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Ising model in a transverse field: I. Basic theory

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Abstract. A brief review is first made of systems for which the spin-$\frac{1}{2}$ Ising model in a transverse field provides a useful description (insulating magnetic systems, order–disorder ferroelectrics, cooperative Jahn–Teller systems and other systems with 'pseudo-spin'–phonon interactions). A perturbation expansion is then developed which provides for all temperatures an approximate description of the model. The perturbation series is classified with respect to the small parameter $1/z$, where z is the number of spins interacting with a given spin; this generates the molecular-field approximation and the random-phase approximation as the lowest-order description of the thermodynamic functions and correlation functions respectively. The leading-order approximations for the correlation functions, susceptibilities and spectral functions are discussed in detail. The formalism, which is the first application of such techniques to systems with varying magnetization direction, provides a basis for subsequent higher-order calculations of the free energy and correlation functions.

1. Introduction

This is the first of three papers investigating the properties of systems approximating to the Ising model in a transverse field. The model hamiltonian is

$$\mathscr{H} = -\Gamma \sum_i S_i^x - \tfrac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z \tag{1.1}$$

where S^α, $\alpha = x$, y or z are the components of spin, here taken to have magnitude $S = \frac{1}{2}$, J is an exchange interaction and Γ is the magnitude of the transverse field.

This hamiltonian was introduced by de Gennes (1963) as a model for hydrogen-bonded ferroelectrics, such as KH_2PO_4, where the proton sits in one or other minimum (corresponding to $S^z = \pm \frac{1}{2}$) of a double well, the transverse-field term represents the ability of the proton to tunnel between the two minima, and the exchange term represents the correlation energy of possible proton arrangements.

The model also applies in the limit of small Γ to order–disorder ferroelectrics without tunnelling, such as $NaNO_2$ where the two values of S^z give the two orientations of the NO_2 radical (Yamada and Yamada 1966, Yamada et al 1968). The possible use of the model for displacive ferroelectrics has been suggested by Elliott (1971a) and discussed in this context by Vaks and co-workers (Vaks 1968, Vaks and Larkin 1966, Larkin and Pikin 1969).

The model also applies in principle to ferromagnets with strong uniaxial anisotropy, such as Dy $(C_2H_5SO_4)_3 \cdot 9H_2O$, in a transverse magnetic field but because in such cases

Table 1. Systems related to Ising model in a transverse field

Category	Some specific examples	Notes on applicability of (a) Transverse Ising model	(b) Molecular-field approximation	References
Order–disorder ferroelectrics		1		Kanzig (1957), Jona and Shirane (1962), Cochran (1969)
(a) With tunnelling		2		de Gennes (1963), Kobayashi (1968)
	KH_2PO_4	3, 4	6	Samara (1971), Kaminow and Damen (1968)
	KD_2PO_4	3, 4	6	Samara (1971), Buyers et al (1968), Skalyo et al (1970)
	KH_2AsO_4			
	RbH_2AsO_4	4		
	RbD_2AsO_4	4		
	$NH_4H_2AsO_4$			
	$LiH_3(SeO_3)_2$	3, 4, 7		Samara (1970)
	$LiD_3(SeO_3)_2$	3, 4, 7		Samara (1970)
(b) Without tunnelling	TGS	5	6	Yamada et al (1970)
	Rochelle salt			
	$NaNO_3$	5, 8		Yamada et al (1970)
	$NaNO_2$	5	6	Yamada and Yamada (1966), Yamada et al (1968)
	NH_4Cl	5		Itoh and Yamagata (1962)
	$KNbO_3$			
Simple ferromagnets with uniaxial anisotropy	$Dy(C_2H_5SO_4)_39H_2O$	9	11, 12	Cooke et al (1962), Wolf (1971)
	$FeCl_22H_2O$ and related compounds	9	11	Narath and Schirber (1966)
	$CoCl_2$	9	13	Stout and Chisholm (1962)
	EuS	10	14	Moruzzi and Teaney (1963)
	$Cu(NH_4)_2Br_4 . 2H_2O$	10	14	Wielinga and Huiskamp (1969)
Rare earth compounds with singlet crystal-field ground state	Rare earth–group V compounds with NaCl structure. Rare earth–group VI anion compounds with NaCl structure	15	14	Trammel (1960, 1963), Wang and Cooper (1968), Cooper and Vogt (1971)
Simple Jahn–Teller systems	$DyVO_4$	16	17	Cooke et al (1970, 1971), Gehring et al (1971)
	$TbVO_4$	16	18	Ellis et al (1971)
			18	Harley et al (1971), Elliott (1971b), Elliott et al (1971)
	$TmVO_4$			Cooke et al (1972),
	$TmAsO_4$			Mangum et al (1971)
Other systems with 'pseudo-spin'–phonon interactions	$CeEthylSO_4$	19	20	Stevens and Van Eekelen (1967), Elliott and Parkinson (1967), Fletcher and Sheard (1971)

1. Evidence for order–disorder character from greater entropy difference between ferro-electric and paraelectric phases and smaller Curie constant than in displacive ferroelectrics, such as double oxides with perovskite structure (Blinc and Svetina 1966a, b).

2. Proton–lattice coupling, which gives rise to the spontaneous polarization, is neglected in transverse Ising model. Kobayashi (1968) has extended the model to include the coupling to the phonons.

3. Importance of tunnelling is indicated by decrease in T_c on application of pressure, due to increased tunnelling through lower and narrower barrier (Samara 1970).

4. Isotope effect in T_c indicates importance of tunnelling (which decreases on deuteration), though isotope effect due in part to change in exchange interaction, J (Blinc 1960).

5. Ising model without tunnelling seems to apply: limiting case of tunnelling model.

6. Use of molecular-field theory as leading approximation supported by largely dipolar character of exchange.

7. High T_c implies large J, implying tunnelling effects less important than in other hydrogen-bonded ferroelectrics.

8. Not ferroelectric: NO_3^- carries no dipole moment.

9. Very strong uniaxial anisotropy; $g_\perp \sim 0$.

10. Weak anisotropy.

11. One-dimensional magnetic character (weak interaction between chains): small number of nearest neighbours.

12. Interaction predominantly dipolar.

13. Two-dimensional magnetic character (small antiferromagnetic coupling between planes): small coordination number z.

14. Nearest-neighbour coupling with $z \sim 10$: molecular-field theory reasonable leading approximation.

15. Spin-$\frac{1}{2}$ transverse Ising model applies well if first excited state is also a singlet.

16. Transverse field small.

17. Predominance of optical phonon exchange as source of coupling suggests molecular-field theory only a crude approximation for $DyVO_4$.

18. Use of molecular-field theory supported by moderately strong strain coupling in $TbVO_4$, and by shape of specific heat curve in $TmVO_4$.

19. Weak coupling to phonons and consequent weak exchange.

20. Molecular-field theory can account for shape of Shottky anomaly (Fletcher and Sheard 1971).

the anisotropy arises from $g_\perp \sim 0$, the effect of the transverse field is much reduced (Wolf 1971).

The model can also be used (as has been fully discussed by Wang and Cooper 1968) to describe magnetic ordering in rare earth compounds with a singlet crystal-field ground state, such as certain rare earth–group V compounds with the NaCl structure.

It also applies to some Jahn–Teller systems, such as $DyVO_4$, $TbVO_4$, where spin up or down correspond approximately to the two doublets of the distorted phase, and modification of the crystal field by atomic displacements gives rise to an effective spin-spin interaction of the Ising type (Elliott 1971b). The transverse-field term arises from residual crystal-field effects. The same model also arises in the treatment of other systems, such as $CeEthSO_4$, whose crystal-field levels are modified by interaction with phonons (Elliott and Parkinson 1967, Elliott 1971a, and Stinchcombe, unpublished).

Table 1 gives a list of these systems related to the 'transverse Ising model' together with specific examples and further references, as well as notes about the applicability of the model and of the molecular-field approximations to it.

The model shows for $\Gamma \leqslant \Gamma_c$ a second-order transition, at a temperature T_c depending on Γ, above which one component of the effective field is zero. For Γ greater than the critical field Γ_c, no ordered phase occurs at any temperature. Below T_c the direction and magnitude of the effective field change continuously, resulting in a mixing of the usual

longitudinal and transverse properties familiar in magnetic systems with isotropic exchange. The associated spin waves have two branches, as in the antiferromagnet, resulting in zero-point effects such as lack of saturation in the low-temperature magnetization. The great variety of such properties in so simple a model makes the model worth study in itself, as well as for its implications about related but more complicated systems, and perhaps accounts for the many theoretical investigations of it.

Previous theoretical work on the model (de Gennes 1963, Brout *et al* 1966, Wang and Cooper 1968, and others) has been largely based on molecular-field theory for the thermodynamic behaviour or random-phase approximation for the correlation functions, though there also exist series expansions (Elliott *et al* 1970) and cluster approaches (Blinc and Svetina 1966a, b) for the thermodynamic quantities and recent treatments (Chock *et al* 1971, Chock and Dagonnier 1971, Williams 1971, and Moore and Williams (1972a, b, c) based on the method of Blume and Hubbard (1970) for correlation functions in the paramagnetic regime.

The molecular-field and random-phase approximations are good if the number z of spins j linked by the exchange J_{ij} to a given spin i is large (*or*, as a special case, the range of the interaction J_{ij} is large). Within certain limitations to be mentioned these approximations appear to be adequate in the magnetic systems where even though J_{ij} usually links only nearest-neighbour spins, coordination numbers z of the order of 6–12 are sufficient to ensure validity. In the hydrogen-bonded ferroelectrics and in such order–disorder ferroelectrics as $NaNO_2$, as well as in some magnetic systems, dipolar coupling is thought to play an important rôle and the long-range nature of this interaction supports the use of molecular-field and random-phase theories as leading approximations. As is well known for other systems, and will be shown for the transverse Ising model in this paper, molecular-field theory and a theory of the randon-phase type are provided respectively by the zeroth-order terms in the expansions in powers of $(1/z)$ of the free energy and of the correlation functions. This suggests the use of $1/z$ as a small parameter in terms of which the free energy or self energies of the correlation functions can be expanded to any desired order (Brout 1960, 1961).

It is the purpose of this series of three papers to apply such a technique to the transverse Ising model in both paramagnetic and ferromagnetic phases. The leading order approximation for the paramagnetic phase has previously been obtained by Houston and Bolton (1971). It will be shown here that by taking the first two terms in the $1/z$ expansion for the correlation functions the leading damping effects are included and one of the two major shortcomings of the leading-order approximations, the omission of damping, is rectified. The other major shortcoming, the inadequate treatment of the critical regime remains to all finite orders in the $1/z$ expansion, though the critical region is narrow if z is large (Thouless 1969).

