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Analysis of ultrasonic anomaly in V_3Si

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Abstract. V_3Si exhibits an ultrasonic anomaly when cooled well below its martensitic and superconducting transition temperatures (T_m and T_c), and a magnetic field is applied on to the sample. The anomaly is thought to be due to reorientation of micro-domains formed below T_m, to energetically favourable configurations. The effect disappears when the domains are stabilised in new configurations in the presence of the magnetic field. An analysis of these results is presented in this paper by relating the ultrasonic attenuation coefficient to strain fluctuations, arising here from domain reorientations. The treatment is based on a master equation for the probability matrix whose elements yield the probabilities of transitions between domain configurations, in the presence of both the magnetic field and the stress wave. Arguments for the validity of this master equation, when the oscillatory stress is weak, are given in a longish appendix. The derived results are used to analyse, in qualitative terms, the observed experimental facts. Also, new measurements are suggested which may help interpret the experimental data in a satisfactory manner.

Keywords. A-15 compounds; ultrasonic attenuation; magnetostriction; strain fluctuations.

1. Introduction

The A-15 structure compounds such as V_3Si and Nb_3Sn have recently been receiving considerable attention in view of their high superconducting transition temperatures T_c. The superconducting transition is believed to be closely related to the martensitic transformation that occurs above T_c (see for example, Bhatt 1976). While carrying out ultrasonic measurements in V_3Si, Fukase *et al* (1976) observed some anomalous attenuation below T_c. They found a sharp peak on increasing the temperature, after first cooling the sample to 4 K, and then applying a magnetic field (figure 1). However, on lowering the temperature, the peak disappeared, suggesting that the contributory process had 'annealed out'. The field H^* corresponding to the peak had a value between the lower critical field H_{c1} and the upper critical field H_{c2} and it varied with temperature.

Tachiki and Koyama (1977; henceforth abbreviated as TK; see also Tachiki and Umezawa 1977) have proposed an explanation for the anomaly. Their model is centred around the fact that below the martensitic transition temperature, micro-domains with tetragonal distortions around an array of defects in the crystal, are formed. When $H = 0$, the stable configuration in V_3Si corresponds to domains elongated along the three cubic axes. Application of the magnetic field changes the situation, and a calculation by TK shows that the free energy of the system is the lowest when the long axis of the domains is perpendicular to the field. Accordingly, the observed anomalous attenuation peak is thought to be related to the reorientations

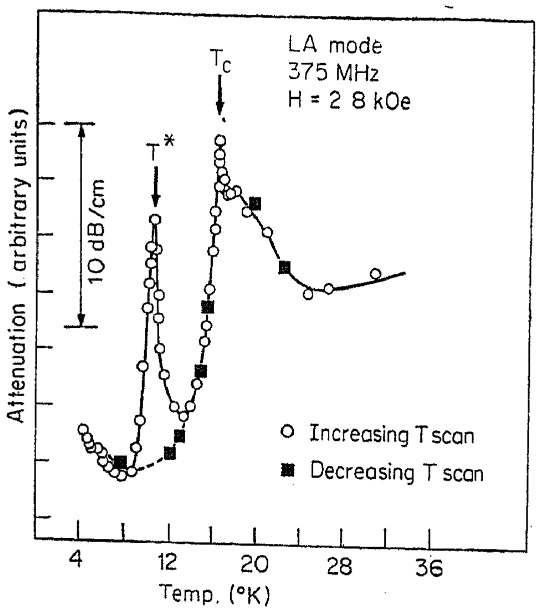

Figure 1. Anomaly in ultrasonic attenuation in V_3Si. The temperature T^* at which the peak appears is a function of the applied magnetic field (after Fukase *et al* 1976).

of the domains to an energetically favourable configuration, a process that is aided by temperature-increase. Once the reorientation to the lower energy state is complete —as happens during the first scan—there is no further scope for such motions and consequently the peak vanishes during subsequent scans.

TK do not calculate the ultrasonic attenuation as such, but merely propose an explanation for the occurrence of the peak, as described above, on the basis of their free energy calculation. In this paper, we adopt the interpretation of TK and actually explore the reorientational motion of the microdomains and its contribution to the observed attenuation. The calculational approach is related to a treatment given earlier by Balakrishnan *et al* (1978; hereafter referred to as (I)) in connection with anelastic relaxation. As in I, the energy dissipated by the sound wave, assumed to be a weak probe, is linked to strain fluctuations (arising here from domain reorientations). An important difference between the present formalism and that of I is that the probe here acts on a state that is *not* in equilibrium.

