \rho(H - \langle \rho H \rangle)^2 \rangle}. \quad (88)$$

Therefore, for our model $M(t)$ will be ergodic if, in the limit $N \rightarrow \infty$

$$\lim_{t \rightarrow \infty} R(t) = \frac{1}{N} \frac{\langle \rho(M - \langle \rho M \rangle)(H - \langle \rho H \rangle) \rangle^2}{\langle \rho(H - \langle \rho H \rangle)^2 \rangle}. \quad (89)$$

The l.h.s. of (89) has been evaluated above (see (83)). As for the r.h.s. of this equation we may, with (51) and (75), write it in the form:

$$\begin{aligned} \lim_{N \rightarrow \infty} \frac{1}{N} \frac{\langle \rho(M - \langle \rho M \rangle)(H - \langle \rho H \rangle) \rangle^2}{\langle \rho(H - \langle \rho H \rangle)^2 \rangle} &= \\ &= \left[-\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \frac{B}{2(\gamma^2 \{f(\theta)\}^2 + B^2 \{f(\theta) + \frac{1}{4} B^2\})^{\frac{1}{2}}} \times \right. \\ &\times \left. \left\{ \frac{\hbar^2 \omega_+^2(\theta)}{4 \sinh^2 \frac{1}{2} \beta \hbar \omega_+(\theta)} - \frac{\hbar^2 \omega_-^2(\theta)}{4 \sinh^2 \frac{1}{2} \beta \hbar \omega_-(\theta)} \right\}^2 \right] \times \\ &\times \left[\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \left\{ \frac{\hbar^2 \omega_+^2(\theta)}{4 \sinh^2 \frac{1}{2} \beta \hbar \omega_+(\theta)} + \frac{\hbar^2 \omega_-^2(\theta)}{4 \sinh^2 \frac{1}{2} \beta \hbar \omega_-(\theta)} \right\} \right]^{-1} \quad (90) \end{aligned}$$

which satisfies the following inequalities:

$$\begin{aligned}
 & \left[\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \frac{B}{2(\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\})^{\frac{1}{2}}} \times \right. \\
 & \quad \times \left. \left\{ \frac{\hbar^2\omega_+^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} - \frac{\hbar^2\omega_-^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right\}^2 \right] \times \\
 & \quad \times \left[\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \left\{ \frac{\hbar^2\omega_+^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{\hbar^2\omega_-^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right\} \right]^{-1} \leq \\
 & \leq \left[\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \frac{B}{2(\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\})^{\frac{1}{2}}} \times \right. \\
 & \quad \times \left. \left\{ \frac{\hbar^2\omega_+^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{\hbar^2\omega_-^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right\}^2 \right] \times \\
 & \quad \times \left[\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \left\{ \frac{\hbar^2\omega_+^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{\hbar^2\omega_-^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right\} \right]^{-1} \leq \\
 & \leq \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \frac{B^2}{4[\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\}]} \times \\
 & \quad \times \left\{ \frac{\hbar^2\omega_+^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{\hbar^2\omega_-^2(\theta)}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right\}. \tag{91}
 \end{aligned}$$

The last member of this (Schwarz-)inequality is equal to the r.h.s. of (83). We therefore conclude that in the limit $N \rightarrow \infty$

$$\lim_{t \rightarrow \infty} R(t) \geq \frac{1}{N} \frac{\langle \rho(M - \langle \rho M \rangle)(H - \langle \rho H \rangle) \rangle^2}{\langle \rho(H - \langle \rho H \rangle)^2 \rangle}. \tag{92}$$

It is seen from inspection of the explicit expression for both sides of (92) that in the general case ($B \neq 0$) the l.h.s. is larger than and not equal to the r.h.s. Thus the magnetization is in general not ergodic. However, if $B \rightarrow 0$, we have according to (85):

$$\lim_{B \rightarrow 0} \lim_{t \rightarrow \infty} R(t) = I(\gamma) \frac{\hbar^2}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{1}{\sinh^2 \frac{1}{2}\beta\hbar\sqrt{f(\theta)}},$$

while the r.h.s. of (92) reduces to

$$\lim_{B \rightarrow 0} \lim_{N \rightarrow \infty} \frac{1}{N} \frac{\langle \rho(M - \langle \rho M \rangle)(H - \langle \rho H \rangle) \rangle^2}{\langle \rho(H - \langle \rho H \rangle)^2 \rangle} = 0. \tag{93}$$

Thus we find that, if $B \rightarrow 0$ with $\gamma \neq 0$, the magnetization is ergodic. If $B \rightarrow 0$ with $\gamma = 0$ the magnetization becomes a constant of the motion, and is not ergodic, in agreement with the above result.

In this connection we may mention that a lower bound can be found for time-averaged autocorrelation functions in terms of ensemble averages involving the constants of the motion of the system. The general inequality established by Mazur⁶⁾, reads in our case

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T R(t) dt \geq \frac{1}{N} \sum_{\substack{i=1, \dots, N \\ \alpha=+, -}} \frac{\langle \rho(M - \langle \rho M \rangle)(H_i^\alpha - \langle \rho H_i^\alpha \rangle) \rangle^2}{\langle \rho(H_i^\alpha - \langle \rho H_i^\alpha \rangle)^2 \rangle}, \quad (94)$$

where the H_i^α ($i = 1, \dots, N$; $\alpha = +, -$) are the constants of the motion given by (28) and (29). It can be shown that in general ($B \neq 0$) the r.h.s. of (94) is larger than the r.h.s. of (88), so that the non-ergodicity of the magnetization in this case may already be inferred from the above inequality which is obtained without explicitly solving the dynamics of the system. However, in the limit $B \rightarrow 0$, the r.h.s. of (94) behaves differently for the cases $\gamma = 0$ and $\gamma \neq 0$, due to the non-analytic behaviour in γ of the constants of the motion in the limit $B \rightarrow 0$, and reduces in fact for the infinite system to the r.h.s. of (85). Thus in the case $B \rightarrow 0$ $\gamma \neq 0$, ergodicity of M is not excluded by the inequality (94). We may therefore conclude that there is an intimate relation between the possibility for ergodic behaviour of the magnetization and the non-analytic character of the invariants H_i^α .

5. *Conclusions.* In a recent article Niemeijer⁷⁾ studies the dynamics and statistics of the so called X-Y model for spins $\frac{1}{2}$ as a soluble model for paramagnetic relaxation. He computes the autocorrelation function for the magnetization in this model and shows that for $t \rightarrow \infty$ this function relaxes to a nonzero asymptotic value. He also finds that there is no value of the "anisotropy" parameter γ in this model, for which the correlation function becomes exponential in time, so that no "weak-coupling limit" in the conventional sense exists. Mazur has shown⁶⁾ that the asymptotic value reached by the correlation function in the X-Y model is not the thermodynamically expected value for the autocorrelation function of the magnetization, but is restricted to a higher value by the invariants of the system: the magnetization is not an ergodic function in this model.

In this chapter we studied, as it were, a soluble model for diamagnetic relaxation. We have seen that the magnetization is also in our model in general not an ergodic function, but that it does become one when the static magnetic field B tends to zero. We have pointed out that this ergodic behaviour is connected with the non-analytic nature in γ of the invariants in the limit $B \rightarrow 0$ (In fact in our model the $2N$ non-analytic invariants may be linearly combined to yield N analytic invariants, the energies of

the quasiparticles; however, the remaining N invariants are essentially non-analytic functions in γ). In this connection we may point out that in the X-Y model the invariants expressed in terms of the original operators remain analytic functions in the "coupling" parameter γ for all values of the static field B . Balescu⁸) has derived for oscillator systems conditions necessary to insure that these admit no invariants analytic in the coupling constant (special case of Poincaré's theorem). These conditions are obviously satisfied in our case for a quasiparticle (with $B = 0$) but not in the X-Y model.

Finally we wish to make three remarks:

1. It should be noted that whereas the X-Y model reduces to a fermion-problem the analogous problem treated here is a bosonproblem.
2. The treatment in this chapter has been restricted to linear chains of two-dimensional coupled oscillators, but could easily be extended to simple two-dimensional or three-dimensional arrays of these oscillators.
3. It turns out, from inspection of the expression (82) for the correlation function $R(t)$, that *even in our model and in the limit $B \rightarrow 0$* , no weak coupling limit ($\gamma \rightarrow 0$, $t \rightarrow \infty$; $\gamma^2 t = \text{finite}$) exists for the correlation function $R(t)$. Indeed, if we consider for simplicity's sake the classical case, we find that, for $B \rightarrow 0$, $R(t)$ reduces to (cf. eqs. (78)-(82)):

$$\begin{aligned}
 R(t) = & \frac{1}{8\pi\beta^2} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)} \left[\frac{1}{1-\gamma^2} - \frac{1}{\sqrt{1-\gamma^2}} \right] \times \\
 & \times \cos\{\sqrt{f(\theta)}(\sqrt{1+\gamma} + \sqrt{1-\gamma}) t\} + \\
 & + \frac{1}{8\pi\beta^2} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)} \left[\frac{1}{1-\gamma^2} + \frac{1}{\sqrt{1-\gamma^2}} \right] \times \\
 & \times \cos\{\sqrt{f(\theta)}(\sqrt{1+\gamma} - \sqrt{1-\gamma}) t\}.
 \end{aligned} \tag{95}$$

Thus ergodicity in itself of a dynamical function is not sufficient to ensure the existence of a weak-coupling limit as is customarily assumed for more complicated systems. It would be worthwhile to analyze in more detail under which conditions weak coupling limits do or do not exist. Note, for instance, that the momentum autocorrelation function for a heavy particle in a linear chain of coupled harmonic oscillators does admit a weak coupling limit (the square root of the inverse of the mass ratio M plays the role of coupling constant).

In chapter II we shall apply the results of this chapter to study the behaviour of our model under the influence of time-dependent external magnetic fields and thus obtain information about the frequency-dependent magnetic susceptibility.

APPENDIX I

In this appendix we shall derive the expressions for a_i , c_i , A_i^\pm and B_i^\pm given by (12), (13), (16) and (17) in section 2.

Substituting (10) into (9), H_i becomes (dropping the index i):

$$H = \frac{1}{2}\mathbf{P}\cdot\mathbf{U}\cdot\mathbf{P} + \frac{1}{2}\mathbf{R}\cdot\mathbf{V}\cdot\mathbf{R} + \frac{1}{2}\mathbf{R}\cdot\mathbf{W}\cdot\mathbf{P}, \quad (\text{I.1})$$

where \mathbf{U} , \mathbf{V} and \mathbf{W} are 2×2 matrices given by

$$\mathbf{U} = \{(1 - ac)^2 + c^2(\omega^2 + \frac{1}{4}B^2)\} \mathbf{1} - \{c(1 - ac)B + c^2\gamma\omega^2\} \boldsymbol{\sigma}^z, \quad (\text{I.2})$$

$$\mathbf{V} = (a^2 + \omega^2 + \frac{1}{4}B^2) \mathbf{1} + (\gamma\omega^2 - aB) \boldsymbol{\sigma}^z, \quad (\text{I.3})$$

$$\mathbf{W} = \{2a(1 - ac) - 2c(\omega^2 + \frac{1}{4}B^2)\} \boldsymbol{\sigma}^x - i\{(1 - 2ac)B + 2c\gamma\omega^2\} \boldsymbol{\sigma}^y. \quad (\text{I.4})$$

As we want H to become a sum of Hamiltonians for two independent one-dimensional oscillators we expect \mathbf{U} , \mathbf{V} and \mathbf{W} to satisfy the following conditions:

$$U_{\alpha\beta} = A_\alpha \delta_{\alpha\beta} \quad (\alpha, \beta = x, y), \quad (\text{I.5})$$

$$V_{\alpha\beta} = B_\alpha \delta_{\alpha\beta} \quad (\alpha, \beta = x, y), \quad (\text{I.6})$$

$$W_{\alpha\beta} = 0 \quad \text{for all } \alpha \text{ and } \beta \quad (\alpha, \beta = x, y). \quad (\text{I.7})$$

From (I.2) and (I.3) it is clear that \mathbf{U} and \mathbf{V} are diagonal 2×2 matrices, so the conditions (I.5) and (I.6) are already satisfied for all values of a and c . In order to make \mathbf{W} satisfy condition (I.7) the coefficients of the independent 2×2 matrices $\boldsymbol{\sigma}^x$ and $\boldsymbol{\sigma}^y$ must be equal to zero. Therefore a and c have to obey the following relations:

$$2a(1 - ac) - 2c(\omega^2 + \frac{1}{4}B^2) = 0, \quad (\text{I.8})$$

$$(1 - 2ac)B + 2c\gamma\omega^2 = 0, \quad (\text{I.9})$$

which yield for a and c :

$$a = \frac{\gamma\omega^2 - [\gamma^2\omega^4 + B^2(\omega^2 + \frac{1}{4}B^2)]^{\frac{1}{2}}}{B}, \quad (\text{I.10})$$

$$c = \frac{-B}{2[\gamma^2\omega^4 + B^2(\omega^2 + \frac{1}{4}B^2)]^{\frac{1}{2}}}. \quad (\text{I.11})$$

The other set of solutions for (I.8) and (I.9) given by

$$a = \frac{\gamma\omega^2 + [\gamma^2\omega^4 + B^2(\omega^2 + \frac{1}{4}B^2)]^{\frac{1}{2}}}{B}$$

$$c = \frac{B}{2[\gamma^2\omega^4 + B^2(\omega^2 + \frac{1}{4}B^2)]^{\frac{1}{2}}}$$

must be rejected, since this set does not exist in the limit $B \rightarrow 0$ and $\gamma > 0$. In this limit (I.10) and (I.11) both reduce to zero so that the transformation (10) reduces to the identity transformation.

Substituting now (I.10) and (I.11) into (I.2) and (I.3) we find

$$A^\pm \equiv U_{xx} = \frac{2[\gamma^2\omega^4 + B^2(\omega^2 + \frac{1}{4}B^2)]^\pm + 2\gamma\omega^2 \pm B^2}{4[\gamma^2\omega^4 + B^2(\omega^2 + \frac{1}{4}B^2)]^\pm} \quad (\text{I.12})$$

and

$$B^\pm \equiv V_{xx} = \frac{1}{B^2} \{2\gamma^2\omega^4 + 2B^2(\omega^2 + \frac{1}{4}B^2) - (2\gamma\omega^2 \mp B^2)[\gamma^2\omega^4 + B^2(\omega^2 + \frac{1}{4}B^2)]^\pm\}. \quad (\text{I.13})$$

APPENDIX II

In this appendix we state the theorem that we have used in section 4 in order to replace the summation in (76) over discrete indices by the integral in (82) over a continuous parameter, in the limit $N \rightarrow \infty$.

Theorem

If $f(\theta)$ is a real-valued Lebesgue integrable function whose Fourier coefficients are given by the elements of the $N \times N$ Toeplitz matrix Ω , *i.e.*

$$\Omega_{jk} = \Omega_{j-k} = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta f(\theta) \exp i(j-k)\theta \quad (\text{II.1})$$

$(j = 1, \dots, N; k = 1, \dots, N),$

if furthermore $\lambda_v^{(N)}$ ($v = 1, \dots, N$) are the eigenvalues of the matrix Ω , and if $F(\lambda)$ is a continuous function, we have

$$\lim_{N \rightarrow \infty} \sum_{v=1}^N \frac{F(\lambda_v^{(N)})}{N} = \frac{1}{2\pi} \int_{-\pi}^{\pi} F[f(\theta)] d\theta. \quad (\text{II.2})$$

The above theorem can be found in the monograph of Grenander and Szegő on Toeplitz forms⁹).

APPENDIX III

In this appendix we shall derive that eq. (88) of the main text holds in the limit $N \rightarrow \infty$. We consider the variables H (= total energy of the system) and M_d (= diagonal part of the magnetization in the represen-

tation in which the operators $n_{\alpha k} \equiv a_{\alpha k}^\dagger a_{\alpha k}$ ($\alpha = \pm$; $k = 1, \dots, n$) are diagonal), which are sums of N independent, canonically distributed stochastic variables:

$$H = \sum_{i=1}^N H_i = \sum_{i=1}^N (n_i^+ + \frac{1}{2}) \hbar \omega_{+,i} + (n_i^- + \frac{1}{2}) \hbar \omega_{-,i}, \quad (\text{III.1})$$

$$M_d = \sum_{i=1}^N M_{di} = \sum_{i=1}^N c_i \{ (n_i^+ + \frac{1}{2}) \hbar \omega_{+,i} - (n_i^- + \frac{1}{2}) \hbar \omega_{-,i} \}. \quad (\text{III.2})$$

Next we introduce new sumvariables \tilde{H} and \tilde{M}_d which are each sums of normalized independent stochastic variables:

$$\tilde{H} = \sum_{i=1}^N \tilde{H}_i \quad (\text{III.3})$$

and

$$\tilde{M}_d = \sum_{i=1}^N \tilde{M}_{di}, \quad (\text{III.4})$$

where \tilde{H}_i and \tilde{M}_{di} are defined as:

$$\tilde{H}_i = \frac{H_i - \langle \rho H_i \rangle}{\sigma_{H,N} N^{\frac{1}{2}}} \quad (i = 1, \dots, N) \quad (\text{III.5})$$

and

$$\tilde{M}_{di} = \frac{M_{di} - \langle \rho M_{di} \rangle}{\sigma_{M,N} N^{\frac{1}{2}}} \quad (i = 1, \dots, N). \quad (\text{III.6})$$

The quantities $\sigma_{H,N}$ and $\sigma_{M,N}$ are given by:

$$\sigma_{H,N} = \left\{ \frac{1}{N} \sum_{i=1}^N \langle \rho (H_i - \langle \rho H_i \rangle)^2 \rangle \right\}^{\frac{1}{2}} \quad (\text{III.7})$$

and

$$\sigma_{M,N} = \left\{ \frac{1}{N} \sum_{i=1}^N \langle \rho (M_{di} - \langle \rho M_{di} \rangle)^2 \rangle \right\}^{\frac{1}{2}}. \quad (\text{III.8})$$

The joint distribution function of the variables \tilde{H} and \tilde{M}_d is defined by

$$\begin{aligned} f(\tilde{H} = \tilde{X}, \tilde{M}_d = \tilde{Y}) &= \langle \rho \delta(\tilde{H} - \tilde{X}) \delta(\tilde{M}_d - \tilde{Y}) \rangle = \\ &= \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dt ds \exp(-i\tilde{X}t - i\tilde{Y}s) \langle \rho \exp(i\tilde{H}t + i\tilde{M}_d s) \rangle. \end{aligned} \quad (\text{III.9})$$

The logarithm of the trace in the last member of (III.9) can be developed in a power series in t and s in the following way:

$$\begin{aligned}
\ln \langle \rho \exp(i\tilde{H}t + i\tilde{M}_{aj}s) \rangle &= \sum_{j=1}^N \ln \frac{\langle \exp(-\beta H_j) \exp(i\tilde{H}_j t + i\tilde{M}_{aj}s) \rangle}{\langle \exp(-\beta H_j) \rangle} = \\
&= \sum_{j=1}^N \ln \left\{ 1 - \frac{1}{2} \frac{\langle \rho (H_j - \langle \rho H_j \rangle)^2 \rangle}{\sigma_{H,N}^2} \frac{t^2}{N} - \right. \\
&\quad \left. - \frac{\langle \rho (H_j - \langle \rho H_j \rangle) (M_{aj} - \langle \rho M_{aj} \rangle) \rangle}{\sigma_{H,N} \sigma_{M,N}} \frac{ts}{N} - \right. \\
&\quad \left. - \frac{1}{2} \frac{\langle \rho (M_{aj} - \langle \rho M_{aj} \rangle)^2 \rangle}{\sigma_{M,N}^2} \frac{s^2}{N} + \mathcal{O} \left(\frac{1}{N\sqrt{N}} \right) \right\} = \\
&= -\frac{1}{2} t^2 - Bts - \frac{1}{2} s^2 + \mathcal{O} \left(\frac{1}{\sqrt{N}} \right), \tag{III.10}
\end{aligned}$$

where

$$B \equiv \frac{1}{N} \sum_{j=1}^N \frac{\langle \rho (H_j - \langle \rho H_j \rangle) (M_{aj} - \langle \rho M_{aj} \rangle) \rangle}{\sigma_{H,N} \sigma_{M,N}} \quad (0 \leq B < 1). \tag{III.11}$$

Thus for large N the joint distribution function becomes Gaussian:

$$\begin{aligned}
f(\tilde{X}, \tilde{Y}) &= \frac{1}{(2\pi)^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dt ds \exp(-i\tilde{X}t - i\tilde{Y}s) \exp\{-\frac{1}{2}(t^2 + 2Bts + s^2)\} = \\
&= (2\pi\sqrt{1-B^2})^{-1} \exp \frac{-(\tilde{X}^2 - 2B\tilde{X}\tilde{Y} + \tilde{Y}^2)}{2(1-B^2)}. \tag{III.12}
\end{aligned}$$

Following the argument of the appendix of ref. 6 we finally have as $N \rightarrow \infty$:

$$\langle \rho \tilde{M}_a^2(\tilde{H} = \tilde{E}) \rangle = \frac{\langle \rho \tilde{M}_a \tilde{H}^2 \rangle}{\langle \rho \tilde{H}^2 \rangle} \tag{III.13}$$

or:

$$\frac{1}{N} \langle \rho(\bar{M}_a(E) - \langle \rho M_a \rangle)^2 \rangle = \frac{1}{N} \frac{\langle \rho (M_a - \langle \rho M_a \rangle) (H - \langle \rho H \rangle)^2 \rangle}{\langle \rho (H - \langle \rho H \rangle)^2 \rangle} \tag{III.14}$$

or (as $N \rightarrow \infty$):

$$\frac{1}{N} \langle \rho(\bar{M}(E) - \langle \rho M \rangle)^2 \rangle = \frac{1}{N} \frac{\langle \rho (M - \langle \rho M \rangle) (H - \langle \rho H \rangle)^2 \rangle}{\langle \rho (H - \langle \rho H \rangle)^2 \rangle} \tag{III.15}$$

since the non-diagonal part of M does not contribute to the traces on both sides of this formula, which is just eq. (88) of the main text.