In this work the first two terms in the expansion in powers of $1/z$ of the self energies of the correlation functions and the first three terms in the expansion of the free energy are discussed. Detailed results are given for the leading damping terms, which are of two distinct types, and for the free energy up to $O(1/z)$ for all Γ and T and up to $O(1/z)^2$ for $\Gamma \geqslant \Gamma_c$ *or* $T = (0)$, $\Gamma < \Gamma_c$. Other related quantities, such as spectral functions and components of the magnetization and susceptibility, are derived and the results compared with exact results for the one-dimensional model at zero temperature (Pfeuty 1971, and private communication) and with series expansions in powers of Γ/J or J/Γ (Pfeuty 1970, Elliott *et al* 1970). Most of the new results appear in the second and third papers which are concerned respectively with correlation functions, damping and spectral functions, and with free energy, magnetizations and susceptibilities.

In this first paper the basic theory is developed, certain exact relationships between correlation functions are derived and the leading-order results for the magnetizations (molecular-field theory) and correlation functions (random-phase approximation) are obtained. These leading-order results are mostly not new, though they are obtained by a new method which shows clearly their relationship to the $1/z$ expansion and allows a generalization to arbitrary order.

The perturbation technique used here has been previously applied to the Ising model ferromagnet in a longitudinal field (Brout 1960, 1961, Horwitz and Callen 1961, Englert 1963), to the Heisenberg model ferromagnet (Stinchcombe *et al* 1963, Spencer 1968b, Vaks *et al* 1968a, b, Stinchcombe 1970) and to the antiferromagnet (Solyom 1968, Cottam and Stinchcombe 1970a, b, c) and to the ferromagnet with dipole–dipole interactions (Cottam 1971a, b).

The present paper gives the first application of such a method to systems with varying magnetization direction.

Though their developments are different, the final methods of Stinchcombe *et al* (1963) and of Vaks *et al* (1968a, b) are identical, each using time-ordered cumulant spin averages replacing the propagators of ordinary many-body theory. The method can be applied to spin of any magnitude. Spencer (1968a, b) used a special representation for the spin operators which applies only to spin $\frac{1}{2}$ or 1. Grouping vertex terms within this method leads to the same perturbation rules as Stinchcombe *et al* (1963) and Vaks *et al* (1963). The time-ordered cumulant spin average used in the present work are given in the appendices of this paper.

The structure of this first paper is as follows: §2 gives a brief account of molecular-field theory for the transverse Ising model. Section 3 is divided into three subsections giving in turn the perturbation method, the classification of terms with respect to powers of the small parameter $1/z$, and the full renormalization in order $(1/z)^0$, leading to molecular-field theory. Section 4 gives exact relationships between correlation functions. Section 5 gives the leading approximation for the correlation functions, allowing a preliminary view of their character and how it changes with temperature. The relationship of the results to experiment, and to the exact results of Pfeuty for a zero-temperature spectral function are pointed out.

2. Molecular field theory

In molecular-field theory (de Gennes 1963, Tokunaga and Matsubara 1966) the transverse Ising system reduces to an assembly of spin vectors in the self-consistent molecular field

$$\gamma = \Gamma \hat{x} + J(0) \langle S^z \rangle \hat{z}. \tag{2.1}$$

$\langle S^z \rangle$ is here the z component of the consequent selfconsistently determined spin vector. The average spin vector is of magnitude $R_1 \equiv \frac{1}{2} \tanh \frac{1}{2}\beta\gamma$ and makes an angle θ with the z direction, where $\sin \theta = \Gamma/\gamma$, as shown in figure 1. Thus

$$\langle S^z \rangle = \frac{1}{2} \cos \theta \tanh \frac{1}{2}\beta\gamma = \frac{\gamma \cos \theta}{J(0)}. \tag{2.2}$$

This simple equation of state gives a correct qualitative picture of the behaviour of the system. For $\Gamma/J(0)$ less than $\frac{1}{2}$, $\langle S^z \rangle$ will become nonzero at temperatures less than a critical temperature $T_c(\Gamma)$.
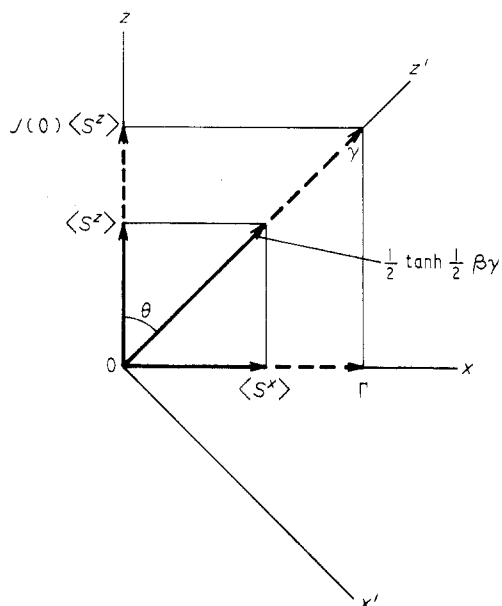
Figure 1. Components of magnetization and molecular field, and transformation of axes.

In this ordered phase $\cos \theta$ is nonzero and the equation of state is

$$\frac{\gamma}{J(0)} = \tfrac{1}{2} \tanh \tfrac{1}{2}\beta\gamma \equiv R_1 \tag{2.3}$$

with

$$\sin \theta = \Gamma/\gamma. \tag{2.4}$$

T_c (at which $\cos \theta$ becomes zero) is given by

$$\frac{\Gamma}{J(0)} = \tfrac{1}{2} \tanh \tfrac{1}{2}\beta_c\Gamma \tag{2.5}$$

and is sketched as a function of Γ in figure 2.

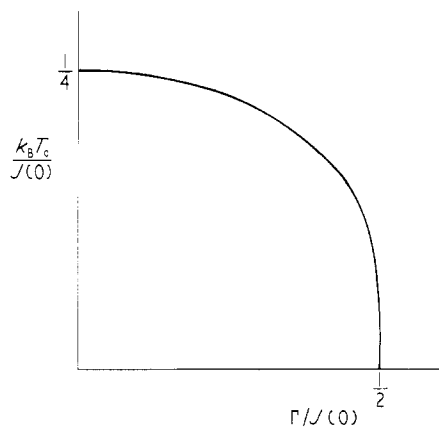

Figure 2. Relationship between critical temperature and transverse field.

In the paramagnetic phase, $T > T_c$, $\cos \theta$ is zero and $\langle S^z \rangle$ vanishes while

$$\langle S^x \rangle = \tfrac{1}{2} \tanh \tfrac{1}{2}\beta\Gamma. \tag{2.6}$$

The type of behaviour illustrated in figure 2 is related to the observed decrease in critical temperature of mixed terbium–yttrium antimonide as the fraction of Tb decreases, corresponding to decreasing J (Cooper and Vogt 1971). Also in hydrogen-bonded ferroelectrics such as KDP application of pressure increases overlap and therefore increases the tunnelling frequency Γ (Samara 1970). The resulting dependence of T_c on pressure has been seen experimentally to have a form similar to figure 2 (Samara 1971). Perhaps the most direct examples of the relationship (2.5) are however provided by the cooperative Jahn–Teller systems $TmAsO_4$ and $TmVO_4$ (Mangum *et al* 1971, Cooke *et al* 1972).

3. Perturbation method and $1/z$ expansion

3.1. Perturbation method

In order to go beyond molecular-field theory in our investigation of the thermodynamic behaviour and correlation functions of the system we use graphical perturbation theory methods starting first with $-\Gamma \sum_i S_i^x$ as unperturbed hamiltonian but subsequently making a renormalization to replace the unperturbed hamiltonian by the molecular-field hamiltonian

$$\mathscr{H}_{MF} = - \sum_i \gamma \cdot S_i. \tag{3.1}$$

In perturbation methods for spin systems the various quantities to be calculated, such as free energy, or Green functions, are as usual given in terms of linked cluster expansions in powers of the interaction J. But the unperturbed time-ordered averages of spin operators occurring in such expansions occur grouped into cumulant averages, hereafter called semi-invariants. The early work of Stinchcombe *et al* (1963) and the subsequent method of Vaks *et al* (1968a, b) lead directly to such averages, while the method of Spencer (1968b) for spin $\tfrac{1}{2}$ in which the spin is first represented by a pair of fermion operators, leads to n-point vertex functions (given in terms of the fermion propagators) which combine naturally to give the time-ordered semi-invariants (see Appendix B of Cottam and Stinchcombe 1970a).

The consequent scheme for calculating for the transverse Ising model the perturbation expansion for $-\beta F$, where F is the free energy, is:

(*a*) Draw all possible diagrams in which wavy lines labelled by q, λ representing interactions $J(q)$ are linked by vertices representing the semi-invariants $M^{zz\cdots z}(\lambda_1 \ldots \lambda_n)$ whose frequency variables correspond to the labels on the interactions incident upon them.

(*b*) The labelling of the diagrams is such that frequency and wavevector are conserved at each vertex.

(*c*) A factor $\beta J(q)$ is associated with each wavy line labelled by q, λ.

(*d*) A factor $M^{zz\cdots z}(\lambda_1 \ldots \lambda_n)$ is associated with each vertex at which n interactions labelled by $q_1\lambda_1$, $q_2\lambda_2$, $\ldots$, $q_n\lambda_n$ are incident. (The low order semivariants are given in Appendix 1. They are independent of wavevector labels.)

(*e*) Associate a factor $(1/p)$ with a graph invariant under p symmetry operations.

(f) Finally sum over all wavevector and frequency labels within the restriction imposed by (b), where each λ goes over the values $2n\pi/(k_{\mathrm{B}}T)$, n integral.