The plan of the paper is as follows. § 2 includes the formulation of the problem. In § 3, we calculate the strain response of the system in the presence of the external agencies, viz., the magnetic field and the sound wave. A discussion of the results is presented in §4, together with an indication of how additional measurements may be made for extracting unambiguously, the physical parameters of the system. The last section offers some concluding remarks. In the appendix, we put forward a theoretical discussion with a view to justify the use (as made here) of the master equation for the probability in describing the response of a *time-evolving* system to a weak probe.

2. Formulation of the problem

Following TK, we show in figure 2 schematic plots of the free energy of the system as a function of domain orientation. During the initial cooling of the sample (with $H = 0$),

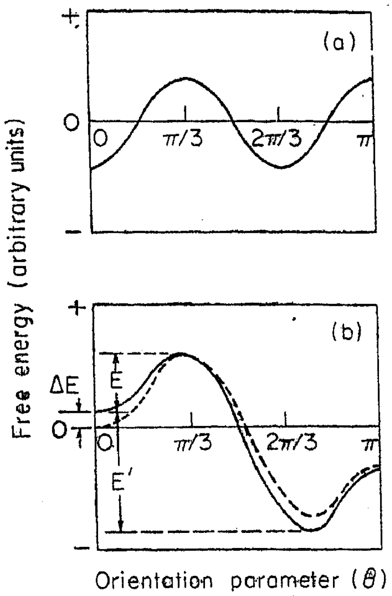

Figure 2. Schematic plots of the free energy of microdomains in V_3Si in **2a**. zero and **2b**. finite magnetic fields (after Tachiki and Koyama 1977). The values $\theta=0$ and $\theta = \frac{2}{3}\pi$ represent microdomains with their long axes parallel and perpendicular to the field H. The microdomains with $\theta = 0$ must overcome the barrier E to get past the saddle point (**2b**). In the presence of a weak static stress σ_0, E is modified to $(E + \triangle E)$ (dashed lines).

curve (a) applies and the stable state is characterised by domains elongated along the three cubic axes. As the magnetic field is switched on, the domains with their long axis parallel to the field (see curve (b)) are in a metastable state which decays to the stable state at a rate governed by, among other quantities, the temperature and barrier parameters. Under favourable conditions, this rate may be so slow as to permit attenuation measurements at various temperatures to be completed before equilibrium is reached.

For calculational simplicity, we assume that corresponding to each measurement temperature, the sample is first cooled from above to that temperature, and the magnetic field is then switched on. The sound wave is also supposed to be impressed at the same instant (which is taken to define $t=0$) and the attenuation measured. This process is visualised to be repeated at every temperature so that the initial state of the system corresponding to each measurement is well-defined. Categorical assumptions of this nature are necessary in this case since we are dealing with a non-equilibrium situation. Although the evolution history of the domains in the actual experiment by Fukase *et al* (1976) may not be faithfully reproduced by these assumptions, no essential physics is lost.

Turning next to the method of calculation, we note that the strain (measured along z-axis, say) for tetragonally distorted domains, may be regarded as a fluctuating quantity in view of domain reorientations. In particular, when reorientations take place among three allowed configurations, as in the present case, the fluctuating strain can be viewed as a 3×3 matrix. The expectation value of the strain variable may then be written as

$$\langle \epsilon_{zz}(t) \rangle = \sum_{n,m=1}^{3} p_n (n\,|\,P(t)\,|\,m)\,(m\,|\,\epsilon_{zz}\,|\,m), \tag{1}$$

where $(1 \mid \epsilon_{zz} \mid 1)$, for example, is the z-component of the strain associated with domains elongated along direction 1, p_n is the weight factor corresponding to the initial orientation n at $t = 0$ and $(n \mid P(t) \mid m)$ is the conditional probability that the orientation is m at time t given that it was n at $t = 0$. As in standard rate theories, $P(t)$ may be modelled on the assumption that the domain reorientation is a stationary Markov process. We remark here that a very similar approach was adopted in I for describing Snoek relaxation in b.c.c. crystals.