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CHAPTER II

THEORY OF DIAMAGNETIC RELAXATION IN HARMONIC OSCILLATOR ASSEMBLIES

Synopsis

A linear response theory for simple diamagnetic systems in a time-dependent magnetic field is presented. It is shown that the average magnetization consists of two components, one following the magnetic field instantaneously, and a second one involving an after-effect function and giving rise to relaxation. Expressions are given for the isothermal, adiabatic, isolated and frequency-dependent susceptibilities per particle for diamagnetic systems. Inequalities between the various susceptibilities are derived. The various relevant quantities are calculated for the case of a linear chain of charged anisotropically coupled two-dimensional harmonic oscillators in a time-dependent magnetic field.

1. *Introduction.* In chapter I¹⁾† we solved the dynamical problem of a linear chain of charged anisotropically coupled two-dimensional harmonic oscillators in a constant magnetic field B . We also studied the autocorrelation function of the magnetization in this system, in particular its asymptotic behaviour for long times. In this chapter we shall investigate the behaviour of the system considered in the presence of a small additional time-dependent magnetic field. To this end we first develop in section 2 a linear response theory for the magnetization, in simple diamagnetic systems, to a time-dependent electromagnetic field. Whereas in the conventional linear response theory one usually deals with dynamical functions which do not explicitly depend on time, the magnetization in diamagnetic systems is a function of the canonical variables *and* of time through the electromagnetic field. As a result we find in this case that in contradistinction to the paramagnetic case, the average magnetization has a component which follows the magnetic field instantaneously, and a second component involving an after-effect function and giving rise to relaxation. As discussed in section 6 this second component becomes relatively less and less important at very low temperatures. This is the reason why the electronic diamagnetism of molecules follows the field, so to speak, instantaneously. However, inter-

† Equations and sections of chapter I, referred to in this chapter, will be preceded by the prefix 1.

molecular interactions may give rise to a small time lag. On the other hand at very high temperatures both contributions to the average magnetization are of the same order of magnitude.

We show in section 3 that in the situation in which the system is in thermal equilibrium for times $t < 0$ with respect to a magnetic field $B + b$, and in which the field b is (unrealistically) thought to be switched off at $t = 0$, the average magnetization first increases discontinuously at $t = 0$, and then has for $t > 0$ a continuous time-dependent behaviour described by the relaxation function. In particular this implies for a classical system that the magnetization which is initially zero according to Miss van Leeuwen's theorem²), jumps to a positive value at $t = 0$, before decreasing again. We give a formal expression for the relaxation function.

In section 4 formal expressions are derived for the isothermal, adiabatic and isolated susceptibilities per article. It is shown that they obey the same inequalities as the corresponding paramagnetic susceptibilities. Special cases, *i.e.* when the system is a classical one and/or ergodic, are considered. We also discuss in this section the frequency-dependent susceptibility per article $\chi(\omega)$, whose asymptotic value for $\omega \rightarrow \infty$ is related to the jump in the relaxation function.

Finally in section 5 we calculate the various quantities and functions considered in sections 2-4 for the system investigated in chapter I, and discuss their behaviour also in the light of the results obtained previously for the autocorrelation function of the magnetization.

2. *Linear response theory for simple diamagnetic systems in a time-dependent external magnetic field.* We consider a system of N interacting identical particles (charge e) moving with respect to fixed centers of force (charge $-e$). The system is subjected to a constant homogeneous external magnetic field \mathbf{B}_1 and a small time-dependent external electromagnetic field, characterized by the vector potential $\mathbf{a}(\mathbf{r}, t)$ and the scalar potential $\varphi(\mathbf{r}, t)$. The hamiltonian of the system is given by†

$$H = \sum_{i=1}^N \frac{1}{2m} \left\{ \mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times (\mathbf{R}_i + \mathbf{r}_i) - \frac{e}{c} \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \right\}^2 + e \sum_{i=1}^N \varphi(\mathbf{R}_i + \mathbf{r}_i, t) + U(\mathbf{r}^N). \quad (1)$$

Here \mathbf{R}_i is the position vector of the center of force of the i th particle, and \mathbf{r}_i and \mathbf{p}_i are the displacement and momentum vector operators of the i th particle. $U(\mathbf{r}^N)$ is the sum of the potential energy of interaction and the potential energy of the particles with respect to their fixed centers of force; m is the mass of a particle, and c is the velocity of light.

† We use rationalized gaussian units.

The operator for the total magnetization of the system is given by

$$\begin{aligned} \mathbf{M}(\mathbf{r}^N, \mathbf{p}^N; t) &= \frac{e}{2mc} \sum_{i=1}^N \left\{ \mathbf{r}_i \times \left[\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times (\mathbf{R}_i + \mathbf{r}_i) - \frac{e}{c} \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \right] \right\}. \quad (2) \end{aligned}$$

The explicit time dependence in \mathbf{M} refers to the terms on the r.h.s. of (2) involving $\mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t)$ ($i = 1, \dots, N$). Performing the canonical transformation

$$\begin{aligned} \mathbf{p}'_i &= \mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{R}_i, & (i = 1, \dots, N), \\ \mathbf{r}'_i &= \mathbf{r}_i, \end{aligned} \quad (3)$$

we obtain for the hamiltonian (omitting the primes)

$$\begin{aligned} H &= \sum_{i=1}^N \frac{1}{2m} \left[\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i - \frac{e}{c} \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \right]^2 \\ &\quad + e \sum_{i=1}^N \varphi(\mathbf{R}_i + \mathbf{r}_i, t) + U(\mathbf{r}^N) \end{aligned} \quad (4)$$

and for the total magnetization

$$\begin{aligned} \mathbf{M}(\mathbf{r}^N, \mathbf{p}^N; t) &= \frac{e}{2mc} \sum_{i=1}^N \left\{ \mathbf{r}_i \times \left[\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i - \frac{e}{c} \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \right] \right\}. \quad (5) \end{aligned}$$

We may rewrite the hamiltonian as follows:

$$\begin{aligned} H &= \sum_{i=1}^N \frac{1}{2m} \left(\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i \right)^2 + U(\mathbf{r}^N) \\ &\quad - \frac{e}{2mc} \sum_{i=1}^N \left(\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i \right) \cdot \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \\ &\quad - \frac{e}{2mc} \sum_{i=1}^N \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \cdot \left(\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i \right) \\ &\quad + e \sum_{i=1}^N \varphi(\mathbf{R}_i + \mathbf{r}_i, t) + \mathcal{O}(a^2). \end{aligned} \quad (6)$$

Taking a gauge in which

$$\operatorname{div} \mathbf{a} = 0, \quad (7)$$

we obtain to first order in \mathbf{a} and φ :

$$\begin{aligned} H &= H_{\mathbf{B}_1} - \frac{e}{mc} \sum_{i=1}^N \left(\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i \right) \cdot \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \\ &\quad + e \sum_{i=1}^N \varphi(\mathbf{R}_i + \mathbf{r}_i, t), \end{aligned} \quad (8)$$

where

$$H_{\mathbf{B}_1} = \sum_{i=1}^N \frac{1}{2m} \left(\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i \right)^2 + U(\mathbf{r}^N). \quad (9)$$

We define the current-density operator $\mathbf{j}_{\mathbf{B}_1}(\mathbf{r})$ in the absence of the external time-dependent electromagnetic field as

$$\mathbf{j}_{\mathbf{B}_1}(\mathbf{r}) \equiv \sum_{i=1}^N \frac{1}{2} e \{ (\dot{\mathbf{r}}_i)_{\mathbf{B}_1} \delta(\mathbf{R}_i + \mathbf{r}_i - \mathbf{r}) + \delta(\mathbf{R}_i + \mathbf{r}_i - \mathbf{r}) (\dot{\mathbf{r}}_i)_{\mathbf{B}_1} \} \quad (10)$$

and the charge-density operator $\rho_e(\mathbf{r})$ as

$$\rho_e(\mathbf{r}) \equiv \sum_{i=1}^N [e \delta(\mathbf{R}_i + \mathbf{r}_i - \mathbf{r}) - e \delta(\mathbf{R}_i - \mathbf{r})]. \quad (11)$$

We may then express the hamiltonian as

$$H = H_{\mathbf{B}_1} - \frac{1}{c} \int_V d\mathbf{r} \mathbf{j}_{\mathbf{B}_1}(\mathbf{r}) \cdot \mathbf{a}(\mathbf{r}, t) + \int_V d\mathbf{r} \rho_e(\mathbf{r}) \varphi(\mathbf{r}, t), \quad (12)$$

where V is a volume enclosing the system.

We now suppose the system to be in thermal equilibrium at $t = -\infty$ in the presence of the static external magnetic field \mathbf{B}_1 . We shall investigate the linear response of the average magnetization to a small external electromagnetic field, characterized by the vector potential $\mathbf{a}(\mathbf{r}, t)$ and the scalar potential $\varphi(\mathbf{r}, t)$ with $\mathbf{a}(\mathbf{r}, -\infty) = \varphi(\mathbf{r}, -\infty) = 0$. In fact we shall first derive an expression linear in $\mathbf{a}(\mathbf{r}, t)$ and $\varphi(\mathbf{r}, t)$ and, making use also of the multipole expansions for $\mathbf{j}_{\mathbf{B}_1}(\mathbf{r})$ and $\rho_e(\mathbf{r})$, convert this expression into a response formula with terms linear in the magnetic field $\mathbf{b}(\mathbf{r}, t)$ and the electric field $\mathbf{e}(\mathbf{r}, t)$ with

$$\mathbf{b}(\mathbf{r}, t) = \nabla_{\mathbf{r}} \times \mathbf{a}(\mathbf{r}, t), \quad (13)$$

$$\mathbf{e}(\mathbf{r}, t) = -\frac{1}{c} \dot{\mathbf{a}}(\mathbf{r}, t) - \nabla_{\mathbf{r}} \varphi(\mathbf{r}, t). \quad (14)$$

From eq. (5) it follows that the average magnetization at time t is given by

$$\bar{\mathbf{M}}(t) = \langle \rho(t) \mathbf{M}(t) \rangle = \langle \rho(t) \mathbf{M}_{\mathbf{B}_1} \rangle + \langle \rho(t) \mathbf{M}_1(t) \rangle, \quad (15)$$

where $\rho(t)$ is the normalized density operator at time t , and where brackets denote quantum-mechanical traces; $\mathbf{M}_{\mathbf{B}_1}$ is the magnetization operator in the absence of the time-dependent electromagnetic field

$$\mathbf{M}_{\mathbf{B}_1} = \frac{e}{2mc} \sum_{i=1}^N \mathbf{r}_i \times \left(\mathbf{p}_i - \frac{e}{2c} \mathbf{B}_1 \times \mathbf{r}_i \right), \quad (16)$$

and the operator $M_1(t)$ is given by

$$M_1(t) = -\frac{e^2}{2mc^2} \sum_{i=1}^N \mathbf{r}_i \times \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t). \quad (17)$$

Note that from eq. (17) it follows that the second term in the last member of eq. (15) itself is linear in \mathbf{a} .

With the form of the hamiltonian given in eq. (12) we can evaluate by standard methods^{3,4} the first term in the last member of eq. (15) to first order in \mathbf{a} and φ , and obtain

$$\begin{aligned} \langle \rho(t) M_{B_1} \rangle &= \langle \rho_{B_1} M_{B_1} \rangle \\ &- \frac{1}{i\hbar c} \int_0^\infty d\tau \int_V d\mathbf{r} \langle M_{B_1}(\tau) [j_{B_1}(\mathbf{r}), \rho_{B_1}] \rangle \cdot \mathbf{a}(\mathbf{r}, t - \tau) \\ &+ \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle M_{B_1}(\tau) [\rho_e(\mathbf{r}), \rho_{B_1}] \rangle \varphi(\mathbf{r}, t - \tau). \end{aligned} \quad (18)$$

For the second term in the last member of eq. (15) we get to first order in \mathbf{a} :

$$\langle \rho(t) M_1(t) \rangle = \langle \rho_{B_1} M_1(t) \rangle. \quad (19)$$

The operator ρ_{B_1} appearing in eqs. (18) and (19) is defined as

$$\rho_{B_1} = \rho(-\infty) = \exp(-\beta H_{B_1}) / \langle \exp(-\beta H_{B_1}) \rangle \quad (\beta = 1/kT). \quad (20)$$

We now make use of the well-known multipole expansions of $j_{B_1}(\mathbf{r})$ and $\rho_e(\mathbf{r})$ up to second-order terms:

$$j_{B_1}(\mathbf{r}) = \dot{\mathbf{p}}(\mathbf{r}) - \nabla_{\mathbf{r}} \cdot \dot{\mathbf{q}}(\mathbf{r}) + c \nabla_{\mathbf{r}} \times \mathbf{m}_{B_1}(\mathbf{r}) \quad (21)$$

and

$$\rho_e(\mathbf{r}) = -\nabla_{\mathbf{r}} \cdot [\mathbf{p}(\mathbf{r}) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r})], \quad (22)$$

where $\mathbf{p}(\mathbf{r})$, $\mathbf{q}(\mathbf{r})$ and $\mathbf{m}_{B_1}(\mathbf{r})$ are the electric dipole moment, quadrupole moment and magnetic dipole moment density operators, respectively:

$$\mathbf{p}(\mathbf{r}) = e \sum_{i=1}^N \mathbf{r}_i \delta(\mathbf{R}_i - \mathbf{r}), \quad (23)$$

$$\mathbf{q}(\mathbf{r}) = \frac{e}{2} \sum_{i=1}^N \mathbf{r}_i \mathbf{r}_i \delta(\mathbf{R}_i - \mathbf{r}), \quad (24)$$

$$\mathbf{m}_{B_1}(\mathbf{r}) = \frac{e}{2c} \sum_{i=1}^N \mathbf{r}_i \times (\dot{\mathbf{r}}_i)_{B_1} \delta(\mathbf{R}_i - \mathbf{r}). \quad (25)$$

One is justified in neglecting the higher-order terms in the multipole expansions, if the fields $\mathbf{a}(\mathbf{r}, t)$ and $\varphi(\mathbf{r}, t)$ do not vary too fast over the average

displacements of the particles from their centers of force. In the same order of approximation we expand in eq. (19) [see also eq. (17)] the vector potential $\mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t)$ as follows

$$\mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) = \mathbf{a}(\mathbf{R}_i, t) + (\mathbf{r}_i \cdot \nabla_{\mathbf{R}_i}) \mathbf{a}(\mathbf{R}_i, t). \quad (26)$$

Inserting eqs. (21) and (22) into eq. (18) and eq. (26) into eq. (19) we obtain after some straightforward calculations (given in detail in appendix I) the following expression for the average magnetization in terms of the fields $\mathbf{b}(\mathbf{r}, t)$ and $\mathbf{e}(\mathbf{r}, t)$

$$\begin{aligned} \bar{\mathbf{M}}(t) = & \langle \rho_{B_1} \mathbf{M}_{B_1} \rangle - \frac{e^2}{4mc^2} \sum_{i=1}^N \langle \rho_{B_1} \{ \mathbf{r}_i \times [\mathbf{b}(\mathbf{R}_i, t) \times \mathbf{r}_i] \} \rangle \\ & - \int_0^\infty d\tau \int_V d\mathbf{r} \int_0^\beta d\lambda \left[\frac{\partial}{\partial \tau} \langle \mathbf{M}_{B_1}(\tau + i\hbar\lambda) \rho_{B_1} \mathbf{m}_{B_1}(\mathbf{r}) \rangle \right] \cdot \mathbf{b}(\mathbf{r}, t - \tau) \\ & - \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [\mathbf{M}_{B_1}, \mathbf{p}(\mathbf{r}, -\tau) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r}, -\tau)] \rangle \cdot \mathbf{e}(\mathbf{r}, t - \tau). \quad (27) \end{aligned}$$

We shall assume the magnetic field to be sufficiently homogeneous over the dimensions of the system, and restrict our considerations to the response of $\mathbf{M}(t)$ to the magnetic component $\mathbf{b}(t)$ of the electromagnetic field alone †. Furthermore we suppose the static field \mathbf{B}_1 and the time-dependent field $\mathbf{b}(t)$ (with magnitudes B_1 and $b(t)$, respectively) to be directed along the z axis, and restrict the analysis to the z component of the magnetization, which will be denoted by M and referred to as the "magnetization". Integrating the third term on the r.h.s. of eq. (27) over \mathbf{r} , we then obtain

$$\begin{aligned} \Delta \bar{M}(t) \equiv \bar{M}(t) - \langle \rho_{B_1} M_{B_1} \rangle = & - \frac{e^2}{4mc^2} \sum_{i=1}^N \langle \rho_{B_1} (x_i^2 + y_i^2) \rangle b(t) \\ & - \int_0^\infty d\tau \int_0^\beta d\lambda \left[\frac{\partial}{\partial \tau} \langle \rho_{B_1} M_{B_1} M_{B_1}(\tau + i\hbar\lambda) \rangle \right] b(t - \tau). \quad (28) \end{aligned}$$

Taking e , m and c to be equal to unity and defining the quantity Q as

$$Q = -\frac{1}{4} \sum_{i=1}^N (x_i^2 + y_i^2), \quad (29)$$

† For the harmonic-oscillator model studied in section 5 it can be shown that the term in eq. (27) characterizing the response of $\mathbf{M}(t)$ to $\mathbf{e}(\mathbf{r}, t)$ vanishes if the contribution arising from the quadrupole moment is neglected.

formula (28) may be written as

$$\Delta \bar{M}(t) = \langle \rho_{B_1} Q \rangle b(t) - \int_0^\infty d\tau \int_0^\beta d\lambda \left[\frac{\partial}{\partial \tau} \langle \rho_{B_1} M_{B_1} M_{B_1}(\tau + i\hbar\lambda) \rangle \right] b(t - \tau). \quad (30)$$

It thus appears that the average magnetization has two time-dependent contributions, one following the magnetic field instantaneously and a second one involving an after-effect function.

3. *The relaxation function.* In this section we shall evaluate the relaxation function of the magnetization. To this end we suppose the system to be initially in thermal equilibrium with respect to an applied magnetic field $B_1 = B + b$ ($B > 0$, $b > 0$). At $t = 0$ the small magnetic field b is thought to be switched off suddenly[†]. We now define a function $\varphi(t)$ as follows:

$$\varphi(t) \equiv \lim_{b \rightarrow 0} \frac{1}{N} \frac{(\bar{M}(t) - \langle \rho_B M_B \rangle)}{b}. \quad (31)$$

For $t < 0$ $\varphi(t)$ represents the isothermal static magnetic susceptibility per particle $\chi_T(B)$:

$$\chi_T(B) \equiv \lim_{b \rightarrow 0} \frac{1}{N} \frac{(\langle \rho_{B+b} M_{B+b} \rangle - \langle \rho_B M_B \rangle)}{b} \equiv \frac{1}{N} \frac{\partial \langle \rho_B M_B \rangle}{\partial B}, \quad (32)$$

while for $t > 0$ $\varphi(t)$ is the relaxation function of the magnetization per particle. Thus in order to calculate $\varphi(t)$ we have to evaluate $\bar{M}(t) - \langle \rho_B M_B \rangle$ up to first order in b . Eq. (30) gives an expression for $\bar{M}(t)$ to first order in $b(t)$ for an arbitrary time dependence of the magnetic field $B(t) = B_1 + b(t)$ with $b(-\infty) = 0$. The specific time dependence of $B(t)$ for our case is

$$B(t) = B + b + b(t), \quad (33)$$

with

$$b(t) = \begin{cases} 0 & \text{for } t < 0, \\ -b & \text{for } t > 0. \end{cases} \quad (34)$$

Inserting eq. (33) into eq. (30), we obtain the following expression for $\bar{M}(t)$ [linear in $b(t)$]:

$$\bar{M}(t) = \langle \rho_{B+b} M_{B+b} \rangle + \langle \rho_{B+b} Q \rangle b(t) - \int_0^\infty d\tau \int_0^\beta d\lambda \left[\frac{\partial}{\partial \tau} \langle \rho_{B+b} M_{B+b} M_{B+b}(\tau + i\hbar\lambda) \rangle \right] b(t - \tau). \quad (35)$$

[†] It is by no means implied here that the instantaneous switching off of the field $b(t)$ can indeed be realized. We only introduce such an unphysical time dependence of $b(t)$ as a formal way to define the relaxation function, which characterizes also the response of $M(t)$ in more realistic situations (*cf.* section 4).