If instead of the free energy it is required to calculate the average of some time-ordered cumulant combination Q of m spin operators a similar procedure is followed except that 'rooted' graphs now arise as follows: it is convenient first to Fourier analyse Q. With

$$Q_{i_1\ldots i_m}^{\alpha_1\ldots\alpha_m}(\tau_1\ldots\tau_m) \equiv \text{cumulant part of } \langle TS_{i_1}^{\alpha_1}(\tau_1)\ldots S_{i_m}^{\alpha_m}(\tau_m)\rangle \tag{3.2}$$

where T is the usual operator ordering the spins with respect to 'times' τ_i and the α_i identify cartesian components, define

$$Q^{\alpha_1\ldots\alpha_m}(q_1\lambda_1',\ldots,q_m\lambda_m')$$

by

$$Q^{\alpha_1\ldots\alpha_m}(q_1\lambda_1',\ldots,q_m\lambda_m') = \frac{1}{\beta^m}\int_0^\beta d\tau_1\ldots\int_0^\beta d\tau_m \sum_{i_1\ldots i_m} Q_{i_1\ldots i_m}^{\alpha_1\ldots\alpha_m}(\tau_1\ldots\tau_m)$$

$$\times \exp\left\{\sum_{i=1}^m (i\lambda_i'\tau_i + i\boldsymbol{r}_i\cdot\boldsymbol{q}_i)\right\}. \tag{3.3}$$

Then because of the m additional spin operators contributed by Q to the terms averaged in arriving at the perturbation series, the diagrams drawn for the evaluation of Q are all those in which the additional frequency, wavevector and component labels λ_i', q_i, α_i are distributed in all possible ways over vertices joined to interactions. The consequent semi-invariant factors $M^{z\ldots z\alpha_i\ldots\alpha_j}(\lambda_1\ldots\lambda_n\lambda_i'\ldots\lambda_j')$ are as before identified by the frequency labels $\lambda_1\ldots\lambda_n$ associated with the n interactions incident upon the vertex and with the frequency and component labels $\lambda_i'\alpha_i,\ldots,\lambda_j'\alpha_j$ of any operators from Q now associated with the vertex. (These 'mixed' semi-invariants are also included in the Appendices). The remaining factors are given by the same rules as for the free-energy calculation.

Simple examples of the use of this procedure are given at the end of this section (where it is used to derive molecular-field theory) and in § 4, § 5 where leading approximations for the Green functions are arrived at.

3.2. The $1/z$ expansion

As in the previous work on the ferromagnet and antiferromagnet referred to in the Introduction we identify a parameter of smallness by means of which diagrams may be
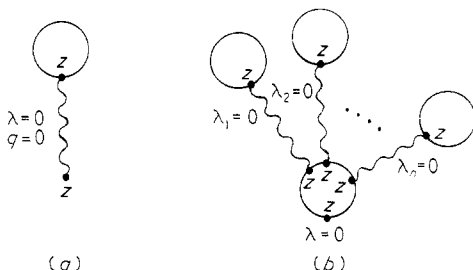

Figure 3. (a) A 'Hartree' insertion. (b) Addition of n Hartree articulations to a vertex.

classified and important terms selected. For systems whose bulk thermodynamic properties are well described by molecular-field theory, the appropriate small parameter is $1/z$ where z is the number of spins linked directly by the exchange interaction J_{ij} to a given spin. This is because, as will be shown shortly, the leading order term $(1/z)^0$ in expansions in powers of $1/z$ of thermodynamic functions is the molecular-field value.

The classification of terms with respect to this parameter is provided by the following rule:

A diagram containing t independent wavevector labels which are eventually summed over and which appear explicitly in one or more of the $J(q)$ is of order $(1/z)^t$. (See for instance Cottam and Stinchcombe 1970a, Appendix A).

3.3. Molecular-field theory, and renormalization in order $(1/z)^0$

According to the rule just stated the addition of the Hartree articulation shown in figure 3a does not alter the $(1/z)$ order of a diagram since the only interaction J in this articulation carries the unsummed wavevector label $q = 0$. Thus any vertex corresponding to a semi-invariant spin average evaluated in the external field can have added to it arbitrarily many such Hartree articulations without altering the $1/z$ order of the diagram in which it appears. The consequent $(1/z)^0$ renormalization of vertices is evaluated as follows.

We first add an additional label to the semi-invariants to denote the external field in the unperturbed hamiltonian which appears in the Heisenberg operators and the density operator with which the averaging is carried out: thus the vertex in figure 3a is now rewritten as $M^z(\lambda; \Gamma)|_{\lambda=0}$ and denotes

$$\beta^{-1} \int_0^\beta d\tau \exp(i\lambda\tau) \frac{\text{Tr}\{\exp(\beta\Gamma S^x) T S^z(\tau)\}}{\text{Tr}\{\exp(\beta\Gamma S^x)\}}$$

evaluated at $\lambda = 0$. $S^z(\tau)$ here means $\exp(\tau\Gamma S^x)S^z \exp(-\tau\Gamma S^x)$ but because of the cyclic invariance of the trace the label and the time ordering in this last expression are redundant. The addition of n Hartree articulations to such a vertex, as shown in figure 3b, gives $(1/n!)(\beta J(0)M^z(0; \Gamma))^n M^{zz\cdots z}(0, 0 \ldots 0; \Gamma)$, since $n!$ is the symmetry factor p for this diagram. Now

$$M^{\alpha_1\cdots\alpha_m x}(\lambda_1', \ldots, \lambda_m', 0; \Gamma) = \frac{\partial}{\partial\beta\Gamma} M^{\alpha_1\cdots\alpha_m}(\lambda_1', \ldots \lambda_m'; \Gamma) \tag{3.4}$$

essentially because (Horwitz and Callen 1961, Englert 1963, Stinchcombe *et al* 1963, Vaks *et al* 1968a, b) differentiation with respect to $\beta\Gamma$ brings down from the density operators $\exp(\beta S^x\Gamma)$ the required additional factor S^x into the spins being averaged. The frequency to be associated with the additional S^x is $\lambda = 0$ since the operator occurs in all possible time orderings with respect to the other operators. Similarly the density operator can be used as a generating function for higher-order semi-invariants involving S^z at zero frequency by adding to the field Γ a small field, $\Gamma_\parallel$ say, in the z direction: defining $\boldsymbol{h}$ by

$$\boldsymbol{h} = \Gamma\hat{\boldsymbol{x}} + \Gamma_\parallel\hat{\boldsymbol{z}}, \tag{3.5}$$

$$M^{\alpha_1\cdots\alpha_m z}(\lambda_1, \ldots, \lambda_m', 0; \boldsymbol{h}) = \frac{\partial}{\partial\beta\Gamma_\parallel} M^{\alpha_1\cdots\alpha_m}(\lambda_1' \ldots \lambda_m'; \boldsymbol{h}). \tag{3.6}$$

Thus the contribution from figure 3b to the renormalization of the semi-invariant $M^z(0; \Gamma)$ is

$$\left[\frac{1}{n!} \left(\beta J(0) M^z(0; \Gamma) \frac{\partial}{\partial \beta \Gamma_{\|}} \right)^n M^z(0; \boldsymbol{h}) \right] \Bigg|_{\Gamma_{\|}=0}.$$

Summing over all n yields the Taylor series for

$$M^z(0; \boldsymbol{h} + J(0) M^z(0; \Gamma) \hat{\boldsymbol{z}}) \big|_{\Gamma_{\|}=0}.$$

The $(1/z)^0$ renormalization is not yet complete, however, since the semi-invariants $M^z(0; \Gamma)$ in the Hartree articulations of figure 3b can also be similarly renormalized without changing the overall $1/z$ order. The complete $(1/z)^0$ renormalization of $M^z(0; \Gamma)$ is thus

$$M^z(0; \Gamma) \to M^z(0; \gamma) \tag{3.7}$$

where

$$\gamma = \Gamma \hat{\boldsymbol{x}} + J(0) M^z(0; \gamma) \hat{\boldsymbol{z}}. \tag{3.8}$$

Similarly

$$M^x(0; \Gamma) \to M^x(0; \gamma). \tag{3.9}$$

Since $M^z(0; \gamma)$ is just the average of S^z in the field γ it can be seen that γ is the selfconsistently determined molecular field of § 2. The full $(1/z)^0$ renormalization of semi-invariants of arbitrary order, and with general frequency labels, is carried out in the same way with the result

$$M^{\alpha_1 \cdots \alpha_n}(\lambda_1' \ldots \lambda_n'; \Gamma) \to M^{\alpha_1 \cdots \alpha_n}(\lambda_1' \ldots \lambda_n'; \gamma) \tag{3.10}$$

corresponding to the replacement of the unperturbed field Γ by the molecular field γ. This proves the statement that molecular-field theory is equivalent to the leading order $(1/z)^0$ in an expansion in powers of $(1/z)$.

Hereafter it will be assumed that the $(1/z)^0$ renormalization has already been carried out, so that the semi-invariants all involve averages in the molecular field, and no Hartree articulations are drawn.

The renormalized semi-invariants $M(\gamma)$ are easily obtained from $M(\Gamma)$, Appendices 1 and 2, by a change of axes from xyz to axes $x'y'z'$ where $\hat{\boldsymbol{z}}'$ is along the molecular field and $\hat{\boldsymbol{y}}' = \hat{\boldsymbol{y}}$ (figure 1).

For, using

$$S^x = \cos \theta \, S^{x'} + \sin \theta \, S^{z'}$$

$$S^y = S^{y'}$$

$$S^z = -\sin \theta \, S^{x'} + \cos \theta \, S^{z'} \tag{3.11}$$

the semi-invariants $M^{\alpha_1 \cdots \alpha_n}(\lambda_1 \ldots \lambda_n; \gamma)$ can be written as linear combinations of $M^{\beta_1 \cdots \beta_n}(\lambda_1 \ldots \lambda_n; \gamma)$ where

$$M^{\beta_1 \cdots \beta_n}(\lambda_1 \ldots \lambda_n; \gamma) = M^{\beta_1 \cdots \beta_n}(\lambda_1 \ldots \lambda_n; \Gamma) \big|_{\Gamma = |\gamma|} \tag{3.12}$$

(Appendix 2). Thus

$$M^z(0; \gamma) = - \sin\theta \, M^{x'}(0;\gamma) + \cos\theta \, M^{z'}(0; \gamma)$$

$$= - \sin\theta \, M^x(0; \Gamma)|_{\Gamma = |\gamma|} + \cos\theta \, M^z(0; \Gamma)|_{\Gamma = |\gamma|}$$

$$= R_1 \cos\theta. \tag{3.13}$$

It follows that (3.8) is equivalent to the molecular-field equations of state given in §2.