To construct ϵ_{zz}, we note that a microdomain with a tetragonal distortion may be regarded as an elastic dipole with principal axis components of the strain tensor as λ_1, λ_2, and $\lambda_3=\lambda_2$ (cf., I). Thus in (1)

$$(1 \mid \epsilon_{zz} \mid 1) = N\lambda_1,\ (2 \mid \epsilon_{zz} \mid 2) = N\lambda_2,\ (3 \mid \epsilon_{zz} \mid 3) = N\lambda_2, \tag{2}$$

where N is the total number of domains.

3. Evaluation of the strain response

In this section, (1) and (2) will be employed first to calculate the strain response to an applied magnetic field alone, and then to compute the response to the combined presence of the magnetic field and the stress wave. The latter calculation will lead then to the required attenuation coefficient.

3·1 *Magnetic field alone present*

The magnetic field is assumed to be switched on at $t = 0$ in the [0 0 1] or Z direction. The resulting reorientation of the domains, from those configurations in which the long axis is aligned along [0 0 1] to the ones in which the long axis points towards [1 0 0] or [0 1 0] (cf. figure 2), gives rise to a kind of magnetostriction effect. We presently wish to calculate the magnitude and time-dependence of the associated macroscopic strain along [0 0 1], using (1) and (2).

As mentioned before, the domain reorientation may be regarded as a stationary Markov process so that we may write (cf., I),

$$P(t) = \exp (Wt), \tag{3}$$

where W is a 3×3 matrix whose elements give the rate of reorientation from one configuration to another. Bearing in mind the free energy diagram of figure 2b, we have

$$(n \mid W \mid m) = \nu\delta_{1n},\ m \neq 1 \text{ and } (1 \mid W \mid 1) = -2\nu, \tag{4}$$

the last equation following from the conservation of probability. According to the classical nucleation theory (see for example, Langer 1969),

$$\nu = \nu_0 \exp (-E/KT), \tag{5}$$

where E is the *free* energy-difference indicated in figure 2b.

From (3) and (4), $(n|P(t)|m)$ can be easily calculated. Noting further that $p_n=\frac{1}{3}$, since at $t=0$ the three domain orientations are equally favoured, we have from (1) and (2),

$$\langle \epsilon_{zz}(t)\rangle = \tfrac{1}{3}\, N(\lambda_1 + 2\lambda_2) + \tfrac{1}{3}\, N(\lambda_2 - \lambda_1)\,[1 - \exp(-2\nu t)]. \tag{6}$$

The corresponding result for the strain in the two perpendicular directions can be shown to be

$$\langle \epsilon_{xx}(t)\rangle = \langle \epsilon_{yy}(t)\rangle = \tfrac{1}{3}N(\lambda_1 + 2\lambda_2) - \tfrac{1}{6}N(\lambda_2 - \lambda_1)\,[1 - \exp(-2\nu t)] \tag{7}$$

We observe that

$$\langle \epsilon_{xx}(0)\rangle = \langle \epsilon_{yy}(0)\rangle = \langle \epsilon_{zz}(0)\rangle = \tfrac{1}{3}\, N(\lambda_1 + 2\lambda_2), \tag{8}$$

while $$\langle \epsilon_{xx}(\infty)\rangle = \langle \epsilon_{yy}(\infty)\rangle = \tfrac{1}{2}\, N(\lambda_1 + \lambda_2), \quad \langle \epsilon_{zz}(\infty)\rangle = N\lambda_2, \tag{9}$$

in conformity with intuitive expectations.

3.2 *Magnetic field and the sound wave both present*

We turn next to the case in which a stress wave $\sigma_0 \cos \omega t$, in addition to H, is assumed to be impressed on the system at $t=0$, also along z axis. The system, under the influence of H alone, evolves from one equilibrium state to another, as discussed in the previous section. This approach to equilibrium is assumed to be *weakly* modulated by the sound wave (linear response considered). The new probability matrix $P'(t)$ can be taken to obey a master equation

$$\frac{dP'(t)}{dt} = P'(t)\,(W + \mathscr{L}_{\text{osc}}(t)), \tag{10}$$

where W is the same as the one appearing in (3), and $\mathscr{L}_{\text{osc}}(t)$ is the (time-dependent) contribution towards the transition matrix arising from the coupling of the system with the oscillatory stress. It is further assumed that

$$\mathscr{L}_{\text{osc}}(t) = \mathscr{L}_0 \cos \omega t, \tag{11}$$

where $\mathscr{L}_0$ is *that* contribution to the transition matrix which would be relevant had the applied stress been completely static, viz. σ_0.