Using also (34), we have in particular, if $t < 0$

$$\bar{M}(t) = \langle \rho_{B+b} M_{B+b} \rangle, \quad (36)$$

and if $t > 0$

$$\begin{aligned} \bar{M}(t) &= \langle \rho_{B+b} M_{B+b} \rangle - b \langle \rho_{B+b} Q \rangle \\ &+ b \int_0^t d\tau \int_0^\beta d\lambda \frac{\partial}{\partial \tau} \langle \rho_{B+b} M_{B+b} M_{B+b}(\tau + i\hbar\lambda) \rangle. \end{aligned} \quad (37)$$

Performing the integration over τ in the last term of the r.h.s. of eq. (37), we obtain

$$\begin{aligned} \bar{M}(t) &= \langle \rho_{B+b} M_{B+b} \rangle - b \langle \rho_{B+b} Q \rangle + b \int_0^\beta d\lambda \{ \langle \rho_{B+b} M_{B+b} M_{B+b}(t + i\hbar\lambda) \rangle \\ &- \langle \rho_{B+b} M_{B+b} M_{B+b}(i\hbar\lambda) \rangle \} \quad (t > 0). \end{aligned} \quad (38)$$

In view of the definition of $\varphi(t)$ we have to linearize the traces on the r.h.s. of (36) and (38) with respect to b .

First we replace M_{B+b} by [cf. eqs. (16) and (29)]

$$M_{B+b} = M_B + bQ. \quad (39)$$

Next we expand ρ_{B+b} to first order in b :

$$\rho_{B+b} = \rho_B [1 + b \int_0^\beta d\lambda \{ M_B(-i\hbar\lambda) - \langle \rho_B M_B \rangle \}]. \quad (40)$$

Inserting (39) into (36) and (38), and subsequently expanding ρ_{B+b} according to (40), we get, neglecting all terms involving 2nd and higher orders in b , the following expressions for $\bar{M}(t)$:

$$\begin{aligned} \bar{M}(t) &= \langle \rho_B M_B \rangle + b \int_0^\beta d\lambda [\langle \rho_B M_B M_B(i\hbar\lambda) \rangle - \langle \rho_B M_B \rangle^2] + b \langle \rho_B Q \rangle \\ &(t < 0), \end{aligned} \quad (41)$$

$$\begin{aligned} \bar{M}(t) &= \langle \rho_B M_B \rangle + b \int_0^\beta d\lambda [\langle \rho_B M_B M_B(i\hbar\lambda) \rangle - \langle \rho_B M_B \rangle^2] \\ &+ b \int_0^\beta d\lambda [\langle \rho_B M_B M_B(t + i\hbar\lambda) \rangle - \langle \rho_B M_B M_B(i\hbar\lambda) \rangle] \quad (t > 0). \end{aligned} \quad (42)$$

Thus in view of the definition (31), we can finally express $\varphi(t)$ as follows:

$$\varphi(t) = \begin{cases} \frac{1}{N} \langle \rho_B Q \rangle + \frac{1}{N} \int_0^\beta d\lambda [\langle \rho_B M_B M_B(i\hbar\lambda) \rangle - \langle \rho_B M_B \rangle^2] & (t < 0), \\ \frac{1}{N} \int_0^\beta d\lambda [\langle \rho_B M_B M_B(t + i\hbar\lambda) \rangle - \langle \rho_B M_B \rangle^2] & (t > 0). \end{cases} \quad (43)$$

For the classical case we have instead of (43) and (44):

$$\varphi(t) = \begin{cases} \frac{1}{N} \langle \rho_B Q \rangle + \frac{\beta}{N} [\langle \rho_B M_B^2 \rangle - \langle \rho_B M_B \rangle^2] & (t < 0), \\ \frac{\beta}{N} [\langle \rho_B M_B M_B(t) \rangle - \langle \rho_B M_B \rangle^2] & (t > 0), \end{cases} \quad (45)$$

where ρ_B , Q and M_B are the classical analogues of the operators defined in section 2, and where the brackets now denote integration over phase space. Since for classical systems in thermal equilibrium the average magnetization is zero at any value of the applied magnetic field (according to Miss van Leeuwen's theorem²), *i.e.*, since

$$\langle \rho_{B+b} M_{B+b} \rangle = \langle \rho_B M_B \rangle = 0, \quad (47)$$

we have furthermore

$$\lim_{b \rightarrow 0} \frac{\bar{M}(t)}{Nb} = \varphi(t) = \begin{cases} 0 & (t < 0), \\ \frac{\beta}{N} \langle \rho_B M_B M_B(t) \rangle & (t > 0). \end{cases} \quad (48)$$

The result (48) can also easily be found directly from eq. (45). A very remarkable feature of diamagnetic relaxation is the discontinuity of $\varphi(t)$:

$$\Delta\varphi \equiv \lim_{t \downarrow 0} \varphi(t) - \lim_{t \uparrow 0} \varphi(t) = -\frac{1}{N} \langle \rho_B Q \rangle. \quad (50)$$

With eq. (29) it follows that the last member of (50) is always positive (both in the classical and the quantum-mechanical case). This discontinuity is characteristic of diamagnetic relaxation.

4. *Isothermal, adiabatic, isolated and frequency-dependent susceptibilities for diamagnetic systems.* a) The isothermal susceptibility χ_T . In section 3 we have already defined the isothermal susceptibility per particle χ_T for diamagnetic systems:

$$\chi_T(B) \equiv \frac{1}{N} \frac{\partial \langle \rho_B M_B \rangle}{\partial B} = \varphi(t) \quad \text{for } t < 0. \quad (51)$$

As we have seen in section 3 [*cf.* eq. (48)] we find for the classical case

$$\chi_T(B) = \varphi(t < 0) = 0 \quad (52)$$

and for the quantum-mechanical case [*cf.* eq. (43)]

$$\chi_T(B) = \frac{1}{N} \langle \rho_B Q \rangle + \int_0^{\beta} d\lambda R(i\hbar\lambda), \quad (53)$$

where $R(z)$ is the autocorrelation function of the magnetization

$$R(z) \equiv \frac{1}{N} (\langle \rho_B M_B M_B(z) \rangle - \langle \rho_B M_B \rangle^2). \quad (54)$$

b) The adiabatic susceptibility χ_s . The adiabatic susceptibility per particle χ_s is given by (*cf.* appendix II and ref. 5)

$$\chi_T - \chi_s = \frac{\beta}{N} \frac{\langle \rho_B \Delta M \Delta H \rangle^2}{\langle \rho_B (\Delta H)^2 \rangle} \geq 0, \quad (55)$$

where $\Delta H \equiv H - \langle \rho_B H \rangle$ and $\Delta M \equiv M_B - \langle \rho_B M_B \rangle$. In the classical case we have, since M is an odd and H is an even function of the velocities \mathbf{r}_i , instead of (55) the following equality:

$$\chi_T - \chi_s = \frac{\beta}{N} \frac{\langle \rho_B \Delta M \Delta H \rangle^2}{\langle \rho_B (\Delta H)^2 \rangle} = 0. \quad (56)$$

Therefore, since χ_T is zero in this case, the adiabatic susceptibility will also vanish for a classical system.

c) The isolated susceptibility χ_{is} . In order to obtain an expression for the isolated susceptibility per particle χ_{is} we first rewrite eq. (30) as follows (with $B_1 = B$):

$$\begin{aligned} \frac{1}{N} \Delta \bar{M}(t) &\equiv \frac{1}{N} [\bar{M}(t) - \langle \rho_B M_B \rangle] \\ &= \frac{1}{N} \langle \rho_B Q \rangle b(t) - \int_0^\infty d\tau \frac{d\varphi}{d\tau} b(t - \tau). \end{aligned} \quad (57)$$

Here we also used eq. (44) defining the relaxation function φ . Suppose now that $b(t)$ has the following form:

$$b(t) = \begin{cases} 0 & t < -T, \\ \frac{T+t}{T} b & -T \leq t \leq 0. \end{cases} \quad (58)$$

Then (57) reduces for $-T \leq t \leq 0$ to:

$$\begin{aligned} \Delta \bar{M}_T(t) &= \frac{1}{N} \langle \rho_B Q \rangle \frac{T+t}{T} b - b \int_0^{T+t} \frac{T+t-\tau}{T} \frac{d\varphi}{d\tau} d\tau \\ &= \frac{1}{N} \langle \rho_B Q \rangle \frac{T+t}{T} b + \varphi(0^+) \frac{T+t}{T} b - \frac{b}{T} \int_0^{T+t} \varphi(\tau) d\tau \\ &= \frac{b}{N} \frac{T+t}{T} \varphi(0^-) - \frac{b}{T} \int_0^{T+t} \varphi(\tau) d\tau, \end{aligned} \quad (59)$$

where we also have used eq. (50). The isolated susceptibility per particle is now defined† as

$$\chi_{is} \equiv \lim_{T \rightarrow \infty} \lim_{b \rightarrow 0} \frac{1}{Nb} \Delta \bar{M}_T(0). \quad (60)$$

It follows therefore with eq. (59) that

$$\chi_{is} = \varphi(0^-) - \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \varphi(t) dt = \chi_T - \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \varphi(t) dt, \quad (61)$$

where χ_T is the isothermal susceptibility [cf. eq. (51)]. It can be shown that the following relation holds [cf. appendix III]:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \varphi(t) dt = \beta \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T R(t) dt. \quad (62)$$

Furthermore it has been shown by Mazur⁶) that the following inequality holds quite generally:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T R(t) dt \geq \frac{1}{N} \frac{\langle \rho \Delta M \Delta H \rangle^2}{\langle \rho (\Delta H)^2 \rangle} \geq 0. \quad (63)$$

When the magnetization is an ergodic function, the first inequality becomes an equality in the limit of an infinite system. In view of eqs. (55), (61), (62) and (63) we obtain the following inequalities:

$$\chi_T \geq \chi_s \geq \chi_{is}. \quad (64)$$

In the classical case this reduces to [cf. eqs. (52) and (56)]:

$$0 = \chi_T = \chi_s \geq \chi_{is}. \quad (65)$$

If the magnetization is an ergodic function, we have

$$\chi_T \geq \chi_s = \chi_{is}, \quad (66)$$

and for a classical ergodic system

$$0 = \chi_T = \chi_s = \chi_{is}. \quad (67)$$

† Many authors define the isolated susceptibility per particle $\tilde{\chi}_{is}$ by choosing $b(t) = b e^{\epsilon t}$, ($t \leq 0$, $\epsilon > 0$) and writing $\tilde{\chi}_{is} \equiv \lim_{\epsilon \rightarrow 0} \lim_{b \rightarrow 0} (1/Nb) \Delta \bar{M}_\epsilon(0)$. One easily verifies, using the fact that $\varphi(t)$ is a relaxation function, that $\tilde{\chi}_{is}$ is identical with χ_{is} defined by (59) and (60). Note also that, when $\lim_{t \rightarrow \infty} \varphi(t)$ exists, χ_{is} is simply $\chi_{is} = \chi_T - \lim_{t \rightarrow \infty} \varphi(t)$. (61a)

In addition to (64) we expect for a diamagnetic system the inequality

$$\chi_T \leq 0,$$

to hold. We note that according to eq. (53) χ_T consists of two contributions of which the first one is negative and the second one positive.

It is easy to show that in the limit $\beta \rightarrow \infty$ for zero magnetic field the second contribution vanishes for a rotationally invariant hamiltonian. χ_T is then given by the conventional expression for the ground-state susceptibility

$$\chi_{T=0}(0) = -\frac{1}{4N} \sum_{i=1}^N \frac{\text{gr. st.}}{(x_i^2 + y_i^2)} = -\frac{1}{6N} \sum_{i=1}^N \frac{\text{gr. st.}}{r_i^2}. \quad (68)$$

Note that as a consequence of this value for $\chi_{T=0} = \varphi(t < 0)$, which also implies that χ_T is now simply equal to $-\Delta\varphi$, $\varphi(0^+)$ and therefore also $\varphi(t > 0)$ vanish. Therefore in this limit there is no relaxation at all and the magnetization follows the field instantaneously.

On the other hand Van Vleck⁷⁾ has given an expression for χ_T for the case of free electrons at arbitrary temperatures, which is indeed negative. For the case of a harmonic oscillator assembly with a hamiltonian which is *not* rotationally invariant, as considered in section 5, we again find that χ_T is negative as expected. We have not been able to establish in general from expression (53), that χ_T must always be negative.

d) The frequency-dependent susceptibility $\chi(\omega)$. The frequency-dependent susceptibility per particle $\chi(\omega)$ is found by Fourier inversion of (57). This leads to:

$$\frac{1}{N} \Delta \bar{M}(\omega) = \chi(\omega) b(\omega), \quad (69)$$

where $\Delta \bar{M}(\omega)$ is given by

$$\Delta \bar{M}(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} \Delta \bar{M}(t), \quad (70)$$

and $b(\omega)$ by

$$b(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} b(t), \quad (71)$$

and where $\chi(\omega)$ is

$$\chi(\omega) = \frac{1}{N} \langle \rho_B Q \rangle - \int_0^{\infty} d\tau e^{i\omega\tau} \frac{d\varphi}{d\tau}. \quad (72)$$

We note that the real part $\chi'(\omega)$ of $\chi(\omega)$ contains a constant (negative) term, which is just minus the jump in the function $\varphi(t)$. It can be shown that for

a large class of functions φ the second term on the r.h.s. of (72) vanishes in the limit $\omega \rightarrow \infty$. In this case (*cf.* also the example in section 5):

$$\lim_{\omega \rightarrow \infty} \chi(\omega) = \lim_{\omega \rightarrow \infty} \chi'(\omega) = \frac{1}{N} \langle \rho_B Q \rangle \equiv -\Delta\varphi. \quad (73)$$

The expression eq. (30) [or eq. (57)] for $\bar{M}(t)$ contains a term following the magnetic field instantaneously. We have seen that this term gives rise to the jump in φ . Here we find that it is just this same term which, for a large class of functions φ , is responsible for the non-vanishing asymptotic value of $\chi(\omega)$ in the limit $\omega \rightarrow \infty$. On the other hand we obtain in the limit $\omega \rightarrow 0$:

$$\begin{aligned} \chi(0) &= \frac{1}{N} \langle \rho_B Q \rangle - \int_0^{\infty} d\tau \frac{d\varphi}{d\tau} \\ &= \varphi(0^-) - \varphi(0^+) - \lim_{t \rightarrow \infty} \varphi(t) + \varphi(0^+) = \chi_T - \lim_{t \rightarrow \infty} \varphi(t). \end{aligned} \quad (74)$$

Comparing with (61a) we see that $\chi(0)$ exists and is identical with χ_{is} , whenever $\lim_{t \rightarrow \infty} \varphi(t)$ exists (*cf.* also ref. 4). It should be mentioned that the real and imaginary parts of the complex function $\chi(\omega) - N^{-1} \langle \rho_B Q \rangle$ satisfy Kramers-Kronig dispersion relations, as follows from conventional considerations. Furthermore eq. (72) together with the explicit expression for $\varphi(t)$ ensures that the imaginary part $\chi''(\omega)$ of $\chi(\omega)$ is non-negative for $\omega > 0$ and describes therefore absorption.

5. *Diamagnetic relaxation in harmonic oscillator assemblies.* We shall now apply the theory developed in the previous sections to the system considered in chapter I. This system consists of a linear chain of N charged anisotropically coupled two-dimensional oscillators in a magnetic field.

The hamiltonian of this system is given by†

$$H = \sum_{i=1}^N \frac{1}{2} (\mathbf{p}_i - \frac{1}{2} \mathbf{B} \times \mathbf{r}_i)^2 + \frac{1}{2} \sum_{\substack{i,j=1 \\ \alpha,\beta=x,y}}^N r_i^\alpha \Omega_{ij} (1 + \gamma \sigma_z)^{\alpha\beta} r_j^\beta. \quad (75)$$

This hamiltonian has the form of the time-independent part of the general hamiltonian eq. (4). Since the dynamical problem for this hamiltonian has been solved in chapter I, where we have also calculated the corresponding autocorrelation function for the magnetization $R(t)$, we can evaluate in a straightforward way for this model the various quantities defined in sections 2-4. In the first place we calculate with (1.46), (1.52) and (1.68) the average magnetization per particle in thermal equilibrium in the presence of a

† For notations used in this section *cf.* chapter I.

magnetic field B :

$$\frac{1}{N} \langle \rho_B M_B \rangle = -\frac{1}{N} \sum_{i=1}^N \frac{B}{4[\gamma^2 \omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]^{\frac{1}{2}}} \times (\hbar \omega_{+,i} \coth \frac{1}{2} \beta \hbar \omega_{+,i} - \hbar \omega_{-,i} \coth \frac{1}{2} \beta \hbar \omega_{-,i}) \leq 0. \quad (76)$$

The inequality follows with $\omega_{+,i} \geq \omega_{-,i} \geq 0$.

For high temperatures ($\beta \hbar \omega_{\pm,i} \ll 1$) eq. (76) reduces to

$$\frac{1}{N} \langle \rho_B M_B \rangle = -\frac{1}{12} \beta \hbar^2 B. \quad (77)$$

On the other hand for very low temperatures ($\beta \hbar \omega_{\pm,i} \gg 1$) we have:

$$\frac{1}{N} \langle \rho_B M_B \rangle = -\frac{1}{N} \sum_{i=1}^N \frac{B}{4[\gamma^2 \omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]^{\frac{1}{2}}} (\hbar \omega_{+,i} - \hbar \omega_{-,i}). \quad (78)$$

From eq. (76) we obtain according to eq. (51) an expression for the isothermal susceptibility per particle:

$$\begin{aligned} \chi_T(B) &= \frac{1}{N} \frac{\partial \langle \rho_B M_B \rangle}{\partial B} \\ &= -\frac{1}{8N} \sum_{i=1}^N \frac{2\gamma^2 \omega_i^4 - \frac{1}{2}B^4}{[\gamma^2 \omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]^{\frac{3}{2}}} \\ &\quad \times (\hbar \omega_{+,i} \coth \frac{1}{2} \beta \hbar \omega_{+,i} - \hbar \omega_{-,i} \coth \frac{1}{2} \beta \hbar \omega_{-,i}) \\ &\quad - \frac{1}{8N} \sum_{i=1}^N \frac{B^2}{[\gamma^2 \omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]} \\ &\quad \times \left(\hbar \omega_{+,i} \coth \frac{1}{2} \beta \hbar \omega_{+,i} + \hbar \omega_{-,i} \coth \frac{1}{2} \beta \hbar \omega_{-,i} \right. \\ &\quad \left. - \frac{\beta \hbar^2 \omega_{+,i}^2}{2 \sinh^2 \frac{1}{2} \beta \hbar \omega_{+,i}} - \frac{\beta \hbar^2 \omega_{-,i}^2}{2 \sinh^2 \frac{1}{2} \beta \hbar \omega_{-,i}} \right) \leq 0. \quad (79) \end{aligned}$$

The inequality follows with the help of standard inequalities involving the functions $x \coth x$ and $x \sinh^{-1} x$. We see that $\chi_T(B)$ is indeed negative for all values of B , γ and $T = (k\beta)^{-1}$.

For high temperatures ($\beta \hbar \omega_{\pm,i} \ll 1$) we have

$$\chi_T(B) = -\frac{1}{12} \beta \hbar^2, \quad (80)$$

whereas for low temperatures the susceptibility becomes

$$\begin{aligned} \chi_T(B) &= -\frac{1}{8N} \sum_{i=1}^N \frac{2\gamma^2 \omega_i^4 - \frac{1}{2}B^4}{[\gamma^2 \omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]^{\frac{3}{2}}} (\hbar \omega_{+,i} - \hbar \omega_{-,i}) \\ &\quad - \frac{1}{8N} \sum_{i=1}^N \frac{B^2}{[\gamma^2 \omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]} (\hbar \omega_{+,i} + \hbar \omega_{-,i}). \quad (81) \end{aligned}$$

As we have seen in section 3, $\varphi(t)$ has a discontinuity at $t = 0$ and jumps for our model from the negative value $\varphi(0^-)$ to the positive value $\varphi(0^+)$. The value of this jump may be calculated to be [using the transformations (1.7), (1.10), (1.18) and (1.26), as well as (1.68)]:

$$\begin{aligned} \Delta\varphi &\equiv \frac{1}{4N} \langle \rho_B \sum_{i=1}^N (x_i^2 + y_i^2) \rangle \\ &= \frac{1}{8N} \sum_{i=1}^N \frac{1}{\omega_i^2(1-\gamma^2)} \left[\hbar\omega_{+,i} \coth \frac{1}{2}\beta\hbar\omega_{+,i} \right. \\ &\quad \left. + \hbar\omega_{-,i} \coth \frac{1}{2}\beta\hbar\omega_{-,i} - \frac{2\gamma^2\omega_i^2 + B^2}{2[\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]^{\frac{1}{2}}} \right. \\ &\quad \left. \times (\hbar\omega_{+,i} \coth \frac{1}{2}\beta\hbar\omega_{+,i} - \hbar\omega_{-,i} \coth \frac{1}{2}\beta\hbar\omega_{-,i}) \right] > 0. \end{aligned} \quad (82)$$

In the classical limit ($\hbar \rightarrow 0$) the jump of $\varphi(t)$ is given by

$$\Delta\varphi = \frac{1}{2N\beta} \sum_{i=1}^N 1/\omega_i^2(1-\gamma^2). \quad (83)$$

As for the relaxation function $\varphi(t)$ [cf. eqs. (44) and (54)]

$$\varphi(t) = \int_0^\beta d\lambda R(t + i\hbar\lambda), \quad (84)$$

it can be found with the explicit expression (1.76) for $R(t)$, replacing the real argument t by $t + i\hbar\lambda$. This yields:

$$\begin{aligned} \varphi(t) &= \frac{\beta\hbar^2}{4N} \sum_{i=1}^N \frac{B^2}{4[\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]} \\ &\quad \times \left(\frac{\omega_{+,i}^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_{+,i}} + \frac{\omega_{-,i}^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_{-,i}} \right) \\ &\quad + \frac{\hbar}{4N} \sum_{i=1}^N K_i^2 \frac{\coth \frac{1}{2}\beta\hbar\omega_{+,i} + \coth \frac{1}{2}\beta\hbar\omega_{-,i}}{\omega_{+,i} + \omega_{-,i}} \cos(\omega_{+,i} + \omega_{-,i}) t \\ &\quad + \frac{\hbar}{4N} \sum_{i=1}^N L_i^2 \frac{\coth \frac{1}{2}\beta\hbar\omega_{-,i} - \coth \frac{1}{2}\beta\hbar\omega_{+,i}}{\omega_{+,i} - \omega_{-,i}} \cos(\omega_{+,i} - \omega_{-,i}) t, \end{aligned} \quad (85)$$

where K_i and L_i are defined by (1.53) and (1.54).