4. Exact relationships for generalized susceptibilities

The generalized susceptibilities

$$G^{\alpha\beta}(q_1\lambda_1, q_2\lambda_2) = \frac{1}{\beta^2} \sum_{ij} \int_0^\beta \int_0^\beta d\tau_1 \, d\tau_2 \exp\{i(\lambda_1\tau_1 + \lambda_2\tau_2) + i(\boldsymbol{q}_1 \cdot \boldsymbol{r}_i + \boldsymbol{q}_2 \cdot \boldsymbol{r}_j)\}$$

$$\times \{\langle TS_i^\alpha(\tau_1)S_j^\beta(\tau_2)\rangle - \langle S_i^\alpha(\tau_1)\rangle\langle S_j^\beta(\tau_2)\rangle\}$$

$$\equiv \delta(\boldsymbol{q}_1 + \boldsymbol{q}_2)\delta_{\lambda_1 + \lambda_2, 0} \, G^{\alpha\beta}(q_1\lambda_1) \tag{4.1}$$

reduce in the case $q_1 = 0$, $\lambda_1 = 0$ to $(1/\beta)$ times the usual susceptibilities $\chi^{\alpha\beta}$ obtained by differentiating the free energy with respect to external fields in the α and β directions.

These generalized susceptibilities and the related Green functions

$$\tilde{G}^{\alpha\beta}(q_1\lambda_1, q_2\lambda_2) = \frac{1}{\beta^2} \sum_{ij} \int_0^\beta \int_0^\beta d\tau_1 \, d\tau_2 \exp\{i(\lambda_1\tau_1 + \lambda_2\tau_2) + i(\boldsymbol{q}_1 \cdot \boldsymbol{r}_i + \boldsymbol{q}_2 \cdot \boldsymbol{r}_j)\}$$

$$\times \langle TS_i^\alpha(\tau_1)S_j^\beta(\tau_2)\rangle$$

$$\equiv \delta(\boldsymbol{q}_1 + \boldsymbol{q}_2)\delta_{\lambda_1 + \lambda_2, 0} \, \tilde{G}^{\alpha\beta}(q_1\lambda_1) \tag{4.2}$$

of which they are the cumulant part, play an important rôle in the theory of the transverse Ising model. They are directly related to the cross section for inelastic scattering of slow neutrons (Marshall and Lowde 1968, Buyers *et al* 1968, Skalyo *et al* 1970) and light (Kaminow and Damen 1968) as well as to x-ray diffuse scattering (Yamada *et al* 1970). They also give direct information about the collective modes of the system (the spin waves of the simple magnetic systems, the tunnelling modes of the hydrogen-bonded ferroelectric, or the magnetic excitons of the singlet ground state magnetic systems).
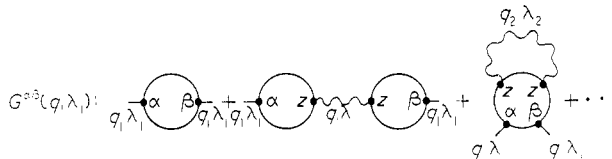

Figure 4. Some simple terms in the graphical expansion of the generalized susceptibility.

Some simple terms in the graphical expansion of $G^{\alpha\beta}(q_1\lambda_1)$ are shown in figure 4 where it has been assumed, as in all the subsequent development, that the $(1/z)^0$ renormalization has been carried out, and so no Hartree articulations appear.

If we define a 'polarization part' $\mathcal{M}^{\alpha\beta}(q\lambda)$ of $G^{\alpha\beta}(q\lambda)$ as the contribution from all those graphs for $G^{\alpha\beta}$ which cannot be separated into two by breaking a single interaction (including, for example, the first and third terms of figure 4), we have

$$G^{\alpha\beta}(q\lambda) = \mathcal{M}^{\alpha\beta}(q\lambda) + \mathcal{M}^{\alpha z}(q\lambda)\beta J(q)G^{z\beta}(q\lambda) \tag{4.3}$$

so that

$$G^{\alpha\beta}(q\lambda) = \mathcal{M}^{\alpha\beta}(q\lambda) + \frac{\mathcal{M}^{\alpha z}(q\lambda)\beta J(q)\mathcal{M}^{z\beta}(q\lambda)}{1 - \beta J(q)\mathcal{M}^{zz}(q\lambda)}. \tag{4.4}$$

In the $1/z$ expansion the lowest-order contribution to $G^{\alpha\beta}$ contains no internal wavevector summations and is given by the chain graphs obtained by taking $M^{\alpha\beta}(\lambda, -\lambda; \gamma)$ for $\mathcal{M}^{\alpha\beta}(q\lambda)$ in (4.4). The properties of this simplest approximation will be discussed in §5.

It might appear that each of the nine components of $G^{\alpha\beta}$ (or $\mathcal{M}^{\alpha\beta}$) has to be calculated individually. This is not necessary because simple exact relationships exist between the components: first of all, from (4.1),

$$G^{\alpha\beta}(q_1\lambda_1, q_2\lambda_2) = G^{\beta\alpha}(q_2\lambda_2, q_1\lambda_1) \tag{4.5}$$

and similarly for $\mathcal{M}^{\alpha\beta}$. Secondly, since

$$\frac{\partial}{\partial \tau} S_j^z(\tau) = [\mathcal{H}, S_j^z(\tau)] = i\Gamma S_j^y(\tau) \tag{4.6}$$

it follows that

$$i\lambda G^{zz}(q\lambda) = -i\Gamma G^{yz}(q\lambda)$$

$$i\lambda G^{zy}(q\lambda) = -i\Gamma G^{yy}(q\lambda) + \left(\frac{i}{\beta}\right)\langle S_0^x \rangle$$

$$i\lambda G^{zx}(q\lambda) = -i\Gamma G^{yx}(q\lambda) - \left(\frac{i}{\beta}\right)\langle S_0^y \rangle. \tag{4.7}$$

The last terms in the second and third equations come from the commutators $[S_q^y, S_{-q}^z]$ and $[S_q^z, S_{-q}^x]$ arising from the time ordering in the τ derivative of the spin averages $\langle TS_q^\alpha(\tau)S_{-q}^\beta(\tau')\rangle$ in $G^{\alpha\beta}(q\lambda)$. $\langle S_0^y \rangle$ is in general zero.

It follows from (4.4) that $\mathcal{M}^{\alpha\beta}$ satisfies similar equations:

$$i\lambda \mathcal{M}^{zz}(q\lambda) = -i\Gamma \mathcal{M}^{yz}(q\lambda)$$

$$i\lambda \mathcal{M}^{zy}(q\lambda) = -i\Gamma \mathcal{M}^{yy}(q\lambda) + \left(\frac{i}{\beta}\right)\langle S_0^x \rangle$$

$$i\lambda \mathcal{M}^{zx}(q\lambda) = -i\Gamma \mathcal{M}^{yx}(q\lambda). \tag{4.8}$$

So also do the unperturbed and molecular field semi-invariants $M^{\alpha\beta}(\lambda, -\lambda; \Gamma)$ and $M^{\alpha\beta}(\lambda, -\lambda; \gamma)$: the commutator of S_j^z with the unperturbed hamiltonian or the molecular-field hamiltonian is again $i\Gamma S^y$, so that each of $M^{\alpha\beta}(\lambda, -\lambda; \Gamma)$ and $M^{\alpha\beta}(\lambda, -\lambda; \gamma)$ satisfy equations identical to those (4.8) satisfied by $\mathcal{M}^{\alpha\beta}$ but with the exact $\langle S_0^x \rangle$ replaced by the unperturbed average or the molecular-field average of S_0^x respectively. This can be

demonstrated explicitly using the expressions of the appendices for the semi-invariants. For instance from equations (A2.6) and (A2.7) of Appendix 2

$$M^{zy}(\lambda, -\lambda; \gamma) = \frac{R_1 \beta \lambda \sin \theta}{\beta^2 \{\gamma^2 - (i\lambda)^2\}} \tag{4.9}$$

and

$$M^{yy}(\lambda, -\lambda; \gamma) = \frac{R_1 \beta \gamma}{\beta^2 \{\gamma^2 - (i\lambda)^2\}} \tag{4.10}$$

where $\sin \theta = \Gamma/\gamma$. It therefore follows that

$$i\lambda M^{zy}(\lambda, -\lambda; \gamma) = -i\Gamma M^{yy}(\lambda, -\lambda; \gamma) + \left(\frac{i}{\beta}\right) \langle S_0^x \rangle_0 \tag{4.11}$$

where

$$\langle S_0^x \rangle_0 \equiv \frac{\Gamma}{\gamma} R_1 \tag{4.12}$$

the molecular-field result.

The exact relationships (4.5) and (4.7) reduce the number of components of G (or $\mathcal{M}$) to be calculated to three, for example G^{zz}, G^{zx} and G^{xx}. These are given in terms of $\mathcal{M}^{zz}$, $\mathcal{M}^{zx}$ and $\mathcal{M}^{xx}$ by

$$G^{xx}(q\lambda) = \mathcal{M}^{xx}(q\lambda) + \frac{\mathcal{M}^{xz}(q\lambda)\beta J(q)\mathcal{M}^{zx}(q\lambda)}{1 - \beta J(q)\mathcal{M}^{zz}(q\lambda)}$$

$$G^{zx}(q\lambda) = \frac{\mathcal{M}^{zx}(q\lambda)}{1 - \beta J(q)\mathcal{M}^{zz}(q\lambda)}$$

$$G^{zz}(q\lambda) = \frac{\mathcal{M}^{zz}(q\lambda)}{1 - \beta J(q)\mathcal{M}^{zz}(q\lambda)}. \tag{4.13}$$

This completes the formal part of our work. In the next section and in the subsequent papers the $(1/z)$ expansion is used to arrive at approximations for these exact expressions.