In the classical limit we obtain instead of (85):

$$\begin{aligned} \varphi(t) &= \frac{1}{2N\beta} \sum_{i=1}^N \frac{B^2}{[\gamma^2\omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)]} \\ &\quad + \frac{1}{2N\beta} \sum_{i=1}^N \frac{K_i^2}{\omega_i^2(1-\gamma^2)^{\frac{1}{2}}} \cos(\omega_{+,i} + \omega_{-,i}) t \\ &\quad + \frac{1}{2N\beta} \sum_{i=1}^N \frac{L_i^2}{\omega_i^2(1-\gamma^2)^{\frac{1}{2}}} \cos(\omega_{+,i} - \omega_{-,i}) t. \end{aligned} \quad (86)$$

Since we are especially interested in the behaviour of the system in the limit $N \rightarrow \infty$, we require, as in chapter I, the interaction matrix Ω to obey eq. (1.77). Using furthermore the definitions (1.78)–(1.81), we can easily express the results obtained above, in the limit $N \rightarrow \infty$, as follows: For the average magnetization per particle we have

$$\begin{aligned} \lim_{N \rightarrow \infty} \frac{1}{N} \langle \rho_B M_B \rangle &= -\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \left\{ \frac{B^2}{4\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}^{\frac{1}{2}}} \right. \\ &\quad \left. \times [\hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) - \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \right\}. \end{aligned} \quad (87)$$

For $\chi_T(B)$ we obtain:

$$\begin{aligned} \lim_{N \rightarrow \infty} \chi_T(B) &= \lim_{N \rightarrow \infty} \frac{1}{N} \frac{\partial \langle \rho_B M_B \rangle}{\partial B} \\ &= -\frac{1}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{2\gamma^2[f(\theta)]^2 - \frac{1}{2}B^4}{\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}^{\frac{3}{2}}} \\ &\quad \times [\hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) - \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \\ &\quad - \frac{1}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{B^2}{\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}^{\frac{3}{2}}} \\ &\quad \times \left\{ \hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta) \right. \\ &\quad \left. - \frac{\beta\hbar^2[\omega_+(\theta)]^2}{2 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} - \frac{\beta\hbar^2[\omega_-(\theta)]^2}{2 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right\}. \end{aligned} \quad (88)$$

For the jump of $\varphi(t)$ at $t = 0$ we get

$$\begin{aligned} \lim_{N \rightarrow \infty} \Delta\varphi &= \frac{1}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)(1 - \gamma^2)} \\ &\quad \times \left\{ \hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta) \right. \\ &\quad \left. - \frac{2\gamma^2 f(\theta) + B^2}{2\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}^{\frac{1}{2}}} \right. \\ &\quad \left. \times [\hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) - \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \right\}, \end{aligned} \quad (89)$$

and in the classical limit:

$$\lim_{N \rightarrow \infty} \Delta\varphi = \frac{1}{4\pi\beta} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)(1-\gamma^2)}. \quad (90)$$

The relaxation function $\varphi(t)$ ($t > 0$) becomes in the limit $N \rightarrow \infty$:

$$\begin{aligned} \lim_{N \rightarrow \infty} \varphi(t) &= \frac{\beta\hbar^2}{8\pi} \int_{-\pi}^{\pi} d\theta \frac{B^2}{4\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}} \\ &\times \left(\frac{[\omega_+(\theta)]^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{[\omega_-(\theta)]^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right) \\ &+ \frac{\hbar}{8\pi} \int_{-\pi}^{\pi} d\theta [\kappa(\theta)]^2 \frac{\coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \coth \frac{1}{2}\beta\hbar\omega_-(\theta)}{g_+(\theta)} \cos g_+(\theta) t \\ &+ \frac{\hbar}{8\pi} \int_{-\pi}^{\pi} d\theta [\lambda(\theta)]^2 \frac{\coth \frac{1}{2}\beta\hbar\omega_-(\theta) - \coth \frac{1}{2}\beta\hbar\omega_+(\theta)}{g_-(\theta)} \cos g_-(\theta) t, \quad (91) \end{aligned}$$

and in the classical limit:

$$\begin{aligned} \lim_{N \rightarrow \infty} \varphi(t) &= \frac{1}{4\pi\beta} \int_{-\pi}^{\pi} d\theta \frac{B^2}{\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}} \\ &+ \frac{1}{4\pi\beta} \int_{-\pi}^{\pi} d\theta \frac{[\kappa(\theta)]^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \cos g_+(\theta) t \\ &+ \frac{1}{4\pi\beta} \int_{-\pi}^{\pi} d\theta \frac{[\lambda(\theta)]^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \cos g_-(\theta) t. \quad (92) \end{aligned}$$

Now that we have taken the limit $N \rightarrow \infty$ for the relaxation function, we are in a position to evaluate the asymptotic value of $\varphi(t)$ in the limit $t \rightarrow \infty$. From eq. (91) we find for the quantum-mechanical case, with the conditions we have imposed on the function $f(\theta)$ in 1. section 4, and making use of the Riemann-Lebesgue theorem

$$\begin{aligned} \lim_{N \rightarrow \infty} (\chi_T - \chi_{is}) &\equiv \lim_{t \rightarrow \infty} \lim_{N \rightarrow \infty} \varphi(t) \\ &= \frac{\beta\hbar^2}{8\pi} \int_{-\pi}^{\pi} d\theta \frac{B^2}{4\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}} \\ &\times \left(\frac{[\omega_+(\theta)]^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{[\omega_-(\theta)]^2}{\sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right). \quad (93) \end{aligned}$$

For $\hbar \rightarrow 0$ this reduces to

$$\begin{aligned} \lim_{N \rightarrow \infty} (\chi_T - \chi_{1s}) &= \lim_{t \rightarrow \infty} \lim_{N \rightarrow \infty} \varphi(t) \\ &= \frac{1}{4\pi\beta} \int_{-\pi}^{\pi} d\theta \frac{B^2}{\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}}. \end{aligned} \quad (94)$$

If, however, the magnetization were to relax to its new thermodynamic equilibrium value, we should have found as asymptotic value of $\varphi(t)$ for $t \rightarrow \infty$:

$$\lim_{t \rightarrow \infty} \lim_{N \rightarrow \infty} \varphi(t) = \lim_{N \rightarrow \infty} \frac{\beta}{N} \frac{\langle \rho \Delta M \Delta H \rangle^2}{\langle \rho (\Delta H)^2 \rangle} \equiv \lim_{N \rightarrow \infty} [(\chi_T - \chi_s)]. \quad (95)$$

The second member of (95) is given explicitly by [cf. eq. (1.90)]:

$$\begin{aligned} &\lim_{N \rightarrow \infty} \frac{\beta}{N} \frac{\langle \rho \Delta M \Delta H \rangle^2}{\langle \rho (\Delta H)^2 \rangle} \\ &= \beta \left[\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \frac{B}{2\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}^{\frac{1}{2}}} \right. \\ &\quad \times \left. \left(\frac{\hbar^2[\omega_+(\theta)]^2}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} - \frac{\hbar^2[\omega_-(\theta)]^2}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right) \right]^2 \\ &\quad \times \left[\frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \left(\frac{\hbar^2[\omega_+(\theta)]^2}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_+(\theta)} + \frac{\hbar^2[\omega_-(\theta)]^2}{4 \sinh^2 \frac{1}{2}\beta\hbar\omega_-(\theta)} \right) \right]^{-1}, \end{aligned} \quad (96)$$

which vanishes in the classical limit:

$$\lim_{\hbar \rightarrow 0} \lim_{N \rightarrow \infty} \frac{\beta}{N} \frac{\langle \rho \Delta M \Delta H \rangle^2}{\langle \rho (\Delta H)^2 \rangle} = 0. \quad (97)$$

Comparing the r.h.s. of (96) with the last member of (93) (cf. 1. section 4) and the r.h.s. of (97) with the last member of (94), we can easily check that for our model the general inequalities (64) and (65) hold.

Furthermore the asymptotic value of $\varphi(t)$ for our model is in the quantum-mechanical case in general not equal to the r.h.s. of (96) and in the classical case in general not equal to zero, so that true thermodynamic equilibrium is not established in general, or equivalently:

$$\chi_s > \chi_{1s}. \quad (98)$$

However, if we also take the limit $B \rightarrow 0$, we find instead of (93):

$$\lim_{B \rightarrow 0} \lim_{t \rightarrow \infty} \lim_{N \rightarrow \infty} \varphi(t) = I(\gamma) \frac{\beta\hbar^2}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{1}{\sinh^2 \frac{1}{2}\beta\hbar[f(\theta)]^{\frac{1}{2}}}, \quad (99)$$

where $I(\gamma)$ is the function defined by (1.34).

In the classical case we obtain instead of (94):

$$\lim_{B \rightarrow 0} \lim_{t \rightarrow \infty} \lim_{N \rightarrow \infty} \varphi(t) = I(\gamma) \frac{1}{4\pi\beta} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)}. \quad (100)$$

Note that the results (99) and (100) are insensitive to the interchange of the limits $B \rightarrow 0$ and $t \rightarrow \infty$. Thus both classically and quantum-mechanically $\varphi(t)$ vanishes as $t \rightarrow \infty$, when $B \rightarrow 0$ with $\gamma \neq 0$. This implies that in this special case ($B \rightarrow 0, \gamma \neq 0$) we have:

$$\chi_T = \chi_{is}, \quad (101)$$

and thus with (64):

$$\chi_T = \chi_s = \chi_{is}, \quad (102)$$

while we have in addition in the classical limit $\chi_T = 0$. The equality sign between χ_s and χ_{is} in (102) expresses the fact, that in the case ($B \rightarrow 0, \gamma \neq 0$), the magnetization relaxes to its new thermodynamic equilibrium value. This is a consequence of the fact that the magnetization is in this case ergodic as shown in 1. section 4, where we also discussed the connection between this property and the nature of the constants of the motion for varying values of B and γ .

To summarize: we have found the following general behaviour of $\varphi(t)$ for our model (in the limit $N \rightarrow \infty$) in the quantum-mechanical case

$$\left. \begin{aligned} \varphi(t) &= \chi_T(B) \frac{1}{2} < 0 & \text{for } t < 0, \\ \varphi(0^+) &> 0, \\ |\varphi(t)| &\leq \varphi(0^+) & \text{for } t > 0, \\ \lim_{t \rightarrow \infty} \varphi(t) &= \chi_T - \chi_{is} \geq \chi_T - \chi_s \geq 0, \end{aligned} \right\} \quad (103)$$

i.e. the function $\varphi(t)$ is first negative, then jumps to a positive value at $t = 0$, and finally relaxes to a non-negative value. True equilibrium is again established only in the case $B \rightarrow 0, \gamma \neq 0$, (*i.e.* when $\chi_T = \chi_s = \chi_{is}$).

Finally we want to give an explicit expression for the frequency-dependent susceptibility per particle for our model. In the limit of an infinite system we obtain with eqs. (72), (89) and (91):

$$\begin{aligned} \chi(\omega) &= -\frac{1}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)(1-\gamma^2)} \\ &\times \left\{ \hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta) \right. \\ &\quad \left. - \frac{2\gamma^2 f(\theta) + B^2}{2\{\gamma^2[f(\theta)]^2 + B^2[f(\theta) + \frac{1}{4}B^2]\}^{\frac{1}{2}}} \right\} \end{aligned}$$

$$\begin{aligned}
& \times [\hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) - \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \Big\} \\
& + \frac{\hbar}{8\pi} \int_0^\infty d\tau e^{i\omega\tau} \int_{-\pi}^\pi d\theta \{ [\kappa(\theta)]^2 [\coth \frac{1}{2}\beta\hbar\omega_+(\theta) \\
& + \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \sin g_+(\theta) \tau + \\
& + [\lambda(\theta)]^2 [\coth \frac{1}{2}\beta\hbar\omega_-(\theta) - \coth \frac{1}{2}\beta\hbar\omega_+(\theta)] \sin g_-(\theta) \tau \}. \quad (104)
\end{aligned}$$

Using now the following relation:

$$\int_0^\infty e^{ixt} dt = \pi\delta(x) - P(1/ix), \quad (105)$$

where P stands for principal value, we have:

$$\begin{aligned}
\chi(\omega) &= \chi(\infty) \\
&+ \frac{\hbar}{8\pi} \int_{-\pi}^\pi d\theta \left\{ [\kappa(\theta)]^2 [\coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \right. \\
&\times \frac{1}{2i} \{ \pi\delta[\omega + g_+(\theta)] - \pi\delta[\omega - g_+(\theta)] \} \Big\} \\
&+ \frac{\hbar}{8\pi} P \int_{-\pi}^\pi d\theta \left\{ [\kappa(\theta)]^2 [\coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \right. \\
&\times \frac{1}{2} \left(\frac{1}{\omega + g_+(\theta)} - \frac{1}{\omega - g_+(\theta)} \right) \Big\} \\
&+ \frac{\hbar}{8\pi} \int_{-\pi}^\pi d\theta \left\{ [\lambda(\theta)]^2 [\coth \frac{1}{2}\beta\hbar\omega_-(\theta) - \coth \frac{1}{2}\beta\hbar\omega_+(\theta)] \right. \\
&\times \frac{1}{2i} \{ \pi\delta[\omega + g_-(\theta)] - \pi\delta[\omega - g_-(\theta)] \} \Big\} \\
&+ \frac{\hbar}{8\pi} P \int_{-\pi}^\pi d\theta \left\{ [\lambda(\theta)]^2 [\coth \frac{1}{2}\beta\hbar\omega_-(\theta) - \coth \frac{1}{2}\beta\hbar\omega_+(\theta)] \right. \\
&\times \frac{1}{2} \left(\frac{1}{\omega + g_-(\theta)} - \frac{1}{\omega - g_-(\theta)} \right) \Big\}, \quad (106)
\end{aligned}$$

with

$$\begin{aligned} \chi(\infty) = \lim_{\omega \rightarrow \infty} \chi(\omega) = & -\frac{1}{16\pi} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)(1-\gamma^2)} \\ & \times \left\{ \hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) + \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta) \right. \\ & - \frac{[2\gamma^2 f(\theta) + B^2]}{2\{\gamma^2 [f(\theta)]^2 + B^2 [f(\theta) + \frac{1}{4}B^2]\}^{\frac{1}{2}}} \\ & \left. \times [\hbar\omega_+(\theta) \coth \frac{1}{2}\beta\hbar\omega_+(\theta) - \hbar\omega_-(\theta) \coth \frac{1}{2}\beta\hbar\omega_-(\theta)] \right\}, \end{aligned} \quad (107)$$

which is precisely equal to $-\Delta\varphi$, as given by (89) [cf. eq. (73)].

By choosing $\omega > 0$, the delta functions $\delta[\omega + g_+(\theta)]$ and $\delta[\omega + g_-(\theta)]$ vanish in the interval $-\pi \leq \theta \leq \pi$, since $g_{\pm}(\theta) \geq 0$ for $-\pi \leq \theta \leq \pi$. After some simple calculations we obtain the following expressions for $\chi'(\omega)$ and $\chi''(\omega)$ [respectively the real and the imaginary parts of $\chi(\omega)$]:

$$\begin{aligned} \chi'(\omega) = \chi(\infty) - \frac{\hbar}{8\pi} \text{P} \int_{-\pi}^{\pi} d\theta [\kappa(\theta)]^2 \\ & \times \frac{\sinh \frac{1}{2}\beta\hbar g_+(\theta)}{\sinh \frac{1}{2}\beta\hbar\omega_+(\theta) \sinh \frac{1}{2}\beta\hbar\omega_-(\theta)} \frac{g_+(\theta)}{\omega^2 - [g_+(\theta)]^2} \\ & - \frac{\hbar}{8\pi} \text{P} \int_{-\pi}^{\pi} d\theta [\lambda(\theta)]^2 \\ & \times \frac{\sinh \frac{1}{2}\beta\hbar g_-(\theta)}{\sinh \frac{1}{2}\beta\hbar\omega_+(\theta) \sinh \frac{1}{2}\beta\hbar\omega_-(\theta)} \frac{g_-(\theta)}{\omega^2 - [g_-(\theta)]^2}, \end{aligned} \quad (108)$$

and

$$\begin{aligned} \chi''(\omega) = \frac{\hbar}{16} \sinh \frac{1}{2}\beta\hbar\omega \int_{-\pi}^{\pi} d\theta \frac{[\kappa(\theta)]^2}{\sinh \frac{1}{2}\beta\hbar\omega_+(\theta) \sinh \frac{1}{2}\beta\hbar\omega_-(\theta)} \delta[\omega - g_+(\theta)] \\ + \frac{\hbar}{16} \sinh \frac{1}{2}\beta\hbar\omega \int_{-\pi}^{\pi} d\theta \frac{[\lambda(\theta)]^2}{\sinh \frac{1}{2}\beta\hbar\omega_+(\theta) \sinh \frac{1}{2}\beta\hbar\omega_-(\theta)} \delta[\omega - g_-(\theta)]. \end{aligned} \quad (109)$$

In the classical (or high-temperature) limit we have:

$$\begin{aligned} \chi'(\omega) = \chi(\infty) - \frac{1}{4\pi\beta} \text{P} \int_{-\pi}^{\pi} d\theta \frac{[\kappa(\theta)]^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \frac{[g_+(\theta)]^2}{\omega^2 - [g_+(\theta)]^2} \\ - \frac{1}{4\pi\beta} \text{P} \int_{-\pi}^{\pi} d\theta \frac{[\lambda(\theta)]^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \frac{[g_-(\theta)]^2}{\omega^2 - [g_-(\theta)]^2}, \end{aligned} \quad (110)$$

where $\chi(\infty)$ is now given by

$$\chi(\infty) = -\frac{1}{4\pi\beta} \int_{-\pi}^{\pi} d\theta \frac{1}{f(\theta)(1-\gamma^2)}. \quad (111)$$

The imaginary part can in the classical limit be expressed as:

$$\begin{aligned} \chi''(\omega) &= \frac{\omega}{8\beta} \int_{-\pi}^{\pi} d\theta \frac{[\kappa(\theta)]^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \delta[\omega - g_+(\theta)] \\ &+ \frac{\omega}{8\beta} \int_{-\pi}^{\pi} d\theta \frac{[\lambda(\theta)]^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \delta[\omega - g_-(\theta)]. \end{aligned} \quad (112)$$

It is seen from eq. (109) that $\chi''(\omega)$ is non-negative for $\omega > 0$ as expected. One can finally check from eq. (106) that $\chi(0)$ is indeed equal to χ_{is} .

6. *Conclusions.* In the preceding sections we have developed a theory of diamagnetic relaxation and pointed out the essential differences of this phenomenon with paramagnetic relaxation. The main difference was the occurrence of a discontinuity in the relaxation function. We have illustrated this specific behaviour of diamagnetic relaxation for the case of the linear chain of two-dimensional harmonic oscillators. For this model we can therefore estimate the magnitude of the discontinuity in terms of the characteristic quantities of the system. Defining the ratio

$$D = \Delta\varphi/|\chi_T|, \quad (113)$$

as a measure for the relative importance of the discontinuity, we find quite generally from eqs. (79) and (82) that for this model

$$D \geq 1. \quad (114)$$

In particular we have for high temperatures

$$D = \frac{6}{1-\gamma^2} \frac{1}{N} \sum_{i=1}^N \frac{1}{\beta^2 \hbar^2 \omega_i^2}. \quad (115)$$

and for very low temperatures

$$D \geq \frac{1}{2} [1 + (1 - \gamma^2)^{\frac{1}{2}}] / (1 - \gamma^2)^{\frac{1}{2}}. \quad (116)$$

Thus D depends under all circumstances on the magnitude of the anisotropy parameter γ , and becomes large for large $|\gamma|$ ($|\gamma| \leq 1$), as well as at high temperatures. (Experimentally the discontinuity could be found from the asymptotic value of the dispersion $\chi'(\omega)$ for $\omega \rightarrow \infty$.)