5. Leading approximations for generalized susceptibilities

By applying the classification of § 3.2, the leading term $G_0^{\alpha\beta}$ in the expansion of $G^{\alpha\beta}$ in inverse powers of z is obtained by replacing $\mathcal{M}^{\alpha\beta}(q\lambda)$ in (4.4) by the molecular-field renormalized semi-invariants $M^{\alpha\beta}(\lambda, -\lambda; \gamma)$. The result is

$$G_0^{xx}(q\lambda) = M^{xx}(\lambda, -\lambda; \gamma) + \frac{M^{xz}(\lambda, -\lambda; \gamma)\beta J(q)M^{zx}(\lambda, -\lambda; \gamma)}{1 - \beta J(q)M^{zz}(\lambda, -\lambda; \gamma)}$$

$$= (1 - \delta_{\lambda, 0}) \frac{R_1 \beta \gamma \cos^2 \theta}{\beta^2 [\omega(q)^2 - (i\lambda)^2]} + \delta_{\lambda, 0} \frac{1}{\beta J(0)}$$

$$\times \left(\frac{\cos^2 \theta + (\sin^2 \theta \beta J(0) - \beta J(q))(\tfrac{1}{4} - R_1^2)}{1 - \{J(q)/J(0)\} \sin^2 \theta - \beta J(q)(\tfrac{1}{4} - R_1^2) \cos^2 \theta} \right) \tag{5.1}$$

$$G_0^{zx}(q\lambda) = -(1 - \delta_{\lambda,0}) \frac{R_1 \beta\gamma \cos\theta \sin\theta}{\beta^2 \{\omega(q)^2 - (i\lambda)^2\}} - \delta_{\lambda,0} \frac{\cos\theta \sin\theta \{(R_1/\beta\gamma) - (\frac{1}{4} - R_1^2)\}}{1 - \beta J(q)\{(R_1/\beta\gamma)\sin^2\theta + (\frac{1}{4} - R_1^2)\cos^2\theta\}}$$

(5.2)

$$G_0^{zz}(q\lambda) = (1 - \delta_{\lambda,0}) \frac{R_1 \beta\gamma \sin^2\theta}{\beta^2[\omega(q)^2 - (i\lambda)^2]}$$

$$+ \delta_{\lambda,0} \left(\frac{(R_1/\beta\gamma)\sin^2\theta + (\frac{1}{4} - R_1^2)\cos^2\theta}{1 - \beta J(q)\{(R_1/\beta\gamma)\sin^2\theta + (\frac{1}{4} - R_1^2)\cos^2\theta\}} \right)$$

(5.3)

where

$$\omega(q)^2 = \gamma^2 - J(q)R_1\gamma \sin^2\theta.$$

(5.4)

This theory will be seen to have properties similar to the random-phase approximation of Brout et al (1966). $\omega(q)$ is the frequency of the collective mode of wavevector q in the system (spin wave, tunnelling mode or magnetic exciton, here referred to collectively as 'spin wave'). This sort of collective behaviour is a characteristic of the transverse generalized susceptibility in the corresponding approximation for the ordinary Heisenberg model, where the longitudinal susceptibility has a static form (Stinchcombe et al 1963). For the transverse Ising model, because the molecular field is in general not parallel to x, y or z the collective behaviour and the static part each occur in all the components of G_0. The two characteristic parts separate for particular values of θ, such as $\theta = \pi/2$ (the paramagnetic regime). In the paramagnetic regime G_0^{zz} is purely collective, G_0^{xx} becomes purely static, while G_0^{zx} vanishes.

In this leading approximation the collective modes are undamped. The existence of two branches, with energies $\pm |\omega(q)|$ implies the existence of zero-point terms in the low-temperature thermodynamic properties, and these will be investigated in a later
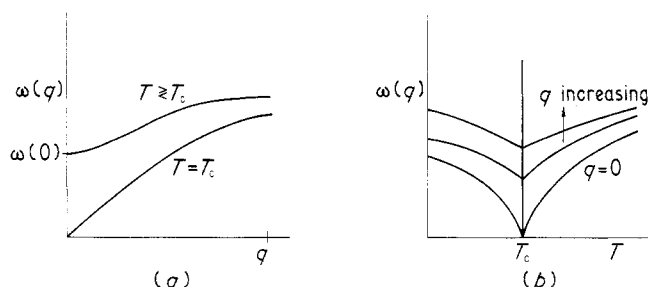

Figure 5. The spin wave or tunnelling-mode frequency as a function of (a) wavevector (b) temperature.

paper. If Γ is less than the critical field the molecular-field transition occurs at a critical temperature T_c given by (2.5) and the frequency $\omega(0)$ of the long-wavelength spin waves becomes zero at T_c. Thus the approximation yields a soft-mode behaviour of the type proposed by Cochran (1961) and others. Figure 5 shows the form of the spin wave frequency (5.4) as a function of q and T. Such behaviour has been observed in both KH_2PO_4, where $\omega(0)$ has been measured by Raman scattering in the paraelectric phase by Kaminow and Damen (1968), and in KD_2PO_4 where neutron diffraction has been used by Buyers et al (1968) to determine $\omega(q)$ for $T > T_c$.

From (5.4), near T_c, $\omega(q)$ behaves as follows:

$$\omega(q)^2 \sim \Gamma^3(\beta_c - \beta)\left(\frac{\frac{1}{4} - R_c^2}{R_c}\right) + \{J(0) - J(q)\}R_c\Gamma \qquad T > T_c$$

$$\sim \frac{2\Gamma^3(\beta - \beta_c)(\frac{1}{4} - R_c^2)}{R_c - \beta_c\Gamma(\frac{1}{4} - R_c^2)} + \{J(0) - J(q)\}R_c\Gamma \qquad T < T_c \qquad (5.5)$$

where

$$R_c \equiv \tfrac{1}{2}\tanh\tfrac{1}{2}\beta_c\Gamma = \frac{\Gamma}{J(0)}. \qquad (5.6)$$

Thus, in agreement with the experimental observations,

$$\omega(q)^2 = A|T - T_c| + Bq^2 \qquad (5.7)$$

for T near T_c and small q, where B is the same just above and below T_c and A takes different values $A_>$, $A_<$ (whose ratio is $\{1 - \beta_c\Gamma(\frac{1}{4} - R_c^2)/R_c\}:2$) on either side of the transition. Associated correlation lengths $\xi_{\lessgtr}$ can be defined with

$$\xi_{\lessgtr} = B^{1/2}(A_{\lessgtr}|T - T_c|)^{-1/2}. \qquad (5.8)$$

If Γ is sufficiently small that the system orders at low temperatures, the character of the generalized susceptibilities varies as follows with decreasing temperature:

(i) In the whole of the paramagnetic regime, $T > T_c$, where $\cos\theta$ vanishes

$$G_0^{xx}(q\lambda) = \delta_{\lambda,0}(\tfrac{1}{4} - R_1^2) \qquad G_0^{zx} = 0 \qquad G_0^{zz}(q\lambda) = \frac{R_1\beta\gamma}{\beta^2\{\omega(q)^2 - (i\lambda)^2\}}. \qquad (5.9)$$

(ii) As T tends to T_c, $G_0^{xx}(q, 0)$ decreases regularly to $\{\beta_c J(0)\}^{-1}$ while $G_0^{zz}(0, 0)$ diverges like $\omega(0)^{-2} \propto (T - T_c)^{-1}$.

(iii) For T slightly below T_c, where $\cos\theta \propto (T_c - T)^{1/2}$ is small, $G_0^{zx}(q\lambda)$ becomes nonzero but being in general proportional to $\cos\theta$ is small (except in the long-wavelength limit where, for example, $G_0^{zx}(0, 0) \sim -\delta_{\lambda 0}\tan\theta/\{\beta_c J(0)\}$.) The weight of the collective part in G_0^{xx} is even smaller, being proportional to $\cos^2\theta$, than in G_0^{xz}.

(iv) As T decreases still further to $T \sim 0$, $\cos\theta$ increases but remains small if $J \ll \Gamma$. As $T \to 0$, the factors $(\frac{1}{4} - R_1^2)$ vanish and $G_0^{xx}(q, \lambda)$, $G_0^{zx}(q, \lambda)$ and $G_0^{zz}(q, \lambda)$ become respectively $\cos\theta$, $-\cos\theta\sin\theta$ and $\sin^2\theta$ times $R_1\beta\gamma\cos^2\theta\{\beta^2(\omega(q)^2 - (i\lambda)^2)\}^{-1}$, that is, purely collective.

(v) If $J \gg \Gamma$, for low temperatures $\sin\theta$ becomes small since the effective field is then dominated by its exchange component. The collective modes then appear only in $G_0^{xx}(q, \lambda)$ and their frequency $\omega(q)$ approaches the frequency γ of Larmor procession in the molecular field. G_0^{zx} vanishes like $\sin\theta$, and G_0^{zz} becomes purely static. This type of behaviour is characteristic of the Ising model without an external field and would apply for instance to order–disorder ferroelectrics without tunnelling, such as $NaNO_2$ (Yamada *et al* 1968) or to the highly anisotropic magnets in table 1.

We now discuss more fully the static, long-wavelength parts of $G_0^{\alpha\beta}(q, \lambda)$, which are related to the $(1/z)^0$ approximations $\chi_0^{\alpha\beta}$ to the usual static susceptibilities or dielectric constants $\chi^{\alpha\beta}$ through

$$\chi_0^{\alpha\beta} = \beta G_0^{\alpha\beta}(0, 0). \qquad (5.10)$$

Thus

$$\chi_0^{xx} = \beta(\tfrac{1}{4} - R_1^2) \qquad T > T_c$$

$$= \frac{1}{J(0)} \qquad T < T_c \tag{5.11}$$

$$\chi_0^{zx} = 0 \qquad T > T_c$$

$$= -\frac{\tan\theta}{J(0)} \qquad T < T_c \tag{5.12}$$

$$\chi_0^{zz} = R_1(\Gamma - J(0)R_1)^{-1} \qquad T > T_c$$

$$= \frac{1}{J(0)} \frac{\{\tan^2\theta + \beta J(0)(\tfrac{1}{4} - R_1^2)\}}{\{1 - \beta J(0)(\tfrac{1}{4} - R_1^2)\}} \qquad T < T_c. \tag{5.13}$$

It can be checked that these are the usual molecular-field susceptibilities by differentiating the molecular-field magnetization components (§2) with respect to Γ or $\Gamma_\parallel$. The temperature dependence of the inverses of these susceptibility components are
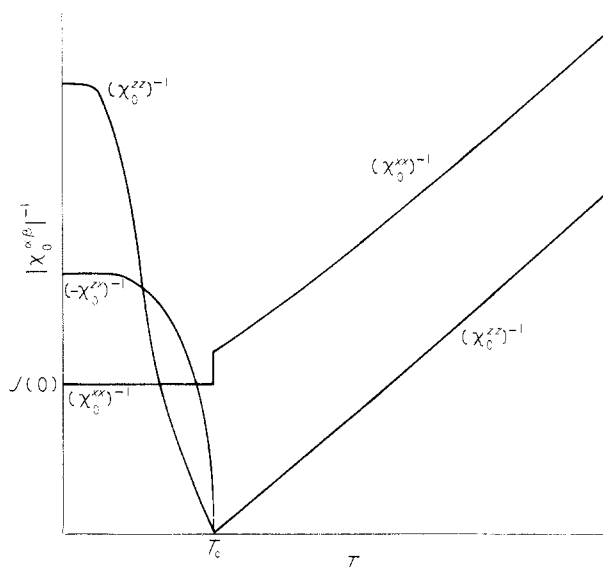

Figure 6. Temperature dependence of the inverse susceptibilities.

sketched in figure 6. The nonvanishing components show a Curie-law behaviour at high temperatures. χ_0^{xx} is discontinuous through the transition below which it is constant. χ_0^{zx} diverges like $(\cos\theta)^{-1} \propto (T_c - T)^{-1/2}$ just below the transition while χ_0^{zz} diverges like $(\cos\theta)^{-2} \propto (T_c - T)^{-1}$ just below the transition and like $(T - T_c)^{-1}$ just above.

For q small but nonzero, the static susceptibility $\beta G_0^{\alpha\beta}(q, 0) \equiv \chi_0^{\alpha\beta}(q, 0)$ behaves as follows near the transition:

For $T > T_c$ only $\chi_0^{zz}(q, 0)$ is q dependent, and since it is proportional to $\omega(q)^{-2}$ it has a screened Coulomb (Ornstein–Zernicke) form with correlation range

$$\xi_>(T - T_c) \propto |T - T_c|^{-1/2}.$$

For $T < T_c$ it follows from (5.3) that $\chi_0^{zz}(q, 0)$ is characterized by the correlation length $\xi_>(T - T_c)/\sqrt{2}$, rather than the length $\xi_<$ associated with $\omega(q)^2$ in the same regime. The same characteristic length $\xi_>/\sqrt{2}$ also determines the range of correlations in $\chi_0^{zx}(q,0)$ and $\chi_0^{xx}(q,0)$ just below the transition, where these two functions have the same denominator as $\chi_0^{zz}(q,0)$. Data for TGS on the x-ray diffuse scattering due to critical fluctuations, which is proportional to $\chi_0^{\alpha\beta}(q,0)$, have been moderately successfully fitted by Nakamura *et al* (1970) to the above Ornstein–Zernicke form with correlation ranges $\xi_>$ and $\xi_>/\sqrt{2}$ above and below T_c respectively.

We conclude this analysis of the properties of the leading approximation for the Green functions with an investigation of the corresponding approximations $\rho_0^{\alpha\beta}(q, \omega)$ for the spectral functions $\rho^{\alpha\beta}(q\omega)$. These are defined by

$$G^{\alpha\beta}(q\lambda) = \frac{1}{\beta} \int_{-\infty}^{\infty} (1 - e^{-\beta\omega}) \rho^{\alpha\beta}(q\omega) \frac{d\omega}{\omega + i\lambda} \tag{5.14}$$

and given by

$$\rho^{\alpha\beta}(q\omega) = \frac{\beta}{2\pi i} (1 - e^{-\beta\omega})^{-1} \lim_{\epsilon \to 0} \{G^{\alpha\beta}(q, i\omega - \epsilon) - G^{\alpha\beta}(q, i\omega + \epsilon)\} \tag{5.15}$$

where the thermodynamic Green functions have here been analytically continued so that $i\lambda \to -\omega \pm i\epsilon$. The spectral functions give the spectral density at frequency ω and wavevector q and are therefore a factor in the cross section for processes involving energy transfer $\hbar\omega$ and wavevector change q, such as inelastic neutron scattering, or Raman scattering of light (where $q = 0$) (Cowley 1966).

For ω nonzero (5.3) yields

$$\rho_0^{zz}(q\omega) = \frac{\gamma R_1 \sin^2\theta}{2\omega(q)} \{(n(q) + 1)\delta(\omega - \omega(q)) + n(q)\delta(\omega + \omega(q))\} \tag{5.16}$$

where $n(q) \equiv \{\exp \beta\omega(q) - 1\}^{-1}$. For $T > T_c$, G_0^{zx} and the nonstatic part of G_0^{xx} vanish so their spectral functions vanish at finite ω in the paramagnetic regime. For $T < T_c$, $\rho_0^{zx}(q\omega)$ and $\rho_0^{xx}(q\omega)$ have a form similar to $\rho_0^{zz}(q\omega)$, $T < T_c$, but scaled by the factors $-\cot\theta$ and $\cot^2\theta$ respectively.

It is of some interest to compute also the single-site spectral function

$$\rho_0^{zz}(r_{ij}, \omega)\big|_{r_{ij}=0} = \sum_q \rho_0^{zz}(q, \omega) \tag{5.17}$$

for which an exact result is known.

For small ω and $|T - T_c|$ since $\rho_0^{zz}(q\omega)$ vanishes except at small q, where in a d-dimensional system the density of states in q space is proportional to q^{d-1}, we obtain from (5.16) the result

$$\rho_0^{zz}(r_{ij} = 0, \omega) \propto Q^{d-2} \theta(Q^2) \tag{5.18}$$

where

$$BQ^2 = \omega^2 - \omega(0)^2 \tag{5.19}$$

and θ is the unit step function which is 1 for positive argument and zero otherwise. This gives

$$\rho_0^{zz}(r_{ij} = 0, \omega) \propto (\omega - \omega(0)) \qquad\qquad T \gtrsim T_c, \omega \sim \omega(0)$$

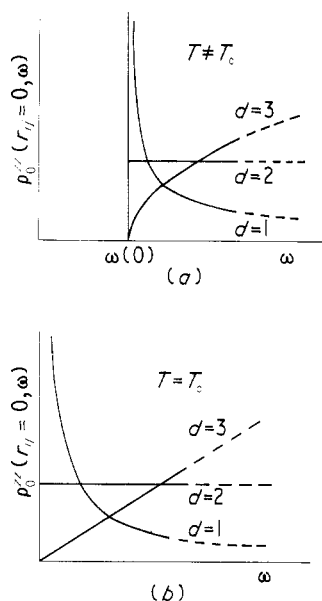$$\propto \omega^{d-2} \qquad\qquad T = T_c, \omega \sim 0. \tag{5.20}$$

Figure 7. Single-site spectral function ρ_0^{zz} against frequency for one, two and three dimensions.

This is sketched in figure 7. Pfeuty (1971, and private communication) has derived an exact expression for the spectral function $\rho^{zz}(r_{ij} = 0,\omega)$ of the one-dimensional transverse Ising model at zero temperatures, whose dynamic functions can be related to the static functions of the two-dimensional Ising model. Pfeuty finds for $\Gamma \lesseqqgtr \Gamma_c$, $T = 0$ (corresponding to the case $T \gtreqqless T_c$ in equation (5.20)) a result of the form $(\omega - \omega(0))^{-1/2}$ $\theta(\omega - \omega(0))$, in agreement with (5.20) for the special case $d = 1$. Pfeuty's dependence of $\omega(0)$ on Γ is identical with ours:

$$\omega(0)^2 = \Gamma_c(\Gamma - \Gamma_c) \qquad \Gamma > \Gamma_c$$

$$= 2\Gamma_c(\Gamma_c - \Gamma) \qquad \Gamma < \Gamma_c. \tag{5.21}$$

For $\Gamma = \Gamma_c$, $T = 0$, Pfeuty finds that the exact single site spectral function diverges like $\omega^{-3/4}$, while (5.20), $T = T_c$, leads to a linear divergence at small ω for $d = 1$.

The extent to which the approximate result agrees with the exact result is due in part to the fact that the latter is for zero temperature. Here damping effects absent from our leading approximation are probably negligible, but they can be expected to substantially modify the spectral functions at higher temperatures. Such effects indeed show up in the Raman and neutron spectroscopy measurements of the spectral function of KH_2PO_4 (Kaminow and Damen 1968, Arsić-Eskinja et al 1971) and of KD_2PO_4 (Buyers et al 1968, Skalyo et al 1970) where the tunnelling modes are seen to be highly damped.

The succeeding paper will give a more detailed study of correlation functions, including damping which first appears one order in the $1/z$ expansion beyond that considered here. An investigation of the thermodynamic behaviour up to $O(1/z)^2$ will be the subject of a third paper.

Acknowledgments

Appendix 1

We give here the unperturbed semi-invariants of low order. They are here defined to be dimensionless, and apart from factors of β are given by taking $l = 1$, $\gamma_1 = \Gamma$, and $-R_{01} = R(\Gamma) \equiv \frac{1}{2}\tanh\frac{1}{2}\beta\Gamma$, and all frequencies as incoming, in Appendix B of Cottam and Stinchcombe (1970a).

(i) First-order semi-invariants.

$$M^z(\lambda_1; \Gamma) = \delta_{\lambda_1, 0}R(\Gamma) \equiv \tfrac{1}{2}\delta_{\lambda_1, 0} \tanh\tfrac{1}{2}\beta\Gamma \tag{A1.1}$$

$$M^x(\lambda_1; \Gamma) = M^y(\lambda_1; \Gamma) = 0. \tag{A1.2}$$

(ii) Second-order semi-invariants.

$$M^{zz}(\lambda_1, \lambda_2; \Gamma) = \delta_{\lambda_1, 0}\delta_{\lambda_2, 0}\left(\tfrac{1}{4} - R(\Gamma)^2\right) \tag{A1.3}$$

$$M^{+-}(\lambda_1, \lambda_2; \Gamma) = M^{-+}(\lambda_2, \lambda_1; \Gamma)$$
$$= \delta_{\lambda_1 + \lambda_2, 0}2R(\Gamma)\{\beta(\Gamma - i\lambda_1)\}^{-1} \tag{A1.4}$$

$$M^{+z}(\lambda_1, \lambda_2; \Gamma) = M^{-z}(\lambda_1, \lambda_2; \Gamma) = M^{--}(\lambda_1, \lambda_2; \Gamma) = \dots$$
$$= 0. \tag{A1.5}$$

Thus, since

$$S^x = \tfrac{1}{2}(S^+ + S^-) \qquad S^y = \frac{1}{2i}(S^+ - S^-) \tag{A1.6}$$

it follows that

$$M^{xx}(\lambda_1, \lambda_2; \Gamma) = M^{yy}(\lambda_1\lambda_2; \Gamma) = \tfrac{1}{4}\{M^{+-}(\lambda_1, \lambda_2; \Gamma) + M^{-+}(\lambda_1, \lambda_2; \Gamma)\}$$
$$= \frac{\delta_{\lambda_1 + \lambda_2, 0}R(\Gamma)\beta\Gamma}{\beta^2\{\Gamma^2 - (i\lambda_1)^2\}} \tag{A1.7}$$

$$M^{xy}(\lambda_1, \lambda_2; \Gamma) = M^{yx}(\lambda_2, \lambda_1; \Gamma) = \frac{-R(\Gamma)\beta\lambda\delta_{\lambda_1 + \lambda_2, 0}}{\beta^2\{\Gamma^2 - (i\lambda_1)^2\}} \tag{A1.8}$$

and

$$M^{xz}(\lambda_1, \lambda_2; \Gamma) = M^{yz}(\lambda_1, \lambda_2; \Gamma) = \dots = 0. \tag{A1.9}$$