We note that even in the low-temperature limit D can be larger than unity. This implies that even in this limit the magnetization after a „sudden“ reduction of the field will at first overshoot its new equilibrium value and must therefore reestablish this value with some time lag. This relaxation phenomenon is described by the function $\varphi(t)$ [eq. (91)] in the corresponding limit ($\beta \rightarrow \infty$):

$$\varphi(t) = \frac{\hbar}{4\pi} \int_{-\pi}^{\pi} d\theta [\kappa(\theta)]^2 \frac{\cos g_+(\theta) t}{g_+(\theta)}. \quad (117)$$

The following comments may now be made:

1. In the above limit $\varphi(t)$ vanishes as t tends to infinity, for all values of γ and B . This implies, in view of the previously derived inequalities, that $\chi_T = \chi_S = \chi_{is}$, as one would expect for a system in its ground state.
2. For $B = 0$ and $\gamma = 0$ $\varphi(t)$ vanishes for all $t \geq 0$. But this is the case, when D is equal to unity, that is, when the magnetization achieves its equilibrium value instantaneously.
3. Even when the system is in its ground state, nonzero values of γ , which characterize the anisotropy of the interaction between the oscillators, give rise to small relaxation effects. In this connection we refer to the controversy concerning the so-called inertia of the Faraday effect⁸).

Although we were able to come to many of these conclusions on the basis of the behaviour of a specific model, it may be expected that they retain in a qualitative way their validity for real diamagnetic systems.

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APPENDIX I

We shall derive here eq. (27) of the main text. Inserting eqs. (21) and (22) into eq. (18) we obtain

$$\begin{aligned} \langle \rho(t) M_{B_1} \rangle &= \langle \rho_{B_1} M_{B_1} \rangle - \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \\ &\langle M_{B_1}(\tau) [\dot{\mathbf{p}}(\mathbf{r}) - \mathbf{V}_r \cdot \dot{\mathbf{q}}(\mathbf{r}) + c \mathbf{V}_r \times \mathbf{m}_{B_1}(\mathbf{r}, \rho_{B_1})] \cdot \mathbf{a}(\mathbf{r}, t - \tau) \\ &+ \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \\ &\langle M_{B_1}(\tau) [-\mathbf{V}_r \cdot \{\mathbf{p}(\mathbf{r}) - \mathbf{V}_r \cdot \mathbf{q}(\mathbf{r})\}, \rho_{B_1}] \rangle \varphi(\mathbf{r}, t - \tau). \end{aligned} \quad (I.1)$$

By cyclic permutation of the operators in the quantum-mechanical traces in eq. (I.1) and splitting up the second term on the r.h.s. of eq. (I.1) into two terms we get

$$\begin{aligned}
 \langle \rho(t) M_{B_1} \rangle &= \langle \rho_{B_1} M_{B_1} \rangle - \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \\
 &\quad \langle \rho_{B_1} [M_{B_1}, \dot{\mathbf{p}}(\mathbf{r}, -\tau) - \nabla_{\mathbf{r}} \cdot \dot{\mathbf{q}}(\mathbf{r}, t - \tau)] \rangle \cdot \mathbf{a}(\mathbf{r}, t - \tau) \\
 &\quad - \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}(\tau), \nabla_{\mathbf{r}} \times \mathbf{m}_{B_1}(\mathbf{r})] \rangle \cdot \mathbf{a}(\mathbf{r}, t - \tau) \\
 &\quad - \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \\
 &\quad \langle \rho_{B_1} [M_{B_1}, \nabla_{\mathbf{r}} \cdot \{\mathbf{p}(\mathbf{r}, -\tau) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r}, -\tau)\}] \rangle \varphi(\mathbf{r}, t - \tau). \quad (\text{I.2})
 \end{aligned}$$

Integration by parts of the terms on the r.h.s. of eq. (I.2) (the second term with respect to τ , the third and fourth term with respect to \mathbf{r}) yields

$$\begin{aligned}
 \langle \rho(t) M_{B_1} \rangle &= \langle \rho_{B_1} M_{B_1} \rangle \\
 &\quad - \frac{1}{i\hbar} \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r})] \rangle \cdot \mathbf{a}(\mathbf{r}, t) \\
 &\quad + \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}, -\tau) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r}, -\tau)] \rangle \cdot \mathbf{a}(\mathbf{r}, t - \tau) \\
 &\quad - \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}(\tau), \mathbf{m}_{B_1}(\mathbf{r})] \rangle \cdot \nabla_{\mathbf{r}} \times \mathbf{a}(\mathbf{r}, t - \tau) \\
 &\quad + \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}, -\tau) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r}, -\tau)] \rangle \cdot \nabla_{\mathbf{r}} \varphi(\mathbf{r}, t - \tau). \quad (\text{I.3})
 \end{aligned}$$

Making use of eqs. (13) and (14) we obtain the following expression

$$\begin{aligned}
 \langle \rho(t) M_{B_1} \rangle &= \langle \rho_{B_1} M_{B_1} \rangle - \frac{1}{i\hbar} \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r})] \rangle \cdot \mathbf{a}(\mathbf{r}, t) \\
 &\quad - \frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}, -\tau) - \nabla_{\mathbf{r}} \cdot \mathbf{q}(\mathbf{r}, -\tau)] \rangle \cdot \mathbf{e}(\mathbf{r}, t - \tau)
 \end{aligned}$$

$$-\frac{1}{i\hbar} \int_0^{\infty} d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}(\tau), \mathbf{m}_{B_1}(\mathbf{r})] \rangle \cdot \mathbf{b}(\mathbf{r}, t - \tau). \quad (\text{I.4})$$

The last term on the r.h.s. of eq. (I.4) may be transformed in the usual way to yield

$$\begin{aligned} & -\frac{1}{i\hbar} \int_0^{\infty} d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}(\tau), \mathbf{m}_{B_1}(\mathbf{r})] \rangle \cdot \mathbf{b}(\mathbf{r}, t - \tau) \\ &= -\frac{1}{i\hbar} \int_0^{\infty} d\tau \int_V d\mathbf{r} \int_0^{\beta} d\lambda \frac{\partial}{\partial \lambda} \langle M_{B_1}(\tau + i\hbar\lambda) \rho_{B_1} \mathbf{m}_{B_1}(\mathbf{r}) \rangle \cdot \mathbf{b}(\mathbf{r}, t - \tau) \\ &= -\int_0^{\infty} d\tau \int_V d\mathbf{r} \int_0^{\beta} d\lambda \left[\frac{\partial}{\partial \tau} \langle M_{B_1}(\tau + i\hbar\lambda) \rho_{B_1} \mathbf{m}_{B_1}(\mathbf{r}) \rangle \right] \cdot \mathbf{b}(\mathbf{r}, t - \tau). \quad (\text{I.5}) \end{aligned}$$

The second term on the r.h.s. of eq. (I.4) becomes after partial integration with respect to \mathbf{r}

$$\begin{aligned} & -\frac{1}{ic\hbar} \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}) - \mathbf{V}_r \cdot \mathbf{q}(\mathbf{r})] \rangle \cdot \mathbf{a}(\mathbf{r}, t) \\ &= -\frac{e^2}{2ic^2\hbar} \sum_{i=1}^N \{ \langle \rho_{B_1} [\mathbf{r}_i \times \dot{\mathbf{r}}_i, \mathbf{r}_i] \rangle \cdot \mathbf{a}(\mathbf{R}_i, t) \\ &+ \frac{1}{2} \langle \rho_{B_1} [\mathbf{r}_i \times \dot{\mathbf{r}}_i, \mathbf{r}_i \mathbf{r}_i] \rangle : \mathbf{V}_{R_i} \mathbf{a}(\mathbf{R}_i, t) \}, \quad (\text{I.6}) \end{aligned}$$

where use has been made of the symmetry of the tensor \mathbf{q} . The first term on the r.h.s. of eq. (I.6) is given by

$$\begin{aligned} & -\frac{e^2}{2c^2} \frac{1}{i\hbar} \sum_{i=1}^N \langle \rho_{B_1} [\mathbf{r}_i \times \dot{\mathbf{r}}_i, \mathbf{r}_i] \rangle \cdot \mathbf{a}(\mathbf{R}_i, t) \\ &= -\frac{e^2}{2c^2} \frac{1}{i\hbar} \sum_{i=1}^N \langle \rho_{B_1} \mathbf{r}_i \times [\dot{\mathbf{r}}_i, \mathbf{r}_i] \rangle \cdot \mathbf{a}(\mathbf{R}_i, t) \\ &= -\frac{e^2}{2c^2} \frac{1}{i\hbar} \sum_{i=1}^N \langle \rho_{B_1} \mathbf{r}_i \rangle \times \frac{\hbar}{i} \frac{1}{m} \mathbf{a}(\mathbf{R}_i, t) \\ &= \frac{e^2}{2mc^2} \sum_{i=1}^N \langle \rho_{B_1} \mathbf{r}_i \times \mathbf{a}(\mathbf{R}_i, t) \rangle. \quad (\text{I.7}) \end{aligned}$$

Next we consider the vector given by the second term on the r.h.s. of eq. (I.6). Apart from a factor $-e^2(4ic^2\hbar)^{-1}$ the α component of this vector is given by

(restricting the argument to the i th particle and omitting the index i)

$$\begin{aligned}
 & \langle \rho_{\mathbf{B}_1}[\mathbf{r} \times \dot{\mathbf{r}}, \mathbf{r}\mathbf{r}] : \mathbf{V}_{\mathbf{R}}\mathbf{a}(\mathbf{R}, t) \rangle_{\alpha} \\
 &= \sum_{\beta, \gamma, \mu, \nu} \langle \rho_{\mathbf{B}_1} \varepsilon_{\alpha\beta\gamma} r_{\beta} [\dot{r}_{\gamma}, r_{\mu} r_{\nu}] \rangle \frac{\partial a_{\mu}(\mathbf{R}, t)}{\partial R_{\nu}} \\
 &= \sum_{\beta, \gamma, \mu, \nu} \langle \rho_{\mathbf{B}_1} \varepsilon_{\alpha\beta\gamma} r_{\beta} ([\dot{r}_{\gamma}, r_{\mu}] r_{\nu} + r_{\mu} [\dot{r}_{\gamma}, r_{\nu}]) \rangle \frac{\partial a_{\mu}(\mathbf{R}, t)}{\partial R_{\nu}} \\
 &= \frac{\hbar}{i} \frac{1}{m} \sum_{\beta, \gamma, \mu, \nu} \langle \rho_{\mathbf{B}_1} \varepsilon_{\alpha\beta\gamma} (r_{\beta} r_{\nu} \delta_{\gamma\mu} + r_{\beta} r_{\mu} \delta_{\gamma\nu}) \rangle \frac{\partial a_{\mu}(\mathbf{R}, t)}{\partial R_{\nu}} \\
 &= \frac{\hbar}{i} \frac{1}{m} \left\{ \sum_{\beta, \gamma, \nu} \left\langle \rho_{\mathbf{B}_1} \varepsilon_{\alpha\beta\gamma} r_{\beta} r_{\nu} \frac{\partial a_{\gamma}(\mathbf{R}, t)}{\partial R_{\nu}} \right\rangle \right. \\
 & \quad \left. + \sum_{\beta, \gamma, \mu} \left\langle \rho_{\mathbf{B}_1} \varepsilon_{\alpha\beta\gamma} r_{\beta} r_{\mu} \frac{\partial a_{\mu}(\mathbf{R}, t)}{\partial R_{\gamma}} \right\rangle \right\} \\
 &= \frac{\hbar}{i} \frac{1}{m} \{ \langle \rho_{\mathbf{B}_1} \mathbf{r} \times (\mathbf{r} \cdot \mathbf{V}_{\mathbf{R}}) \mathbf{a}(\mathbf{R}, t) \rangle + \langle \rho_{\mathbf{B}_1} \mathbf{r} \times \mathbf{V}_{\mathbf{R}}[\mathbf{r} \cdot \mathbf{a}(\mathbf{R}, t)] \rangle \}_{\alpha}, \quad (\text{I.8})
 \end{aligned}$$

where $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor

$$\varepsilon_{\alpha\beta\gamma} = \begin{cases} 1 & \text{if } \alpha, \beta, \gamma = 1, 2, 3 \text{ cycl.}, \\ -1 & \text{if } \alpha, \beta, \gamma = 2, 1, 3 \text{ cycl.}, \\ 0 & \text{otherwise.} \end{cases} \quad (\text{I.9})$$

The second term on the r.h.s. of eq. (I.6) may thus be written as

$$\begin{aligned}
 & - \frac{e^2}{4ic^2\hbar} \sum_{i=1}^N \langle \rho_{\mathbf{B}_1}[\mathbf{r}_i \times \dot{\mathbf{r}}_i, \mathbf{r}_i \mathbf{r}_i] : \mathbf{V}_{\mathbf{R}_i} \mathbf{a}(\mathbf{R}_i, t) \rangle \\
 &= \frac{e^2}{4mc^2} \sum_{i=1}^N \{ \langle \rho_{\mathbf{B}_1} \mathbf{r}_i \times (\mathbf{r}_i \cdot \mathbf{V}_{\mathbf{R}_i}) \mathbf{a}(\mathbf{R}_i, t) \rangle \\
 & \quad + \langle \rho_{\mathbf{B}_1} \mathbf{r}_i \times \mathbf{V}_{\mathbf{R}_i}[\mathbf{r}_i \cdot \mathbf{a}(\mathbf{R}_i, t)] \rangle \}. \quad (\text{I.10})
 \end{aligned}$$

Inserting now eqs. (I.5), (I.6), (I.7) and (I.10) into eq. (I.4), we obtain

$$\begin{aligned}
 \langle \rho(t) \mathbf{M}_{\mathbf{B}_1} \rangle &= \langle \rho_{\mathbf{B}_1} \mathbf{M}_{\mathbf{B}_1} \rangle + \frac{e^2}{2mc^2} \sum_{i=1}^N \langle \rho_{\mathbf{B}_1} \mathbf{r}_i \times \mathbf{a}(\mathbf{R}_i, t) \rangle \\
 & \quad + \frac{e^2}{4mc^2} \sum_{i=1}^N \{ \langle \rho_{\mathbf{B}_1} \mathbf{r}_i \times (\mathbf{r}_i \cdot \mathbf{V}_{\mathbf{R}_i}) \mathbf{a}(\mathbf{R}_i, t) \rangle \\
 & \quad + \langle \rho_{\mathbf{B}_1} \mathbf{r}_i \times \mathbf{V}_{\mathbf{R}_i}[\mathbf{r}_i \cdot \mathbf{a}(\mathbf{R}_i, t)] \rangle \} \\
 & \quad - \int_0^{\infty} d\tau \int_{\mathbf{V}} d\mathbf{r} \int_0^{\beta} d\lambda \left[\frac{\partial}{\partial \tau} \langle \mathbf{M}_{\mathbf{B}_1}(\tau + i\hbar\lambda) \rho_{\mathbf{B}_1} \mathbf{m}_{\mathbf{B}_1}(\mathbf{r}) \rangle \right] \cdot \mathbf{b}(\mathbf{r}, t - \tau)
 \end{aligned}$$

$$-\frac{1}{i\hbar} \int_0^{\infty} d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}, -\tau) - \mathbf{V}_r \cdot \mathbf{q}(\mathbf{r}, -\tau)] \rangle \cdot \mathbf{e}(\mathbf{r}, t - \tau). \quad (\text{I.11})$$

So far we have found an expression for $\langle \rho(t) M_{B_1} \rangle$ [cf. eq. (15)]. Next we have to evaluate $\langle \rho_{B_1} M_1(t) \rangle$ [cf. eqs. (15) and (19)]. With the definition (17) of $M_1(t)$ we obtain, using the expansion (26) for $\mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t)$, the following expression

$$\begin{aligned} \langle \rho_{B_1} M_1(t) \rangle &= -\frac{e^2}{2mc^2} \sum_{i=1}^N \langle \rho_{B_1} \mathbf{r}_i \times \mathbf{a}(\mathbf{R}_i + \mathbf{r}_i, t) \rangle \\ &= -\frac{e^2}{2mc^2} \sum_{i=1}^N \langle \rho_{B_1} \mathbf{r}_i \times \mathbf{a}(\mathbf{R}_i, t) \rangle \\ &\quad - \frac{e^2}{2mc^2} \sum_{i=1}^N \langle \rho_{B_1} \mathbf{r}_i \times (\mathbf{r}_i \cdot \mathbf{V}_{R_i}) \mathbf{a}(\mathbf{R}_i, t) \rangle. \end{aligned} \quad (\text{I.12})$$

With eqs. (I.11) and (I.12) we thus find for $\bar{M}(t)$

$$\begin{aligned} \bar{M}(t) &= \langle \rho(t) M_{B_1} \rangle + \langle \rho_{B_1} M_1(t) \rangle \\ &= \langle \rho_{B_1} M_{B_1} \rangle + \frac{e^2}{4mc^2} \sum_{i=1}^N \{ \langle \rho_{B_1} \mathbf{r}_i \times \mathbf{V}_{R_i} [\mathbf{r}_i \cdot \mathbf{a}(\mathbf{R}_i, t)] \rangle \\ &\quad - \langle \rho_{B_1} \mathbf{r}_i \times (\mathbf{r}_i \cdot \mathbf{V}_{R_i}) \mathbf{a}(\mathbf{R}_i, t) \rangle \} \\ &\quad - \int_0^{\infty} d\tau \int_V d\mathbf{r} \int_0^{\beta} d\lambda \left[\frac{\partial}{\partial \tau} \langle M_{B_1}(\tau + i\hbar\lambda) \rho_{B_1} \mathbf{m}_{B_1}(\mathbf{r}) \rangle \right] \cdot \mathbf{b}(\mathbf{r}, t - \tau) \\ &\quad - \frac{1}{i\hbar} \int_0^{\infty} d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}, -\tau) - \mathbf{V}_r \cdot \mathbf{q}(\mathbf{r}, -\tau)] \rangle \cdot \mathbf{e}(\mathbf{r}, t - \tau). \end{aligned} \quad (\text{I.13})$$

Making use of the identity

$$(\mathbf{r}_i \cdot \mathbf{V}_{R_i}) \mathbf{a}(\mathbf{R}_i, t) - \mathbf{V}_{R_i} [\mathbf{r}_i \cdot \mathbf{a}(\mathbf{R}_i, t)] = [\mathbf{V}_{R_i} \times \mathbf{a}(\mathbf{R}_i, t)] \times \mathbf{r}_i, \quad (\text{I.14})$$

we finally obtain

$$\begin{aligned} \bar{M}(t) &= \langle \rho_{B_1} M_{B_1} \rangle - \frac{e^2}{4mc^2} \sum_{i=1}^N \langle \rho_{B_1} \mathbf{r}_i \times (\mathbf{b}(\mathbf{R}_i, t) \times \mathbf{r}_i) \rangle \\ &\quad - \int_0^{\infty} d\tau \int_V d\mathbf{r} \int_0^{\beta} d\lambda \left[\frac{\partial}{\partial \tau} \langle M_{B_1}(\tau + i\hbar\lambda) \rho_{B_1} \mathbf{m}_{B_1}(\mathbf{r}) \rangle \right] \cdot \mathbf{b}(\mathbf{r}, t - \tau) \end{aligned}$$

$$-\frac{1}{i\hbar} \int_0^\infty d\tau \int_V d\mathbf{r} \langle \rho_{B_1} [M_{B_1}, \mathbf{p}(\mathbf{r}, -\tau) - \mathbf{V}_r \cdot \mathbf{q}(\mathbf{r}, -\tau)] \rangle \cdot \mathbf{e}(\mathbf{r}, t - \tau), \quad (\text{I.15})$$

which is eq. (27) of the main text.

APPENDIX II

We prove, closely following the argument of ref. 5 for the paramagnetic case, that the conventional definition of the diamagnetic adiabatic susceptibility per particle

$$\chi_s \equiv \frac{1}{N} \left(\frac{\partial \langle \rho_B M_B \rangle}{\partial B} \right)_s \quad (\text{II.1})$$

is identical with the one given in section 4 [eq. (55)]. From (II.1) it follows that

$$\begin{aligned} \chi_s &= \frac{1}{N} \left(\frac{\partial \langle \rho_B M_B \rangle}{\partial B} \right)_\beta + \frac{1}{N} \left(\frac{\partial \langle \rho_B M_B \rangle}{\partial \beta} \right) \left(\frac{\partial \beta}{\partial B} \right)_s \\ &= \chi_T - \frac{1}{N} \langle \rho_B \Delta M \Delta H \rangle \left(\frac{\partial \beta}{\partial B} \right)_s. \end{aligned} \quad (\text{II.2})$$

From statistical thermodynamics it follows that:

$$(d \langle \rho_B H \rangle)_s = \left\langle \rho_B \frac{\partial H}{\partial B} \right\rangle dB, \quad (\text{II.3})$$

or

$$(d \langle \rho_B H \rangle)_s - \left\langle \rho_B \frac{\partial H}{\partial B} \right\rangle dB = 0. \quad (\text{II.4})$$

On the other hand,

$$d \langle \rho_B H \rangle = \left(\frac{\partial \langle \rho_B H \rangle}{\partial B} \right)_\beta dB + \left(\frac{\partial \langle \rho_B H \rangle}{\partial \beta} \right)_B d\beta, \quad (\text{II.5})$$

or

$$d \langle \rho_B H \rangle = \left\langle \rho_B \frac{\partial H}{\partial B} \right\rangle dB + \beta \langle \rho_B \Delta M \Delta H \rangle dB - \langle \rho_B (\Delta H)^2 \rangle d\beta, \quad (\text{II.6})$$

where use has been made of the operator identity⁹⁾

$$\frac{\partial (\exp -\beta H)}{\partial B} = - \int_0^\beta d\lambda \exp[-(\beta - \lambda) H] \frac{\partial H}{\partial B} \exp(-\lambda H), \quad (\text{II.7})$$

and of the relation

$$M_B = - \frac{\partial H}{\partial B}. \quad (\text{II.8})$$

For an adiabatic process we obtain from eqs. (II.4) and (II.6)

$$0 = (d\langle \rho_B H \rangle)_s - \left\langle \rho_B \frac{\partial H}{\partial B} \right\rangle dB = \beta \langle \rho_B \Delta M \Delta H \rangle dB - \langle \rho_B (\Delta H)^2 \rangle d\beta. \quad (\text{II.9})$$

Thus we have

$$\left(\frac{\partial \beta}{\partial B} \right)_s = \beta \frac{\langle \rho_B \Delta M \Delta H \rangle}{\langle \rho_B (\Delta H)^2 \rangle}. \quad (\text{II.10})$$

Inserting (II.10) into (II.2) we finally obtain:

$$\chi_s = \chi_T - \frac{\beta}{N} \frac{\langle \rho_B \Delta M \Delta H \rangle^2}{\langle \rho_B (\Delta H)^2 \rangle}, \quad (\text{II.11})$$

which is just the definition eq. (55) of χ_s .