(iii) Third-order semi-invariants.

$$M^{zzz}(\lambda_1\lambda_2\lambda_3;\Gamma) = -\delta_{\lambda_1,0}\delta_{\lambda_2,0}\delta_{\lambda_3,0}2R(\Gamma)(\tfrac{1}{4} - R(\Gamma)^2). \tag{A1.10}$$

$$M^{+-z}(\lambda_1\lambda_2\lambda_3;\Gamma) = \delta_{\lambda_1+\lambda_3,0}2\left\{\frac{R(\Gamma)}{\beta^2(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)} - \delta_{\lambda_3,0}\frac{(\tfrac{1}{4} - R(\Gamma)^2)}{\beta(\Gamma - i\lambda_1)}\right\}. \tag{A1.11}$$

Thus

$$M^{xxz}(\lambda_1\lambda_2\lambda_3;\Gamma) = \delta_{\lambda_1+\lambda_2+\lambda_3,0}\tfrac{1}{2}\left\{\begin{array}{l}\dfrac{R(\Gamma)}{\beta^2(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)} + \dfrac{R(\Gamma)}{\beta^2(\Gamma + i\lambda)(\Gamma - i\lambda_2)} \\[2mm] -\delta_{\lambda_3,0}(\tfrac{1}{4} - R(\Gamma)^2)\dfrac{2\beta\Gamma}{\beta^2(\Gamma^2 - (i\lambda_1)^2)}\end{array}\right\} \tag{A1.12}$$

(iv) Fourth-order semi-invariants.

$$M^{+-+-}(\lambda_1\lambda_2\lambda_3\lambda_4;\Gamma)$$

$$= -4\delta_{\lambda_1+\lambda_2+\lambda_3+\lambda_4,0}\left\{\begin{array}{l}\dfrac{R(\Gamma)(2\Gamma - i\lambda_1 - i\lambda_3)}{\beta^3(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)(\Gamma - i\lambda_3)(\Gamma + i\lambda_4)} \\[2mm] -\delta_{\lambda_2+\lambda_3,0}\dfrac{(\tfrac{1}{4} - R(\Gamma)^2)}{\beta^2(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)} - \delta_{\lambda_3+\lambda_4,0}\dfrac{(\tfrac{1}{4} - R(\Gamma)^2)}{\beta^2(\Gamma - i\lambda_1)(\Gamma - i\lambda_3)}\end{array}\right\} \tag{A1.13}$$

$$M^{+-zz}(\lambda_1\lambda_2\lambda_3\lambda_4;\Gamma)$$

$$= \delta_{\lambda_1+\lambda_2+\lambda_3+\lambda_4,0}\left\{\begin{array}{l}\dfrac{2R(\Gamma)(2\Gamma - i\lambda_1 + i\lambda_2)}{\beta^3(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)(\Gamma - i\lambda_1 - i\lambda_3)(\Gamma - i\lambda_1 - i\lambda_4)} \\[2mm] -(\delta_{\lambda_3,0} + \delta_{\lambda_4,0})\dfrac{2(\tfrac{1}{4} - R(\Gamma)^2)}{\beta^2(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)} + \delta_{\lambda_3,0}\delta_{\lambda_4,0}\dfrac{4R(\Gamma)(\tfrac{1}{4} - R(\Gamma)^2)}{\beta(\Gamma - i\lambda_1)}\end{array}\right\} \tag{A1.14}$$

$$M^{zzzz}(\lambda_1\lambda_2\lambda_3\lambda_4;\Gamma) = -\delta_{\lambda_1,0}\delta_{\lambda_2,0}\delta_{\lambda_3,0}\delta_{\lambda_4,0}2(\tfrac{1}{4} - R(\Gamma)^2)(\tfrac{1}{4} - 3R(\Gamma)^2). \tag{A1.15}$$

It follows that

$$M^{xxzz}(\lambda_1\lambda_2\lambda_3\lambda_4;\Gamma)$$

$$= \tfrac{1}{4}\delta_{\lambda_1+\lambda_2+\lambda_3+\lambda_4,0}\left\{\frac{2R(\Gamma)(2\Gamma - i\lambda_1 + i\lambda_2)}{\beta^3(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)(\Gamma - i\lambda_1 - i\lambda_3)(\Gamma - i\lambda_1 - i\lambda_4)}\right.$$

$$+ \frac{2R(\Gamma)(2\Gamma + i\lambda_1 - i\lambda_2)}{\beta^3(\Gamma + i\lambda_1)(\Gamma - i\lambda_2)(\Gamma + i\lambda_1 + i\lambda_3)(\Gamma + i\lambda_1 + i\lambda_4)}$$

$$- (\delta_{\lambda_3,0} + \delta_{\lambda_4,0})\frac{2(\tfrac{1}{4} - R(\Gamma)^2)}{\beta^2}\left(\frac{1}{(\Gamma - i\lambda_1)(\Gamma + i\lambda_2)} + \frac{1}{(\Gamma + i\lambda_1)(\Gamma - i\lambda_2)}\right)$$

$$\left.+ \delta_{\lambda_3,0}\delta_{\lambda_4,0}\frac{8\Gamma R(\Gamma)(\tfrac{1}{4} - R(\Gamma)^2)}{\beta\{\Gamma^2 - (i\lambda_1)^2\}}\right\} \tag{A1.16}$$

$$M^{xxxx}(\lambda_1\lambda_2\lambda_3\lambda_4;\Gamma)$$

$$= -\tfrac{1}{4}\delta_{\lambda_1+\lambda_2+\lambda_3+\lambda_4,0}\left[\frac{R(\Gamma)}{\beta^3}\left\{\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_3)^2}\right)\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_4)^2}\right)\left(\frac{1}{\Gamma + i\lambda_2} + \frac{1}{\Gamma + i\lambda_1}\right)\right.\right.$$

$$+ \left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_1)^2}\right)\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_2)^2}\right)\left(\frac{1}{\Gamma + i\lambda_3} + \frac{1}{\Gamma + i\lambda_4}\right)$$

$$- \frac{4\Gamma}{(\Gamma + i\lambda_1)(\Gamma + i\lambda_2)(\Gamma + i\lambda_3)(\Gamma + i\lambda_4)}\Bigg\} - \frac{(\frac{1}{4} - R(\Gamma)^2)}{\beta^2}$$

$$\times \Bigg\{ \delta_{\lambda_2 + \lambda_3, 0}\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_1)^2}\right)\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_3)^2}\right) + \delta_{\lambda_1 + \lambda_2, 0}\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_2)^2}\right)$$

$$\times \left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_3)^2}\right) + \delta_{\lambda_1 + \lambda_3, 0}\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_1)^2}\right)\left(\frac{2\Gamma}{\Gamma^2 - (i\lambda_2)^2}\right)\Bigg\}\Bigg]. \tag{A1.17}$$

Appendix 2

The results of Appendix 1 are used to evaluate molecular-field renormalized semi-invariants by first rotating axis from xyz to $x'y'z'$, where z' lies along the molecular field, and then using equation (3.12) of § 3.3. In the following

$$R_1 \equiv R(\gamma) = \tfrac{1}{2}\tanh\tfrac{1}{2}\beta\gamma.$$

(i) First-order semi-invariants $M^{\alpha}(\lambda_1; \gamma)$.

$$M^x(\lambda_1; \gamma) = M^{x'}(\lambda_1; \gamma)\cos\theta + M^{z'}(\lambda_1; \gamma)\sin\theta = \delta_{\lambda_1, 0}R_1\sin\theta \tag{A2.1}$$

$$M^z(\lambda_1; \gamma) = -M^{x'}(\lambda_1; \gamma)\sin\theta + M^{z'}(\lambda_1; \gamma)\cos\theta = \delta_{\lambda_1, 0}R_1\cos\theta. \tag{A2.2}$$

(ii) Second-order semi-invariants $M^{\alpha\beta}(\lambda_1\lambda_2; \gamma)$.

$$M^{xx}(\lambda_1\lambda_2; \gamma) = M^{x'x'}(\lambda_1\lambda_2; \gamma)\cos^2\theta + \{M^{x'z'}(\lambda_1\lambda_2; \gamma) + M^{z'x'}(\lambda_1\lambda_2; \gamma)\}\cos\theta\sin\theta$$

$$+ M^{z'z'}(\lambda_1\lambda_2; \gamma)\sin^2\theta$$

$$= \left(\frac{R_1\beta\gamma\cos^2\theta}{\beta^2\{\gamma^2 - (i\lambda_1)^2\}} + \delta_{\lambda_1, 0}\sin^2\theta\,(\tfrac{1}{4} - R_1^2)\right)\delta_{\lambda_1 + \lambda_2, 0}. \tag{A2.3}$$

$$M^{zz}(\lambda_1\lambda_2; \gamma) = M^{z'z'}(\lambda_1\lambda_2; \gamma)\cos^2\theta + M^{x'x'}(\lambda_1\lambda_2; \gamma)\sin^2\theta$$

(omitting semi-invariants $M^{z'x'}$, $M^{x'z'}$, which vanish)

$$= \delta_{\lambda_1 + \lambda_2, 0}\left(\frac{R_1\beta\gamma\sin^2\theta}{\beta^2(\gamma^2 - (i\lambda_1)^2)} + \delta_{\lambda_1, 0}\cos^2\theta(\tfrac{1}{4} - R_1^2)\right). \tag{A2.4}$$

$$M^{zx}(\lambda_1\lambda_2; \gamma) = \cos\theta\sin\theta\{M^{z'z'}(\lambda_1\lambda_2; \gamma) - M^{x'x'}(\lambda_1\lambda_2; \gamma)\}$$

$$= \cos\theta\sin\theta\,\delta_{\lambda_1 + \lambda_2, 0}\left(-\frac{R_1\beta\gamma}{\beta^2(\gamma^2 - (i\lambda_1)^2)} + \delta_{\lambda_1, 0}(\tfrac{1}{4} - R_1^2)\right) \tag{A2.5}$$

$$M^{yz}(\lambda_1\lambda_2; \gamma) = M^{y'z'}(\lambda_1\lambda_2; \gamma)\cos\theta - M^{y'x'}(\lambda_1\lambda_2; \gamma)\sin\theta$$

$$= \frac{-R_1\beta\lambda_1\sin\theta}{\beta^2\{\gamma^2 - (i\lambda_1)^2\}}\delta_{\lambda_1 + \lambda_2, 0} \tag{A2.6}$$

$$M^{yy}(\lambda_1\lambda_2; \gamma) = M^{y'y'}(\lambda_1\lambda_2; \gamma) = \frac{R_1\beta\gamma\delta}{\beta^2\{\gamma^2 - (i\lambda_1)^2\}}\delta_{\lambda_1 + \lambda_2, 0} \tag{A2.7}$$