APPENDIX III

We shall give a proof of eq. (57) of the main text.

By definition we know that

$$\frac{1}{T} \int_0^T dt \varphi(t) = \frac{1}{T} \int_0^T dt \int_0^\beta d\lambda R(t + i\hbar\lambda), \quad (\text{III.1})$$

or

$$\frac{1}{T} \int_0^T dt \varphi(t) = \int_0^\beta d\lambda \frac{1}{T} \int_0^T dt R(t + i\hbar\lambda). \quad (\text{III.2})$$

The autocorrelation function $R(z)$ is an analytic function in the strip $0 < \text{Im } z < \hbar\beta$, and furthermore $R(z)$ is continuous at the boundaries.

Thus for every contour in the strip $0 \leq \text{Im } z \leq \hbar\beta$ it follows that:

$$\oint R(z) dz = 0. \quad (\text{III.3})$$

Therefore with (III.3) we can show that

$$\begin{aligned} \frac{1}{T} \int_0^T dt R(t) + \frac{i\hbar}{T} \int_0^\lambda d\lambda' R(T + i\hbar\lambda') - \frac{1}{T} \int_0^T dt R(t + i\hbar\lambda) \\ - \frac{i\hbar}{T} \int_0^\lambda d\lambda' R(i\hbar\lambda') = 0 \quad (\text{for } 0 \leq \lambda \leq \beta). \end{aligned} \quad (\text{III.4})$$

From (III.4) it follows that

$$\begin{aligned}
 & \left| \frac{1}{T} \int_0^T dt R(t) - \frac{1}{T} \int_0^T dt R(t + i\hbar\lambda) \right| \\
 &= \left| \frac{i\hbar}{T} \int_0^\lambda d\lambda' R(i\hbar\lambda') - \frac{i\hbar}{T} \int_0^\lambda d\lambda' R(T + i\hbar\lambda') \right| \\
 &\leq 2 \frac{\hbar}{T} \int_0^\lambda d\lambda' R(i\hbar\lambda') \leq 2 \frac{\hbar}{T} \int_0^\beta d\lambda' R(i\hbar\lambda') \\
 &= 2\varphi(0^+) \hbar/T \quad (\text{for } 0 \leq \lambda \leq \beta), \tag{III.5}
 \end{aligned}$$

where we have made use of the following inequalities:

$$\left| \int_0^\lambda d\lambda' R(T + i\hbar\lambda') \right| \leq \int_0^\lambda d\lambda' R(i\hbar\lambda') \quad \text{for every real } T \tag{III.6}$$

and

$$R(i\hbar\lambda') > 0 \quad \text{for } 0 \leq \lambda' \leq \beta. \tag{III.7}$$

Using (III.2) and (III.5) we finally obtain the following inequality:

$$\begin{aligned}
 & \left| \frac{1}{T} \int_0^T dt \varphi(t) - \frac{\beta}{T} \int_0^T dt R(t) \right| \\
 &= \left| \int_0^\beta d\lambda \frac{1}{T} \int_0^T dt R(t + i\hbar\lambda) - \int_0^\beta d\lambda \frac{1}{T} \int_0^T dt R(t) \right| \\
 &\leq \int_0^\beta d\lambda \left| \frac{1}{T} \int_0^T dt R(t + i\hbar\lambda) - \frac{1}{T} \int_0^T dt R(t) \right| \\
 &\leq \int_0^\beta d\lambda 2\varphi(0^+) \hbar/T = 2\varphi(0^+) \beta \hbar/T. \tag{III.8}
 \end{aligned}$$

Or,

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \varphi(t) = \beta \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt R(t), \tag{III.9}$$

and this is just eq. (57) of the main text.

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CHAPTER III

ERGODIC PROPERTIES OF THE MAGNETIZATION IN HARMONIC OSCILLATOR ASSEMBLIES

Synopsis

The stochastic behaviour of the normalized total magnetization $X(t)$ of a linear chain of charged anisotropically coupled two-dimensional harmonic oscillators in a magnetic field B is studied in the limit of an infinite system. Expressions are derived for the joint and conditional distribution functions in the microcanonical ensemble. The process $X(t)$ is found to be a stationary, gaussian, non-markoffian process. The asymptotic time behaviour of the conditional distribution function and the conditional average of $X(t)$ is studied in connection with the ergodic properties of $X(t)$ for varying values of B and the anisotropy parameter γ . If $\gamma \neq 0$, $B \rightarrow 0$, the gaussian process $X(t)$ is found to be ergodic (*i.e.* all square-integrable functions of $X(t)$ are ergodic functions). In the limit of an infinite system an equality is derived, connecting microcanonical and canonical autocorrelation functions of sumvariables. Mazur's condition for ergodicity of certain phase functions is found as a corollary of this equality.

1. *Introduction.* The stochastic types of motion of one single particle in harmonic-oscillator assemblies have been studied extensively (*cf.* section 1 of chapter I¹).

In this chapter we shall discuss the stochastic behaviour of a property of such an assembly as a whole, *viz.* the total magnetization of a linear chain of charged anisotropically coupled two-dimensional harmonic oscillators in a magnetic field B . In chapter I we solved the dynamics of this system, and derived an explicit expression for the autocorrelation function of the magnetization in the canonical ensemble. Furthermore we discussed the ergodic properties of the total magnetization of the chain for varying values of B and the anisotropy parameter γ . We considered both the quantummechanical and the classical case in chapter I. In this chapter we shall restrict the discussion to the classical limit.

In section 2 we derive, in the limit of an infinite system, expressions for the joint and conditional distribution functions (d.f.'s) for the normalized magnetization $X(t)$ in the microcanonical ensemble. The process $X(t)$ is found to be a stationary, gaussian, non-markoffian process. Furthermore it is

shown that, in the limit of an infinite system, the microcanonical and canonical autocorrelation functions of the magnetization are equal for all times t .

In section 3 the asymptotic time behaviour of the conditional d.f. and the conditional average of $X(t)$ is studied in connection with the ergodic properties of $X(t)$. It is shown that, if $B \neq 0$, when $X(t)$ is a non-ergodic function, there remains a "memory" with respect to the initial value X_0 of $X(t)$. If $\gamma \neq 0$, $B \rightarrow 0$, when $X(t)$ is an ergodic function, the conditional d.f. tends to the "equilibrium" d.f. and the conditional average tends to zero as $t \rightarrow \infty$. In this case it is also shown that the process $X(t)$ is ergodic (*i.e.* that all square-integrable functions of $X(t)$ are ergodic functions).

In section 4 we derive, in the limit of an infinite system, an equality connecting microcanonical and canonical autocorrelation functions of sum-variables. Mazur's²⁾ condition for ergodicity of certain phase functions is found as a corollary of this equality.

2. *Microcanonical joint and conditional distribution functions for the magnetization in a linear chain of two-dimensional oscillators.* We consider, in the classical limit, the model studied in chapter I*, *i.e.* a linear chain of N identical anisotropically coupled charged harmonic oscillators, whose motions are restricted to the xy plane. The system is subjected to a time-independent homogeneous external magnetic field B along the z axis. The hamiltonian is given by†

$$H = \sum_{i=1}^N \frac{1}{2}(\mathbf{p}_i - \frac{1}{2}\mathbf{B} \wedge \mathbf{r}_i)^2 + \sum_{\substack{i,j=1,\dots,N \\ \alpha,\beta=x,y}} \frac{1}{2}r_i^\alpha \Omega_{ij} (1 + \gamma\sigma^z)^{\alpha\beta} r_j^\beta. \quad (1)$$

By performing the canonical transformation given by eqs. (1.6) and (1.7) we obtain (dropping the primes denoting the new variables)

$$H = \sum_{i=1}^N H_i, \quad (2)$$

with

$$H_i = \frac{1}{2}\mathbf{p}_i^2 - \frac{1}{2}B(\mathbf{r}_i \wedge \mathbf{p}_i)_z + \frac{1}{2}\mathbf{r}_i \cdot \{(\omega_i^2 + \frac{1}{4}B^2)\mathbf{1} + \gamma\omega_i^2\boldsymbol{\sigma}^z\} \cdot \mathbf{r}_i. \quad (3)$$

In terms of the quasiparticle coordinates and momenta the z component of the magnetization for this system is given by

$$M = \sum_{i=1}^N M_i \quad (4)$$

with

$$M_i = \frac{1}{2}\{(\mathbf{r}_i \wedge \mathbf{p}_i)_z - \frac{1}{2}B(\mathbf{r}_i \cdot \mathbf{r}_i)\}. \quad (5)$$

* Equations and sections of chapter I, referred to in this chapter are preceded by the prefix 1.

† For notations *cf.* 1. section 2.

We shall now, in the limit of an infinite system, derive an expression for the joint d.f. $W_m(X_0, X; t)$ and the conditional d.f. $P_m(X, t|X_0)$ in the microcanonical ensemble on the energy surface E_N (with $E_N/N = c$ (constant)) for the normalized magnetization $X(t)$ *. The variable $X(t)$ is defined in the following way:

$$X(t) = \sum_{i=1}^N X_i(t) \quad (6)$$

with

$$X_i(t) = \frac{M_i(t)}{\sigma_{M,N} \sqrt{N}}, \quad (7)$$

where

$$\sigma_{M,N} = \left\{ \frac{1}{N} \sum_{i=1}^N \langle \rho_1 M_i^2 \rangle \right\}^{\frac{1}{2}} \quad (8)$$

and

$$\rho_1 = \frac{\exp - \beta_1 H}{\langle \exp (-\beta_1 H) \rangle}. \quad (9)$$

Here $\langle \dots \rangle$ denotes integration over phase space. The parameter β_1 is chosen in such a way that the corresponding canonical average of the energy is equal to E_N :

$$2N\beta_1^{-1} = \langle \rho_1 H \rangle = E_N. \quad (10)$$

It follows from eqs. (3) - (9) that

$$\langle \rho_1 X_i(t) \rangle = 0 \quad (i = 1, \dots, N) \quad (11)$$

and

$$\langle \rho_1 X^2(t) \rangle = \sum_{i=1}^N \langle \rho_1 X_i^2(t) \rangle = 1. \quad (12)$$

Furthermore the autocorrelation function of $X(t)$ in the canonical ensemble corresponding with the parameter β_1 can be written as

$$\bar{R}_N(\beta_1, \tau) = \langle \rho_1 X(t) X(t + \tau) \rangle = \frac{1}{N} \frac{\langle \rho_1 M M(\tau) \rangle}{\sigma_{M,N}^2} = \frac{R_N(\beta_1, \tau)}{R_N(\beta_1, 0)}, \quad (13)$$

where $R_N(\beta_1, \tau)$ is the canonical autocorrelation function of the magnetization. From eq. (1.76) we can obtain an explicit expression for $R_N(\beta_1, \tau)$ by substituting $\beta = \beta_1$ and taking the limit $\hbar \rightarrow 0$.

For finite N we obtain

* We note that the *stationary* microcanonical ensemble generates a *stationary* process $X(t)$, e.g.,

$$W_m(X_0, X; t_0, t_0 + t) = W_m(X_0, X; t).$$

$$\begin{aligned}
 R_N(\beta_1, \tau) &= \frac{1}{2N\beta_1^2} \sum_{i=1}^N \frac{B^2}{\gamma^2 \omega_i^4 + B^2(\omega_i^2 + \frac{1}{4}B^2)} \\
 &+ \frac{1}{2N\beta_1^2} \sum_{i=1}^N \frac{K_i^2}{\omega_i^2(1-\gamma^2)^{\frac{1}{2}}} \cos(\omega_{+,i} + \omega_{-,i})\tau \\
 &+ \frac{1}{2N\beta_1^2} \sum_{i=1}^N \frac{L_i^2}{\omega_i^2(1-\gamma^2)^{\frac{1}{2}}} \cos(\omega_{+,i} - \omega_{-,i})\tau,
 \end{aligned} \tag{14}$$

so that the limit of an infinite system

$$\bar{R}(\beta_1, \tau) \equiv \lim_{N \rightarrow \infty} \frac{R_N(\beta_1, \tau)}{R_N(\beta_1, 0)} = \frac{R(\beta_1, \tau)}{R(\beta_1, 0)}, \tag{15}$$

with

$$\begin{aligned}
 R(\beta_1, \tau) &= \frac{1}{4\pi\beta_1^2} \int_{-\pi}^{\pi} d\theta \frac{B^2}{\gamma^2\{f(\theta)\}^2 + B^2\{f(\theta) + \frac{1}{4}B^2\}} \\
 &+ \frac{1}{4\pi\beta_1^2} \int_{-\pi}^{\pi} d\theta \frac{\{\kappa(\theta)\}^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \cos g_+(\theta)\tau \\
 &+ \frac{1}{4\pi\beta_1^2} \int_{-\pi}^{\pi} d\theta \frac{\{\lambda(\theta)\}^2}{f(\theta)(1-\gamma^2)^{\frac{1}{2}}} \cos g_-(\theta)\tau
 \end{aligned} \tag{16}$$

(for notations cf. 1. section 4).

Furthermore we introduce the normalized energy Y

$$Y = \sum_{i=1}^N Y_i \tag{17}$$

with

$$Y \equiv \frac{\Delta H_i}{\sigma_{H,N} \sqrt{N}}, \tag{18}$$

where

$$\Delta H \equiv H_i - \langle \rho_1 H_i \rangle \tag{19}$$

and

$$\sigma_{H,N} \equiv \left\{ \frac{1}{N} \sum_{i=1}^N \langle \rho_1 (\Delta H_i)^2 \rangle \right\}^{\frac{1}{2}} \tag{20}$$

It follows that

$$\langle \rho_1 Y_i \rangle = 0 \quad (i = 1, \dots, N) \tag{21}$$

and

$$\langle \rho_1 Y^2 \rangle = \sum_{i=1}^N \langle \rho_1 Y_i^2 \rangle = 1. \tag{22}$$

We shall now compute the joint d.f. $W_m(X_0, X; t)$ and the conditional d.f. $P_m(X, t|X_0)$ for the process $X(t)$ in the limit of an infinite system.

Replacing the restriction $H = E_N$ by the equivalent restriction $Y = 0$, we may define the joint d.f. $W_m^{(N)}(X_0, X; t)$ as follows

$$\begin{aligned} W_m^{(N)}(X_0, X; t) &\equiv W^{(N)}(X_0, X; t|Y = 0) \\ &\equiv \frac{\langle \delta(X(0) - X_0) \delta(X(t) - X) \delta(Y) \rangle}{\langle \delta(Y) \rangle}. \end{aligned} \quad (23)$$

By multiplying the numerator and denominator in the last member of (23) with a factor $(\exp - \beta_1 E_N) / \langle \exp(-\beta_1 H) \rangle$ we can write (23) as a ratio of canonical averages

$$W_m^{(N)}(X_0, X; t|Y = 0) = \frac{\langle \rho_1 \delta(X(0) - X_0) \delta(X(t) - X) \delta(Y) \rangle}{\langle \rho_1 \delta(Y) \rangle}. \quad (24)$$

By using the Fourier-representation of the δ -function we may write

$$\begin{aligned} &\langle \rho_1 \delta(X(0) - X_0) \delta(X(t) - X) \delta(Y) \rangle \\ &= \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} du dv dw \exp(-iX_0 u - iXv) \psi_N(u, v, w), \end{aligned} \quad (25)$$

where the characteristic function $\psi_N(u, v, w)$ is defined as

$$\psi_N(u, v, w) \equiv \langle \rho_1 \exp(iX(0)u + iX(t)v + iYw) \rangle. \quad (26)$$

The function $\psi_N(u, v, w)$ can be expressed as

$$\psi_N(u, v, w) = \prod_{j=1}^N \frac{\langle \exp(-\beta_1 H_j) \exp(iX_j(0)u + iX_j(t)v + iY_j w) \rangle}{\exp\langle(-\beta_1 H_j)\rangle}, \quad (27)$$

where use has been made of the statistical independence of the quasiparticle functions

$$(X_j(0)u + X_j(t)v + Y_j w), \quad (j = 1, \dots, N).$$

The logarithm of $\psi_N(u, v, w)$ can be expanded in a power series in u, v and w

$$\begin{aligned} \ln \psi_N(u, v, w) &= \sum_{j=1}^N \ln \frac{\langle \exp(-\beta_1 H_j) \exp(iX_j(0)u + iX_j(t)v + iY_j w) \rangle}{\langle \exp(-\beta_1 H_j) \rangle} \\ &= \sum_{j=1}^N \ln \left\{ 1 - \frac{1}{2} \langle \rho_1 X_j^2(0) \rangle u^2 - \frac{1}{2} \langle \rho_1 X_j^2(t) \rangle v^2 \right. \\ &\quad - \frac{1}{2} \langle \rho_1 Y_j^2 \rangle w^2 - \langle \rho_1 X_j(0) X_j(t) \rangle uv \\ &\quad \left. - \langle \rho_1 X_j(0) Y_j \rangle uw - \langle \rho_1 X_j(t) Y_j \rangle vw + \mathcal{O}\left(\frac{1}{N\sqrt{N}}\right) \right\} \\ &= -\frac{1}{2} u^2 - \frac{1}{2} v^2 - \frac{1}{2} w^2 - \bar{R}_N(t) uv + \mathcal{O}\left(\frac{1}{\sqrt{N}}\right), \end{aligned} \quad (28)$$

where $\bar{R}_N(t)$ is given by eqs. (13) and (14).

Thus in the limit $N \rightarrow \infty$ (keeping $E_N/N = 2\beta_1^{-1}$ constant) we find that

$$\psi_N(u, v, w) \rightarrow \exp\left\{-\frac{1}{2}u^2 - \frac{1}{2}v^2 - \frac{1}{2}w^2 - \bar{R}(t) uv\right\} \quad (29)$$

uniformly in any finite region of (u, v, w) space³. $\bar{R}(t)$ is given by eqs. (15) and (16). It can then also be shown along the lines of an argument given, *e.g.*, by Van der Linden⁴, that

$$\begin{aligned} \lim_{N \rightarrow \infty} \langle \rho_1 \delta(X(0) - X_0) \delta(X(t) - X) \delta(Y) \rangle \\ = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} du dv dw \exp(-iX_0u - iXv) \\ \times \exp\left\{-\frac{1}{2}u^2 - \frac{1}{2}v^2 - \frac{1}{2}w^2 - \bar{R}(t) uv\right\} \\ = \frac{1}{(2\pi)^{\frac{3}{2}}} \frac{1}{\{1 - \bar{R}^2(t)\}^{\frac{1}{2}}} \exp - \frac{X^2 - 2\bar{R}(t) XX_0 + X_0^2}{2\{1 - \bar{R}^2(t)\}} \end{aligned} \quad (30)$$

uniformly in X and X_0 (for details see appendix).

Integrating (30) over X_0 and X we obtain

$$\lim_{N \rightarrow \infty} \langle \rho_1 \delta(Y) \rangle = \frac{1}{(2\pi)^{\frac{1}{2}}}. \quad (31)$$

Inserting now the results (30) and (31) into (24) we get

$$\begin{aligned} W_m(X_0, X; t) \equiv \lim_{N \rightarrow \infty} W_m^{(N)}(X_0, X; t) = \frac{1}{2\pi\{1 - \bar{R}^2(t)\}^{\frac{1}{2}}} \\ \times \exp - \frac{X^2 - 2\bar{R}(t) XX_0 + X_0^2}{2\{1 - \bar{R}^2(t)\}} \end{aligned} \quad (32)$$

uniformly in X and X_0 . The procedure followed above leads for every finite set $X(t_1), X(t_2), \dots, X(t_n)$ to an n -dimensional gaussian d.f. for the joint d.f. of this set in the microcanonical ensemble. Therefore the process $X(t)$ is a stationary, gaussian process. Integrating both sides of eq. (32) over X we find for the equilibrium d.f. $W_m(X)$

$$W_m(X) \equiv \lim_{N \rightarrow \infty} W_m^{(N)}(X) = \frac{1}{(2\pi)^{\frac{1}{2}}} \exp - \frac{1}{2}X^2 \quad (33)$$

uniformly in X . We thus obtain, in the limit of an infinite system, for the conditional d.f. $P_m(X, t|X_0)$, defined as

$$P_m(X, t|X_0) \equiv \frac{W_m(X_0, X; t)}{W_m(X_0)}, \quad (34)$$

the following expression, which follows from (32) and (33),

$$P_m(X, t|X_0) = \frac{1}{[2\pi\{1 - \bar{R}^2(t)\}]^{\frac{1}{2}}} \exp - \frac{(X - \bar{R}(t)X_0)^2}{2\{1 - \bar{R}^2(t)\}}. \quad (35)$$

With eq. (33) it follows trivially that $\lim_{N \rightarrow \infty} \langle X(t) \rangle_m = 0$, as it should. Eq. (32) enables one to compute the microcanonical autocorrelation function $\rho_m(\tau)$ of the function $X(t)$:

$$\begin{aligned} \rho_m(\tau) &\equiv \lim_{N \rightarrow \infty} \langle X(t) X(t + \tau) \rangle_m \\ &= \iint dX dX_0 X X_0 W_m(X_0, X; \tau) = \bar{R}(\beta_1, \tau), \end{aligned} \quad (36)$$

where $\bar{R}(\beta_1, \tau)$ is the function defined by (15) and (16). Instead of (36) we may also write

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle M(t) M(t + \tau) \rangle_m = \lim_{N \rightarrow \infty} \langle \rho_1 M(t) M(t + \tau) \rangle. \quad (37)$$

In (36) and (37) the microcanonical average is taken on the energy surface E_N ($E_N/N = \text{constant}$) and the canonical average is taken with the corresponding parameter β_1 , defined by eq. (10). Eq. (37) is a special case of a more general equality which will be derived in section 4.

As we have shown already in 1. section 5, the canonical autocorrelation function $R(\beta_1, \tau)$, and consequently $\bar{R}(\beta_1, \tau)$ and $\rho_m(\tau)$, assume for no value of the parameters γ and B the form $\exp(-\alpha\tau)$ ($\alpha > 0$). This implies⁵⁾ that the stationary, gaussian process $X(t)$ is not a Markoff process.

3. *The long-time behaviour of the conditional distribution function $P_m(X, t|X_0)$ and the conditional average $\overline{X(t)}^{X_0}$ in connection with the ergodic properties of $X(t)$.* In chapter I we have investigated the ergodic properties of the total magnetization of the harmonic chain for varying values of the anisotropy parameter γ and the magnetic field B . We found that for our system the magnetization, or equivalently the function $X(t)$, is in general ($B \neq 0$) non-ergodic. In the case $\gamma = 0, B \rightarrow 0$ the magnetization and consequently $X(t)$ are constants of the motion, and non-ergodic. Only if $\gamma \neq 0, B \rightarrow 0$, the function $X(t)$ was found to be ergodic*. Now we are going to investigate, having taken the limit $N \rightarrow \infty$, the conditional d.f. $P_m(X, t|X_0)$ and the conditional average $\overline{X(t)}^{X_0}$ in the limit of infinitely long times. For the general case ($B \neq 0$) we obtain

$$\lim_{t \rightarrow \infty} P_m(X, t|X_0) = \frac{1}{\{2\pi(1 - \hat{\rho}_m^2)\}^{\frac{1}{2}}} \exp - \frac{(X - \hat{\rho}_m X_0)^2}{2(1 - \hat{\rho}_m^2)}, \quad (38)$$

* In chapter I this property was established in the limit of an infinite system. It may, however, be verified that the magnetization, or equivalently $X(t)$, is already an ergodic function, if $\gamma \neq 0, B \rightarrow 0$, for finite N . In this case, however, only the time average of the correlation function $R_N(t)$ vanishes, but its limit as $t \rightarrow \infty$ does not exist. It could furthermore have been checked that for the finite system, even when $X(t)$ is ergodic, the function $X^2(t)$ e.g. is nevertheless a non-ergodic function. It is the purpose of this section to establish that in the limit of an infinite system all square-integrable functions of $X(t)$ are ergodic functions and that the process $X(t)$ is a gaussian, ergodic process, if $\gamma \neq 0, B \rightarrow 0$.

where

$$\hat{\rho}_m \equiv \lim_{t \rightarrow \infty} \rho_m(t) = \lim_{t \rightarrow \infty} \bar{R}(t) = \lim_{t \rightarrow \infty} \frac{R(t)}{R(0)}. \quad (39)$$

$R(t)$ is the function defined by (16).

For the conditional average $\overline{X(t)}^{X_0}$ we get

$$\overline{X(t)}^{X_0} \equiv \int dX X P_m(X, t|X_0) = \rho_m(t) X_0 \quad (40)$$

and in the limit $t \rightarrow \infty$ we find

$$\lim_{t \rightarrow \infty} \overline{X(t)}^{X_0} = \hat{\rho}_m X_0. \quad (41)$$

From inspection of eq. (16) it appears that, if $B \neq 0$, $\hat{\rho}_m$ obeys the inequality

$$0 < \hat{\rho}_m < 1. \quad (42)$$

This implies that in the case $B \neq 0$, when $X(t)$ is non-ergodic, there is a "memory" with respect to the initial value X_0 , in the limit $t \rightarrow \infty$.

In the case $\gamma = 0$, $B \rightarrow 0$, *i.e.* when $X(t)$ is a constant of the motion, it follows from (23) (one does not have to take the limit of an infinite system here) that

$$\lim_{B \rightarrow 0, \gamma = 0} P_m(X, t|X_0) = \delta(X - X_0) \quad (43)$$

and

$$\lim_{B \rightarrow 0, \gamma = 0} \overline{X(t)}^{X_0} = X_0. \quad (44)$$

Both (43) and (44) hold for all times t . It should be noted that one obtains the same result in the limit of an infinite system, by taking the limit $B \rightarrow 0$, $\gamma = 0$ in (35) and (40) ($\hat{\rho}_m \rightarrow 1$).

Finally, if $\gamma \neq 0$ and $B \rightarrow 0$, it follows from (16) that

$$\hat{\rho}_m = \lim_{t \rightarrow \infty} \rho_m(t) = 0. \quad (45)$$

Thus we obtain

$$\lim_{t \rightarrow \infty} P_m(X, t|X_0) = \frac{1}{\sqrt{2\pi}} \exp - \frac{X^2}{2} \quad (46)$$

and

$$\lim_{t \rightarrow \infty} \overline{X(t)}^{X_0} = 0. \quad (47)$$

In this case, when $X(t)$ is an ergodic function, there is no "memory" with respect to the initial value X_0 . The conditional d.f. $P_m(X, t|X_0)$ tends to the "equilibrium" d.f. $W_m(X)$ (*cf.* eq. (33)) as $t \rightarrow \infty$. Or, equivalently, the joint d.f. $W_m(X_0, X; t)$ factorizes into a product of two uncorrelated "equi-

librium" d.f.'s as $t \rightarrow \infty$:

$$\lim_{t \rightarrow \infty} W_m(X_0, X; t) = W_m(X_0) W_m(X). \quad (48)$$

A necessary and sufficient condition for $X(t)$ to be an ergodic function is, that the time average $T^{-1} \int_0^T \rho_m(t) dt$ vanishes as $T \rightarrow \infty$. It is obvious that the property given by eq. (45) is a sufficient but not a necessary condition to ensure the ergodicity of the function $X(t)$. In fact, if $\gamma \neq 0$ and $B \rightarrow 0$, $\rho_m(t) \rightarrow 0$ as $|t| \rightarrow \infty$, and this property is a sufficient condition for the real gaussian stationary process $X(t)$ to be ergodic⁶). The property that the process $X(t)$ is ergodic is of course stronger than the property that the phase function $X(t)$ is ergodic. Indeed, ergodicity of the gaussian process $X(t)$ implies that all functions $f(X(t))$ for which

$$\int dX |f(X)|^2 W_m(X)$$

exists, are ergodic.

4. *An equality connecting microcanonical and canonical autocorrelation functions of sumvariables.* In section 2 we have derived an equality (37) connecting, in the limit of an infinite system, microcanonical and canonical autocorrelation functions of $X(t)$ (with corresponding parameters E_N/N and β_1). In fact this equality is a special case of a more general equality. The reason why we obtained the form (37) lies in the fact that for our model the quantities

$$\langle \rho_1 X_j(t) Y_j \rangle \quad \text{or} \quad \langle \rho_1 M_j(t) (H_j - \langle \rho_1 H_j \rangle) \rangle$$

vanish for all j and N and all times t .

Let us now consider a variable $A(t)$ which is, in terms of the quasi particle coordinates and momenta, a sum of variables $A_i(t)$ with independent distributions in the canonical ensemble. Let the normalized variable $Z(t)$ be defined as

$$Z(t) \equiv \sum_{i=1}^N Z_i(t) \quad (49)$$

with

$$Z_i(t) = \frac{\Delta A_i(t)}{\sigma_{A,N} \sqrt{N}} \quad (i = 1, \dots, N), \quad (50)$$

where

$$\Delta A_i(t) \equiv A_i(t) - \langle \rho_1 A_i \rangle \quad (51)$$

and

$$\sigma_{A,N} \equiv \left\{ \frac{1}{N} \sum_{i=1}^N \langle \rho_1 (\Delta A_i)^2 \rangle \right\}^{\frac{1}{2}}. \quad (52)$$

The canonical ensemble density ρ_1 and the normalized energy variables Y_i ($i = 1, \dots, N$) and Y are defined here in the same way as in section 2. Let us now define the quantity Q as

$$Q \equiv \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N \langle \rho_1 Z_i Y_i \rangle. \quad (53)$$

Substituting (18) and (50) into (53) we have

$$Q = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N \frac{\langle \rho_1 \Delta A_i \Delta H_i \rangle}{\sigma_{A, N} \sigma_{H, N}}. \quad (54)$$

(Note that for the variable studied in section 2 (*i.e.* if $A_i(t) = M_i(t)$) we have $Q = 0$). Applying a Schwartz inequality to the r.h.s. of (54) we obtain the following inequality

$$|Q| \leq 1. \quad (55)$$

Assuming now that the arguments, used in section 2 and in the appendix, which led to eqs. (32), (33) and (35), are valid here too, we obtain in the limit of an infinite system for the microcanonical joint d.f. $W_m(Z_0, Z; t)$

$$\begin{aligned} W_m(Z_0, Z; t) &\equiv \lim_{N \rightarrow \infty} W_m^{(N)}(Z_0, Z; t) \\ &= \frac{1}{2\pi(1-Q^2)\{1-\hat{R}^2(t)\}^{\frac{1}{2}}} \exp - \frac{Z^2 - 2\hat{R}(t)ZZ_0 + Z_0^2}{2(1-Q^2)\{1-\hat{R}^2(t)\}}, \end{aligned} \quad (56)$$

with

$$\hat{R}(t) \equiv \frac{\bar{R}(t) - Q^2}{1 - Q^2}. \quad (57)$$

Here

$$\bar{R}(t) \equiv \lim_{N \rightarrow \infty} \sum_{i=1}^N \langle \rho_1 Z_i Z_i(t) \rangle = \lim_{N \rightarrow \infty} \frac{\langle \rho_1 \Delta A \Delta A(t) \rangle}{\langle \rho_1 (\Delta A)^2 \rangle}, \quad (58)$$

where

$$\Delta A(t) \equiv \sum_{i=1}^N \Delta A_i(t). \quad (59)$$

With the assumption made above the limit in (56) is established uniformly in Z and Z_0 .

For the d.f. $W_m(Z)$ we get

$$W_m(Z) \equiv \lim_{N \rightarrow \infty} W_m^{(N)}(Z) = \frac{1}{\{2\pi(1-Q^2)\}^{\frac{1}{2}}} \exp - \frac{Z^2}{2(1-Q^2)} \quad (60)$$

uniformly in Z .

Consequently we have in the limit $N \rightarrow \infty$ for the conditional d.f. $P_m(Z, t|Z_0)$:

$$P_m(Z, t|Z_0) \equiv \frac{W_m(Z_0, Z; t)}{W_m(Z_0)}$$

$$= \frac{1}{(2\pi)^{\frac{1}{2}}(1-Q^2)^{\frac{1}{2}}\{1-\bar{R}^2(t)\}^{\frac{1}{2}}} \exp - \frac{(Z - \bar{R}(t)Z_0)^2}{2(1-Q^2)\{1-\bar{R}^2(t)\}}. \quad (61)$$

From eq. (60) it follows immediately that

$$\lim_{N \rightarrow \infty} \langle Z(t) \rangle_m = \int dZ Z W_m(Z) = 0 \quad (\text{all } t), \quad (62)$$

which implies

$$\lim_{N \rightarrow \infty} \frac{1}{\sqrt{N}} (\langle A \rangle_m - \langle \rho_1 A \rangle) = 0. \quad (63)$$

For the microcanonical autocorrelation function we obtain in the limit of an infinite system

$$\lim_{N \rightarrow \infty} \langle Z Z(t) \rangle_m = \iint dZ dZ_0 Z Z_0 W_m(Z_0, Z; t)$$

$$= (1 - Q^2) \bar{R}(t) = \bar{R}(t) - Q^2. \quad (64)$$

In terms of the variables A and H eq. (64) becomes

$$\lim_{N \rightarrow \infty} \frac{1}{N} \frac{\langle \Delta A \Delta A \Delta A(t) \rangle_m}{\sigma_{A,N}^2}$$

$$= \lim_{N \rightarrow \infty} \left\{ \frac{1}{N} \frac{\langle \rho_1 \Delta A \Delta A \Delta A(t) \rangle}{\sigma_{A,N}^2} - \frac{1}{N^2} \frac{\langle \rho_1 \Delta A \Delta A \Delta H \rangle^2}{\sigma_{A,N}^2 \sigma_{H,N}^2} \right\} \quad (65)$$

or

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle \Delta A \Delta A \Delta A(t) \rangle_m = \lim_{N \rightarrow \infty} \frac{1}{N} \left\{ \langle \rho_1 \Delta A \Delta A \Delta A(t) \rangle - \frac{\langle \rho_1 \Delta A \Delta A \Delta H \rangle^2}{\langle \rho_1 (\Delta H)^2 \rangle} \right\}. \quad (65)$$

Since in view of (63)

$$\lim_{N \rightarrow \infty} \frac{1}{N} (\langle A \rangle_m - \langle \rho_1 A \rangle)^2 = 0, \quad (67)$$

we finally get the following equality

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle (A - \langle A \rangle_m)(A(t) - \langle A \rangle_m) \rangle_m$$

$$= \lim_{N \rightarrow \infty} \frac{1}{N} \left\{ \langle \rho_1 \Delta A \Delta A \Delta A(t) \rangle - \frac{\langle \rho_1 \Delta A \Delta A \Delta H \rangle^2}{\langle \rho_1 (\Delta H)^2 \rangle} \right\}. \quad (68)$$

It is obvious that, if $A(t) = M(t)$ (the total magnetization of the system), eq. (68) reduces to eq. (37). The term by which the two autocorrelation functions in (68) differ, finds its origin in the energy fluctuations of the canonical ensemble.

A necessary and sufficient condition for the phase function $A(t)$ to be ergodic is that the time average of the l. h.s. of (68) vanishes. Since the time averages of both sides of (68) are equal, Mazur's² condition involving canonical averages, for $A(t)$ to be ergodic, is found as a corollary of the equality (68).

The results obtained in this section are valid in general for phase functions $A(t)$ defined for systems with a hamiltonian H , if both $A(t)$ and H are sums of variables with independent distributions in the canonical ensemble, since then the central limit theorem of probability theory applies, provided certain additional conditions (*cf.* Van der Linden⁴) and the appendix) are satisfied.

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APPENDIX

In this appendix we shall prove, for arbitrary but fixed t , that, as $N \rightarrow \infty$

$$\begin{aligned} & \langle \rho_1 \delta(X(0) - X_0) \delta(X(t) - X) \delta(Y) \rangle \\ & \rightarrow \frac{1}{(2\pi)^{\frac{1}{2}}} \frac{1}{\{1 - \bar{R}^2(t)\}^{\frac{1}{2}}} \exp - \frac{X^2 - 2\bar{R}(t) X X_0 + X_0^2}{2\{1 - \bar{R}^2(t)\}} \end{aligned} \quad (\text{A.1})$$

uniformly in X and X_0 (*cf.* eq. (30) of the main text).

Let $\psi_j(u, v, w)$ be defined as

$$\psi_j(u, v, w) = \frac{\langle \exp(-\beta H_j) \exp(iX_j(0)u + iX_j(t)v + iY_j w) \rangle}{\langle \exp(-\beta H_j) \rangle}. \quad (\text{A.2})$$

With eq. (27) we have

$$\psi_N(u, v, w) = \prod_{j=1}^N \psi_j(u, v, w). \quad (\text{A.3})$$

By performing the canonical transformations (1.10) and (1.18) of chapter I eq. (A.2) becomes

$$\psi_j(u, v, w) = \frac{\langle \exp(-\beta \bar{H}_j) \exp(i\bar{X}_j(0)u + i\bar{X}_j(t)v + i\bar{Y}_j w) \rangle}{\langle \exp(-\beta \bar{H}_j) \rangle}, \quad (\text{A.4})$$

where the functions \bar{H}_j , $\bar{X}_j(0)$, $\bar{X}_j(t)$ and \bar{Y}_j are expressed in terms of the momenta P'_{xj} and P'_{yj} and the coordinates X'_j and Y'_j (*cf.* 1. section 2). The variables P'_{xj} , P'_{yj} , X'_j and Y'_j will be referred to as q_{1j} , q_{2j} , q_{3j} and q_{4j} , respectively, in this appendix.

In terms of the q -variables the hamiltonian \bar{H}_j reads

$$\bar{H}_j = \frac{1}{2}q_{1j}^2 + \frac{1}{2}q_{2j}^2 + \frac{1}{2}\omega_{+,j}^2 q_{3j}^2 + \frac{1}{2}\omega_{-,j}^2 q_{4j}^2. \quad (\text{A.5})$$

For the variable \bar{Y}_j we have

$$\begin{aligned}\bar{Y}_j &= \frac{1}{\sigma_{H,N} \sqrt{N}} \{\bar{H}_j - \langle \rho_1 H_j \rangle\} \\ &= \frac{1}{\sigma_{H,N} \sqrt{N}} \left\{ \frac{1}{2} q_{1j}^2 + \frac{1}{2} q_{2j}^2 + \frac{1}{2} \omega_{+,j}^2 q_{3j}^2 + \frac{1}{2} \omega_{-,j}^2 q_{4j}^2 \right\} + C_j^{(N)},\end{aligned}\quad (\text{A.6})$$

where $C_j^{(N)}$ is a real constant.