(iii) Third-order semi-invariants of the form $M^{\alpha z z}(\lambda_1\lambda_2\lambda_3;\gamma)$.

$$M^{zzz}(\lambda_1\lambda_2\lambda_3;\gamma) = M^{z'z'z'}(\lambda_1\lambda_2\lambda_3;\gamma)\cos^3\theta$$
$$+ \{M^{z'x'x'}(\lambda_1\lambda_2\lambda_3;\gamma) + M^{x'z'x'}(\lambda_1\lambda_2\lambda_3;\gamma) + M^{x'x'z'}(\lambda_1\lambda_2\lambda_3;\gamma)\}\cos\theta\sin^2\theta.$$
$$(A2.8)$$

$$M^{xzz}(\lambda_1\lambda_2\lambda_3;\gamma) = M^{z'z'z'}(\lambda_1\lambda_2\lambda_3;\gamma)\sin\theta\cos^2\theta + M^{z'x'x'}(\lambda_1\lambda_2\lambda_3;\gamma)\sin^3\theta$$
$$+ \{M^{x'z'x'}(\lambda_1\lambda_2\lambda_3;\gamma) + M^{x'x'z'}(\lambda_1\lambda_2\lambda_3;\gamma)\}(-\cos^2\theta\sin\theta). \qquad (A2.9)$$

The following semi-invariants, or groups of semi-invariants, obtained from the results of Appendix 1 by using equation (3.12), are sufficient to give the above $M^{\alpha z z}(\lambda_1\lambda_2\lambda_3;\gamma)$:

$$M^{z'x'x'}(\lambda_1\lambda_2\lambda_3;\gamma)$$

$$= \tfrac{1}{2}\delta_{\lambda_1+\lambda_2+\lambda_3,0}\left(\frac{R_1}{\beta^2(\gamma-i\lambda_3)(\gamma+i\lambda_2)} + \frac{R_1}{\beta^2(\gamma+i\lambda_3)(\gamma-i\lambda_2)}\right.$$

$$\left. - \delta_{\lambda_1,0}(\tfrac{1}{4}-R_1^2)\frac{2\beta\gamma}{\beta^2(\gamma^2-(i\lambda_3)^2)}\right) \qquad (A2.10)$$

$$M^{x'z'x'}(\lambda_1\lambda_2\lambda_3;\gamma) + M^{x'x'z'}(\lambda_1\lambda_2\lambda_3;\gamma)$$

$$= \tfrac{1}{2}\delta_{\lambda_1+\lambda_2+\lambda_3,0}\left\{\frac{R_1}{\beta^2}\left(\frac{1}{(\gamma-i\lambda_1)(\gamma+i\lambda_3)} + \frac{1}{(\gamma-i\lambda_3)(\gamma+i\lambda_1)} + \frac{1}{(\gamma-i\lambda_1)(\gamma+i\lambda_2)}\right.\right.$$

$$\left.\left. + \frac{1}{(\gamma-i\lambda_2)(\gamma+i\lambda_1)}\right) - \frac{2\beta\gamma}{\beta^2(\gamma^2-(i\lambda_1)^2)}(\tfrac{1}{4}-R_1^2)(\delta_{\lambda_2,0}+\delta_{\lambda_3,0})\right\} \quad (A2.11)$$

$$M^{z'z'z'}(\lambda_1\lambda_2\lambda_3;\gamma) = -\delta_{\lambda_1,0}\delta_{\lambda_2,0}\delta_{\lambda_3,0}2R_1(\tfrac{1}{4}-R_1^2). \qquad (A2.12)$$

(iv) Fourth-order semi-invariants of the form $M^{\alpha\beta z z}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$.

$$M^{zzzz}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) = M^{z'z'z'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\cos^4\theta + M^{x'x'x'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\sin^4\theta$$

$$+ \cos^2\theta\sin^2\theta\{M^{z'z'x'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) + M^{z'x'z'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$$
$$+ M^{z'x'x'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) + M^{x'z'z'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$$
$$+ M^{x'z'x'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) + M^{x'z'z'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\} \qquad (A2.13)$$

$$M^{xxzz}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) = M^{z'z'z'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\sin^2\theta\cos^2\theta + M^{x'x'x'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$$
$$\times (\cos^2\theta\sin^2\theta) - \cos^2\theta\sin^2\theta\{M^{z'x'z'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$$
$$+ M^{z'x'x'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) + M^{x'z'z'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) + M^{x'z'x'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma\}$$
$$+ M^{z'z'x'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\sin^4\theta + M^{x'x'z'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\cos^4\theta. \qquad (A2.14)$$

$$M^{zxzz}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) = M^{z'z'z'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\sin\theta\cos^3\theta + M^{x'x'x'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$$
$$\times (-\cos\theta\sin^3\theta) + \{M^{z'x'z'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) + M^{z'x'x'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$$
$$+ M^{x'x'z'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\}(-\cos^3\theta\sin\theta) + \{M^{z'z'x'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)$$
$$+ M^{x'z'z'x'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma) + M^{x'z'x'z'}(\lambda_1\lambda_2\lambda_3\lambda_4;\gamma)\}\cos\theta\sin^3\theta. \qquad (A2.15)$$

For explicit calculations to appear in the subsequent papers, the above fourth-order semi-invariants are only required for the special case $\lambda_2 = -\lambda_1$, $\lambda_4 = -\lambda_3$. They are then given as linear combinations of the following, obtained once again from Appendix 1 by using equation (3.12):

$$M^{z'z'z'z'}(\lambda, -\lambda, \lambda', -\lambda'; \gamma) = -\delta_{\lambda,0}\delta_{\lambda',0}2(\tfrac{1}{4} - R_1^2)(\tfrac{1}{4} - 3R_1^2). \quad (A2.16)$$

$M^{x'x'x'x'}(\lambda, -\lambda, \lambda', -\lambda'; \gamma)$

$$= -\tfrac{1}{4}\left[\frac{R_1}{\beta^3}\left\{\left(\frac{2\gamma}{\gamma^2 - (i\lambda)^2}\right)\left(\frac{2\gamma}{\gamma^2 - (i\lambda')^2}\right)\left(\frac{2\gamma}{\gamma^2 - (i\lambda)^2} + \frac{2\gamma}{\gamma^2 - (i\lambda')^2} - \frac{1}{\gamma}\right)\right\}\right.$$
$$\left. - \frac{(\tfrac{1}{4} - R_1^2)}{\beta^2}\left(\frac{2\gamma}{\gamma^2 - (i\lambda)^2}\right)\left(\frac{2\gamma}{\gamma^2 - (i\lambda')^2}\right)(\delta_{\lambda,\lambda'} + \delta_{\lambda,-\lambda'} + 1)\right] \quad (A2.17)$$

$M^{z'z'x'x'}(\lambda, -\lambda, \lambda', -\lambda'; \gamma)$

$$= \tfrac{1}{4}\left\{\frac{4R_1}{\beta^3(\gamma - i\lambda)\{\gamma - i(\lambda + \lambda')\}\{\gamma - i(\lambda - \lambda')\}}\right.$$
$$+ \frac{4R_1}{\beta^3(\gamma + i\lambda)\{\gamma + i(\lambda + \lambda')\}\{\gamma + i(\lambda - \lambda')\}} - \delta_{\lambda',0}4(\tfrac{1}{4} - R_1^2)$$
$$\left. \times \left(\frac{1}{\beta^2(\gamma - i\lambda)^2} + \frac{1}{\beta^2(\gamma + i\lambda)^2} - \frac{2\gamma R_1}{\beta(\gamma^2 - (i\lambda)^2)}\right)\right\} \quad (A2.18)$$

$M^{z'x'z'x'}(\lambda, -\lambda, \lambda', -\lambda'; \gamma) + M^{z'x'x'z'}(\lambda, -\lambda, \lambda', -\lambda'; \gamma)$

$$= \tfrac{1}{4}\left\{\frac{2R_1}{\beta^3\gamma}\left(\frac{2\gamma + i\lambda - i\lambda'}{(\gamma + i\lambda)(\gamma - i\lambda')(\gamma + i\lambda - i\lambda')}\right.\right.$$
$$+ \frac{2\gamma - i\lambda + i\lambda'}{(\gamma - i\lambda)(\gamma + i\lambda')(\gamma - i\lambda + i\lambda')} + \frac{2\gamma + i\lambda + i\lambda'}{(\gamma + i\lambda)(\gamma + i\lambda')(\gamma + i\lambda + i\lambda')}$$
$$\left. + \frac{2\gamma - i\lambda - i\lambda'}{(\gamma - i\lambda)(\gamma - i\lambda')(\gamma - i\lambda - i\lambda')}\right) - (\delta_{\lambda,0} + \delta_{\lambda',0})\frac{2(\tfrac{1}{4} - R_1^2)}{\beta^2}$$
$$\left. \times \frac{2\gamma}{\gamma^2 - (i\lambda)^2} \cdot \frac{2\gamma}{\gamma^2 - (i\lambda')^2} + \delta_{\lambda,0}\delta_{\lambda',0}\frac{16R_1(\tfrac{1}{4} - R_1^2)}{\beta\gamma}\right\} \quad (A2.19)$$
$$= M^{x'z'x'z'}(\lambda, -\lambda, \lambda', -\lambda', \gamma) + M^{x'z'z'x'}(\lambda, -\lambda, \lambda', -\lambda', \gamma) \quad (A2.20)$$

(since $M^{xxzz}(\lambda_1\lambda_2\lambda_3\lambda_4; \Gamma)$ is invariant under

$$\lambda_1 \rightleftarrows \lambda_2 \quad or \quad \lambda_3 \rightleftarrows \lambda_4 \quad or \quad (\lambda_1\lambda_2\lambda_3\lambda_4) \rightarrow (-\lambda_1, -\lambda_2, -\lambda_3, -\lambda_4)).$$

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