For the variable $\bar{X}_j(0)$ we get

$$\begin{aligned}\bar{X}_j(0) &= \frac{1}{\sigma_{M,N} \sqrt{N}} \left\{ \frac{1}{2} c_j q_{1j}^2 + \frac{1}{2} c_j \omega_{+,j}^2 q_{3j}^2 - \frac{1}{2} c_j q_{2j}^2 - \frac{1}{2} c_j \omega_{-,j}^2 q_{4j}^2 \right. \\ &\quad \left. - \frac{1}{2} c_j A_j \omega_{+,j} q_{2j} q_{3j} + \frac{1}{2} c_j B_j \omega_{-,j} q_{1j} q_{4j} \right\},\end{aligned}\quad (\text{A.7})$$

where A_j , B_j and c_j are defined as

$$A_j = \frac{2\gamma\omega_j^2 - B^2}{B\omega_j(1 + \gamma)^{\frac{1}{2}}},\quad (\text{A.8})$$

$$B_j = \frac{2\gamma\omega_j^2 + B^2}{B\omega_j(1 - \gamma)^{\frac{1}{2}}},\quad (\text{A.9})$$

and

$$c_j = - \frac{B}{2\{\gamma^2\omega_j^4 + B^2(\omega_j^2 + \frac{1}{4}B^2)\}^{\frac{1}{2}}}.\quad (\text{A.10})$$

For the variable $\bar{X}_j(t)$ we finally have

$$\begin{aligned}\bar{X}_j(t) &= \frac{1}{\sigma_{M,N} \sqrt{N}} \left[\frac{1}{2} c_j q_{1j}^2 + \frac{1}{2} c_j \omega_{+,j}^2 q_{3j}^2 - \frac{1}{2} c_j q_{2j}^2 - \frac{1}{2} c_j \omega_{-,j}^2 q_{4j}^2 \right. \\ &\quad \left. - \frac{1}{2} c_j \{ A_j \sin \omega_{+,jt} \cos \omega_{-,jt} - B_j \cos \omega_{+,jt} \sin \omega_{-,jt} \} q_{1j} q_{2j} \right. \\ &\quad \left. + \frac{1}{2} c_j \{ A_j \omega_{-,j} \sin \omega_{+,jt} \sin \omega_{-,jt} + B_j \omega_{-,j} \cos \omega_{+,jt} \cos \omega_{-,jt} \} q_{1j} q_{4j} \right. \\ &\quad \left. - \frac{1}{2} c_j \{ A_j \omega_{+,j} \cos \omega_{+,jt} \cos \omega_{-,jt} + B_j \omega_{+,j} \sin \omega_{+,jt} \sin \omega_{-,jt} \} q_{2j} q_{3j} \right. \\ &\quad \left. + \frac{1}{2} c_j \{ A_j \omega_{+,j} \omega_{-,j} \cos \omega_{+,jt} \sin \omega_{-,jt} \right. \\ &\quad \left. - B_j \omega_{+,j} \omega_{-,j} \sin \omega_{+,jt} \cos \omega_{-,jt} \} q_{3j} q_{4j} \right].\end{aligned}\quad (\text{A.11})$$

Now, with (A.5), (A.6), (A.7) and (A.11), ψ_j defined by (A.2) can be written as

$$\begin{aligned}\psi_j(u, v, w) &= \exp(iC_j^{(N)}) \left[\int_{-\infty}^{\infty} d\mathbf{q}_j \exp\left\{-\frac{1}{2} \sum_{i,k=1}^4 S_{ik}(u, v, w) q_k q_{ij}\right\} \right. \\ &\quad \left. \times \left[\int_{-\infty}^{+\infty} d\mathbf{q}_j \exp\left(-\frac{1}{2} \sum_{i=1}^4 T_i q_{ij}^2\right) \right]^{-1}.\end{aligned}\quad (\text{A.12})$$

Introducing new variables q'_{ij} ($i = 1, \dots, 4$) by

$$\begin{aligned}q'_{1j} &= q_{1j}, & q'_{3j} &= \omega_{+,j} q_{3j}, \\ q'_{2j} &= q_{2j}, & q'_{4j} &= \omega_{-,j} q_{4j},\end{aligned}\quad (\text{A.13})$$

we obtain instead of (A.12)

$$\begin{aligned} \psi_j(u, v, w) = & \exp(iC_j^{(N)}) \left[\int_{-\infty}^{+\infty} d\mathbf{q}' \exp\left\{-\frac{1}{2} \sum_{i,k=1}^4 \bar{S}_{ik}(u, v, w) q'_k q'_i\right\}\right] \\ & \times \left[\int_{-\infty}^{+\infty} d\mathbf{q}' \exp\left\{-\frac{1}{2} \sum_{i=1}^4 \bar{T}_i q'^2\right\}\right]^{-1}. \end{aligned} \quad (\text{A.14})$$

Here the quantities \bar{T}_i are given by

$$\bar{T}_i = \beta \quad (i = 1, \dots, 4). \quad (\text{A.15})$$

The 4×4 matrix \bar{S} is defined as

$$\bar{S} = \beta U + iG(u, v, w), \quad (\text{A.16})$$

where $U = 4 \times 4$ unit matrix and the elements of the real matrix G are given by

$$G_{11} = G_{33} = -\frac{c_j}{\sigma_{M,N} \sqrt{N}} (u + v) - \frac{1}{\sigma_{H,N} \sqrt{N}} w, \quad (\text{A.17})$$

$$G_{22} = G_{44} = \frac{c_j}{\sigma_{M,N} \sqrt{N}} (u + v) - \frac{1}{\sigma_{H,N} \sqrt{N}} w, \quad (\text{A.18})$$

$$\begin{aligned} G_{12} = G_{21} = & \frac{c_j}{2\sigma_{M,N} \sqrt{N}} \{A_j \sin \omega_{+,jt} \cos \omega_{-,jt} \\ & - B_j \cos \omega_{+,jt} \sin \omega_{-,jt}\}v, \end{aligned} \quad (\text{A.19})$$

$$\begin{aligned} G_{34} = G_{43} = & -\frac{c_j}{2\sigma_{M,N} \sqrt{N}} \{A_j \cos \omega_{+,jt} \sin \omega_{-,jt} \\ & - B_j \sin \omega_{+,jt} \cos \omega_{-,jt}\}v, \end{aligned} \quad (\text{A.20})$$

$$\begin{aligned} G_{14} = G_{41} = & -\frac{c_j}{2\sigma_{M,N} \sqrt{N}} [\{A_j \sin \omega_{+,jt} \sin \omega_{-,jt} \\ & + B_j \cos \omega_{+,jt} \cos \omega_{-,jt}\}v + B_j u], \end{aligned} \quad (\text{A.21})$$

$$\begin{aligned} G_{23} = G_{32} = & \frac{c_j}{2\sigma_{M,N} \sqrt{N}} [\{A_j \cos \omega_{+,jt} \cos \omega_{-,jt} \\ & + B_j \sin \omega_{+,jt} \sin \omega_{-,jt}\}v + A_j u], \end{aligned} \quad (\text{A.22})$$

$$G_{13} = G_{31} = G_{24} = G_{42} = 0. \quad (\text{A.23})$$

From (A.14), (A.15) and (A.16) it follows that

$$|\psi_j(u, v, w)| = \frac{|\text{Det } \beta U|^{\frac{1}{2}}}{|\text{Det}(\beta U + iG)|^{\frac{1}{2}}} = \frac{\beta^2}{|\text{Det}(\beta U + iG)|^{\frac{1}{2}}}. \quad (\text{A.24})$$

Since G is a real symmetric matrix, we can diagonalize G by an orthogonal

transformation:

$$(OGO^{-1})_{ik} = A_i \delta_{ik} \quad (i, k = 1, \dots, 4), \quad (\text{A.25})$$

where the eigenvalues A_i of \mathbf{G} are real. It follows now, that

$$\begin{aligned} |\text{Det}(\beta\mathbf{U} + i\mathbf{G})|^2 &= \text{Det}(\beta\mathbf{U} + i\mathbf{G}) \cdot \text{Det}(\beta\mathbf{U} - i\mathbf{G}) \\ &= \text{Det}(\beta^2\mathbf{U} + \mathbf{G}^2) = \text{Det}\{\mathbf{O}(\beta^2\mathbf{U} + \mathbf{G}^2)\mathbf{O}^{-1}\} \\ &= \prod_{i=1}^4 (\beta^2 + A_i^2) \geq \beta^8 + \beta^6 \sum_{i=1}^4 A_i^2 = \beta^8 + \beta^6 \text{Tr } \mathbf{G}^2. \end{aligned} \quad (\text{A.26})$$

Since \mathbf{G} is symmetric, $\text{Tr } \mathbf{G}^2$ is given by

$$\text{Tr } \mathbf{G}^2 = \sum_{i,k=1}^4 (G_{ik})^2. \quad (\text{A.27})$$

With (A.17) - (A.23), eq. (A.27) reads explicitly

$$\begin{aligned} \text{Tr } \mathbf{G}^2 &= \frac{4c_j^2}{\sigma_{M,N}^2} \frac{(u+v)^2}{N} + \frac{4}{\sigma_{H,N}^2} \frac{w^2}{N} + \frac{c_j^2}{2\sigma_{M,N}^2} (A_j^2 + B_j^2) \frac{u^2 + v^2}{N} \\ &+ \frac{c_j^2}{2\sigma_{M,N}^2} \{(A_j^2 + B_j^2) \cos \omega_{+,jt} \cos \omega_{-,jt} + 2A_j B_j \\ &\times \sin \omega_{+,jt} \sin \omega_{-,jt}\} \frac{2uv}{N}. \end{aligned} \quad (\text{A.28})$$

Transforming to cylindrical variables by

$$u = \rho \cos \phi, v = \rho \sin \phi, w = w \quad (\rho \geq 0, 0 \leq \phi < 2\pi), \quad (\text{A.29})$$

we get instead of eq. (A.28)

$$\begin{aligned} \text{Tr } \mathbf{G}^2 &= \frac{4}{\sigma_{H,N}^2} \frac{w^2}{N} + \frac{c_j^2}{2\sigma_{M,N}^2} [8 + A_j^2 + B_j^2 \\ &+ \sin 2\phi \{8 + (A_j^2 + B_j^2) \cos \omega_{+,jt} \cos \omega_{-,jt} \\ &+ 2A_j B_j \sin \omega_{+,jt} \sin \omega_{-,jt}\}] \rho^2 / N. \end{aligned} \quad (\text{A.30})$$

It can now easily be checked, that the following inequality holds for all N, j ($= 1, \dots, N$) and ϕ :

$$\begin{aligned} D_j^{(N)}(\phi) &\equiv c_j^2 [8 + A_j^2 + B_j^2 + \sin 2\phi \{8 + (A_j^2 + B_j^2) \cos \omega_{+,jt} \cos \omega_{-,jt} \\ &+ 2A_j B_j \sin \omega_{+,jt} \sin \omega_{-,jt}\}] \geq 0. \end{aligned} \quad (\text{A.31})$$

Since both $\lim_{N \rightarrow \infty} \sigma_{M,N}$ and $\lim_{N \rightarrow \infty} \sigma_{H,N}$ exist, there are positive constants μ_M and μ_H such that

$$0 < \sigma_{M,N}^2 < \mu_M \quad (\text{A.32})$$

and

$$0 < \sigma_{H,N}^2 < \mu_H \quad (\text{A.33})$$

for all N .

It follows from (A.30) – (A.33) that

$$\text{Tr } G^2 \geq \frac{4}{\mu_H} \frac{w^2}{N} + \frac{1}{2\mu_M} D_j^{(N)}(\phi) \frac{\rho^2}{N}. \quad (\text{A.34})$$

Requiring the interaction matrix Ω for our system (*cf.* eq. (1)) to obey eq. (1.77), one can show that (see eq. (A.31))

$$\begin{aligned} \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N D_j^{(N)}(\phi) &= \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta c^2(\theta) \{8 + A^2(\theta) + B^2(\theta)\} \\ &+ \frac{\sin 2\phi}{2\pi} \int_{\pi}^{\pi} d\theta c^2(\theta) [8 + \{A^2(\theta) + B^2(\theta)\} \cos \omega_+(\theta)t \cos \omega_-(\theta)t \\ &+ 2A(\theta)B(\theta) \sin \omega_+(\theta)t \sin \omega_-(\theta)t], \end{aligned} \quad (\text{A.35})$$

where $c(\theta)$, $A(\theta)$, $B(\theta)$ and $\omega_{\pm}(\theta)$ are connected with the quantities c_j , A_j , B_j and $\omega_{\pm,j}$ in the usual way (*cf.* 1. section 4). The limit in (A.35) is established uniformly in ϕ . With the conditions imposed on the function $f(\theta)$ in 1. section 4, it can be shown, that there is a positive Δ , such that

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N D_j^{(N)}(\phi) \equiv \Delta(\phi) \geq \Delta > 0 \quad (\text{A.36})$$

for all ϕ .

Since the limit in (A.36) is established uniformly in ϕ , there is an N_0 such that, if $N \geq N_0$,

$$\frac{1}{N} \sum_{j=1}^N D_j^{(N)}(\phi) \geq \frac{1}{2}\Delta \quad (\text{A.37})$$

for all ϕ . Now we shall first give an upper bound for $D_j^{(N)}(\phi)$ for all N , $j (= 1, \dots, N)$ and ϕ . From (A.31) it follows that for arbitrary N and j

$$0 \leq D_j^{(N)}(\phi) \leq 2c_j^2(8 + A_j^2 + B_j^2) \quad (\text{A.38})$$

for all ϕ ,

or

$$0 \leq D_j^{(N)}(\phi) \leq \frac{4}{\omega_j^2(1 - \gamma^2)} \quad (\text{A.39})$$

for all ϕ .

Assuming that $\omega_j (= \omega_j^{(N)})$ obeys the inequality

$$\omega_j^2 \geq \omega_0^2 > 0 \quad (\text{A.40})$$

for all N and j , we obtain

$$0 \leq D_j^{(N)}(\phi) \leq \frac{4}{\omega_0^2(1 - \gamma^2)} \equiv D_0 \quad (\text{A.41})$$

for all N, j and ϕ . Let the step-function $E(x)$ be defined as

$$E(x) = \begin{cases} 0 & x < 0 \\ \frac{1}{2} & x = 0 \\ 1 & x > 0. \end{cases} \quad (\text{A.42})$$

From (A.37) it follows with (A.42) that, if $N \geq N_0$,

$$\frac{1}{N} \sum_{j=1}^N D_j^{(N)}(\phi) [E\{D_j^{(N)}(\phi) - \frac{1}{4}\Delta\} + E\{\frac{1}{4}\Delta - D_j^{(N)}(\phi)\}] \geq \frac{1}{2}\Delta \quad (\text{A.43})$$

for all ϕ . Let, for arbitrary $N \geq N_0$ and ϕ , $N_1^{(N)}(\phi)$ be the number of j 's (out of $1, \dots, N$) for which

$$D_j^{(N)}(\phi) > \frac{1}{4}\Delta.$$

One finds with (A.41) and (A.43) that $N_1^{(N)}(\phi)$ satisfies the following inequality

$$\frac{1}{N} \{N_1^{(N)}(\phi)D_0 + (N - N_1^{(N)}(\phi))\frac{1}{4}\Delta\} \geq \frac{1}{N} \sum_{j=1}^N D_j^{(N)}(\phi) \geq \frac{1}{2}\Delta, \quad (\text{A.44})$$

So that, if $N \geq N_0$,

$$\frac{1}{N} \{N_1^{(N)}(\phi)D_0 + (N - N_1^{(N)}(\phi))\frac{1}{4}\Delta\} \geq \frac{1}{2}\Delta \quad (\text{A.45})$$

for all ϕ . More explicitly we obtain, if $N \geq N_0$,

$$N_1^{(N)}(\phi) \geq \frac{\frac{1}{4}\Delta}{D_0 - \frac{1}{4}\Delta} N \equiv \varepsilon N \quad (0 < \varepsilon < 1) \quad (\text{A.46})$$

for all ϕ . Now we define the functions $\bar{\psi}_j(\rho, \phi, w)$ and $\bar{\psi}_N(\rho, \phi, w)$ as (cf. (A.29))

$$\bar{\psi}_j(\rho, \phi, w) \equiv \psi_j(u, v, w) \quad (j = 1, \dots, N) \quad (\text{A.47})$$

and

$$\bar{\psi}_N(\rho, \phi, w) \equiv \prod_{j=1}^N \bar{\psi}_j(\rho, \phi, w) = \psi_N(u, v, w). \quad (\text{A.48})$$

In general we have

$$|\bar{\psi}_j(\rho, \phi, w)| \leq 1 \quad (\text{A.49})$$

for all N, j, ρ, ϕ and w . However, if $N \geq N_0$, we have for at least εN values of $j (= 1, \dots, N)$ the more restrictive upper bound

$$|\bar{\psi}_j(\rho, \phi, w)| \leq \beta^2 \left\{ \beta^8 + \beta^6 \frac{4}{\mu_H} \frac{w^2}{N} + \beta^6 \frac{\frac{1}{4}\Delta}{2\mu_M} \frac{\rho^2}{N} \right\}^{\frac{1}{2}} \quad (\text{A.50})$$

for all ρ, ϕ and w . Here we have made use of eqs. (A.24), (A.26), (A.30), (A.31),

(A.32), (A.33), (A.34) and (A.46). Thus we obtain, if $N \geq N_0$

$$|\bar{\psi}_N(\rho, \phi, w)| \leq \left\{ 1 + \frac{4}{\mu_H} \frac{w^2}{N\beta^2} + \frac{\frac{1}{4}A}{2\mu_M} \frac{\rho^2}{N\beta^2} \right\}^{-\varepsilon N/4} \quad (\text{A.51})$$

for all ρ, ϕ and w . Now there is an N_2 such that, if $N \geq N_2$, the r.h.s. of (A.51) can be bounded by an integrable function. Let N_3 be the larger one of N_0 and N_2 . If $N \geq N_3$, $|\bar{\psi}_N(\rho, \phi, w)|$ and consequently $|\psi_N(u, v, w)|$ can be bounded by an integrable function. The function $\psi(u, v, w)$ defined by

$$\psi(u, v, w) \equiv \exp\left\{-\frac{1}{2}u^2 - \frac{1}{2}v^2 - \frac{1}{2}w^2 - \bar{R}(t)uv\right\} \quad (\text{A.52})$$

(cf. eq. (29) of the main text) is integrable. Since furthermore, as $N \rightarrow \infty$ $\psi_N(u, v, w) \rightarrow \psi(u, v, w)$ uniformly in any finite region of (u, v, w) space, we may finally conclude that, as $N \rightarrow \infty$

$$\begin{aligned} & \langle \rho_1 \delta(X(0) - X_0) \delta(X(t) - X) \delta(Y) \rangle \\ & \rightarrow \frac{1}{(2\pi)^{\frac{1}{2}}} \frac{1}{\{1 - \bar{R}^2(t)\}^{\frac{1}{2}}} \exp - \frac{X^2 - 2\bar{R}(t)XX_0 + X_0^2}{2\{1 - \bar{R}^2(t)\}} \end{aligned} \quad (\text{A.53})$$

uniformly in X and X_0 .

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SAMENVATTING

Het tijdsafhankelijke, statistisch-mechanische gedrag van systemen bestaande uit harmonische oscillatoren is het onderwerp geweest van vele, ook recente, onderzoeken. In het bijzonder hadden deze onderzoeken betrekking op de stochastische bewegingstypen van één enkel deeltje. Hoewel in zulke systemen bijv. niet voldaan wordt aan de macroscopische wet voor de warmtegeleiding van Fourier, is gebleken, dat deze systemen enkele opvallende eigenschappen vertonen, die karakteristiek zijn voor het gedrag van systemen met een meer realistische wisselwerking.

In de bovengenoemde onderzoeken werden grootheden bestudeerd, die essentieel lokaal van aard zijn. Het in dit proefschrift beschreven onderzoek echter betreft een grootheid, die betrekking heeft op het *gehele* systeem, namelijk de totale magnetisatie van een systeem bestaande uit harmonische oscillatoren in een magneetveld. In een tijdsafhankelijk magneetveld kan zo'n systeem dan dienen als model voor diamagnetische relaxatie, d.w.z. men mag verwachten, dat een dergelijk systeem zich, in kwalitatieve zin, gedraagt als een echt diamagnetisch systeem. In de theorie voor diamagnetische relaxatie, die in dit proefschrift wordt gegeven, speelt het tijdsgedrag van de autocorrelatiefunctie van de magnetisatie in het kanoniek ensemble een centrale rol. Mazur heeft onlangs aangetoond dat er een nauw verband bestaat tussen het tijdsgemiddelde van zo'n autocorrelatiefunctie en het ergodisch gedrag van de bewuste fasefunctie (of operator). In verband hiermee wordt ruime aandacht geschonken aan de ergodische eigenschappen van de totale magnetisatie in systemen bestaande uit harmonische oscillatoren.

In hoofdstuk I wordt een oplossing gegeven van de bewegingsvergelijkingen voor een lineaire keten van geladen, anisotroop gekoppelde, tweedimensionale harmonische oscillatoren in een magneetveld B . Een expliciete uitdrukking wordt afgeleid voor de autocorrelatiefunctie $R(t)$ van de magnetisatie in het kanoniek ensemble. Het asymptotisch tijdsgedrag van $R(t)$ wordt, in de limiet van een oneindig systeem, besproken in samenhang met de ergodische eigenschappen van de magnetisatie voor verschillende waar-

den van B en van de anisotropie parameter γ . Het blijkt, dat de magnetisatie alleen ergodisch is, indien $\gamma \neq 0$ en $B \rightarrow 0$.

In hoofdstuk II wordt een lineaire responsietheorie gegeven voor eenvoudige diamagnetische systemen in een tijdsafhankelijk magneetveld. Voorts worden uitdrukkingen gegeven voor de isotherme, adiabatisehe, geïsoleerde en frequentieafhankelijke susceptibiliteit per deeltje van diamagnetische systemen. Ongelijkheden tussen de verschillende susceptibiliteiten worden afgeleid. De theorie wordt toegepast op het in hoofdstuk I bestudeerde systeem.

In hoofdstuk III wordt, in de klassieke limiet, het stochastische gedrag onderzocht van de genormeerde totale magnetisatie $X(t)$ van het in hoofdstuk I bestudeerde systeem. Uitdrukkingen worden, in de limiet van een oneindig systeem, afgeleid voor de simultane en conditionele distributiefunctie van $X(t)$ in het mikrokanoniek ensemble. Het blijkt dat het proces $X(t)$ een stationair, Gaussisch proces, maar niet een Markoff-proces is. Het asymptotisch tijdsgedrag van de conditionele distributiefunctie en het conditionele tijdsgemiddelde van $X(t)$ wordt besproken in samenhang met de ergodische eigenschappen van $X(t)$ voor verschillende waarden van γ en B . Voorts blijkt dat het proces $X(t)$ een ergodisch proces is, indien $\gamma \neq 0$ en $B \rightarrow 0$. Tenslotte wordt een gelijkheid afgeleid die een verband geeft tussen de mikrokanonieke en kanonieke autocorrelatiefuncties van somvariabelen.

Tot slot volgen hier enkele gegevens met betrekking tot mijn studie.

In 1961 behaalde ik het diploma H.B.S.-B aan de Stevin-H.B.S. te 's-Gravenhage. In datzelfde jaar begon ik mijn studie in de wis- en natuurkunde aan de R.U. te Leiden. In december 1964 legde ik het kandidaats-examen (a') af en in april 1968 het doctoraal examen theoretische natuurkunde met bijvakken wiskunde en klassieke mechanica. Sinds januari 1967 ben ik, aanvankelijk als student-assistent en sinds mei 1968 als wetenschappelijk medewerker, verbonden aan het Instituut-Lorentz, waar ik onder leiding van Prof. Dr. P. Mazur onderzoek verrichtte op het gebied van de statistische mechanica, meer in het bijzonder aan modellen voor diamagnetische relaxatie. De resultaten van dit onderzoek worden in dit proefschrift beschreven. Gaarne spreek ik mijn dank uit aan de Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.), die mij in staat stelde deel te nemen aan een zomerschool gewijd aan "The many body problem" te Palma de Mallorca in augustus 1969 en aan "The advanced school for statistical mechanics and thermodynamics" te Austin, Texas, in april 1970.

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