Although it is very difficult to deduce (10) and (11) from first principles, plausible arguments for their validity can be given when σ_0 is small (linear response) and ω is not too large (adiabatic approximation). A detailed meaning of these statements is given in the appendix in terms of a prototype two-level problem.

Consistent with the assumptions made above, the solution of (10) can be obtained as

$$P'(t) = P(t) + \int_0^t dt'\, P(t')\, \mathscr{L}_0\, P(t-t') \cos \omega t', \tag{12}$$

where $P(t)$ again is given by (3). We note further that if a static stress σ_0 causes a shift in the free energy by an amount $\triangle E$ indicated in figure 2b (where $\triangle E \ll KT$), we can write (cf.(5); see also the appendix).

$$\mathscr{L}_0 = - W(\triangle E/KT), \tag{13}$$

where W is given by (4).

Denoting by $\triangle P(t)$ ($\equiv P'(t) - P(t)$), the change in the probability matrix caused by the impressed sound wave, we can easily calculate the additional contribution to the strain by replacing $P(t)$ in (1) by $\triangle P(t)$, and making use of (2), (3), (4), (12) and (13). We obtain

$$\langle \triangle \epsilon_{zz}(t) \rangle = \tfrac{2}{3}(\triangle E/KT)(\nu/\omega)N(\lambda_1 - \lambda_2) \exp(-2\nu t) \sin \omega t. \tag{14}$$

In contrast to the usually encountered relaxation behaviour for systems in equilibrium, the energy dissipated by the sound wave per unit volume, $\triangle \mathscr{W}$ varies from cycle to cycle in the present case. For the nth cycle, we have from (14),

$$\triangle \mathscr{W}_n \equiv \int_{2\pi(n-1)/\omega}^{2\pi n/\omega} dt \sigma_0 \cos \omega t \, (d/dt) \langle \triangle \epsilon_{zz}(t) \rangle$$

$$= \tfrac{1}{3}(\triangle E/KT)N(\lambda_1 - \lambda_2)\sigma_0 \, [\exp(-4\pi\nu\,(n-1)/\omega)$$

$$-\exp(-4\pi\nu n/\omega)] \times [\omega^2/(\nu^2 + \omega^2] \tag{15}$$

4. Discussion

We consider first results (6) and (7). These suggest that conventional magnetostriction studies can also be employed to obtain information about the relaxation process under consideration. However, since the time constants involved in these measurements are usually in the range milliseconds to seconds (as opposed to a hundredth of a microsecond in an ultrasonic experiment), the temperature used corresponding to a given field H must be much less than the peak temperature T^* obtained by Fukase *et al* (1976) for the same field.

One of the advantages of magnetostriction measurements is that ambiguities about the initial preparation of the state can be removed. From the data at various temperatures, the temperature dependence of ν, and hence the barrier parameters can be conveniently extracted. Although it may not be possible to cover a wide enough range of temperature for reasons cited in the preceding paragraph, the technique of magnetostriction can be suitably combined with ultrasonic attenuation to yield the desired information.

Turning next to the result (15), we observe that $\triangle \mathscr{W}_n$ and hence the attenuation coefficient, vanishes at large times (i.e. $n \to \infty$). This is to be expected since by this time domain realignment in accordance with the minimum free energy configuration must be complete. This is also the reason for the disappearance of the peak during the downward scan of temperature (Fukase *et al* 1976). The result (15) in fact suggests a comprehensive way of performing the ultrasonic attenuation experiments. This would consist of preparing the initial state as described earlier, and tracking the attenuation as a function of the cycle number n, with H and T fixed. By systematically repeating the experiment at different temperatures, one can obtain, in addition to the temperature dependent relaxation rate ν, the quantities $\triangle E$ and $(\lambda_1-\lambda_2)$, as well.

We consider next the energy dissipated per unit volume in a given cycle, say the first ($n=1$). From (15),

$$\triangle \mathscr{W}_1 = \eta f(x), \tag{16}$$

where
$$\eta = \tfrac{1}{6}(\triangle E/KT)N(\lambda_1-\lambda_2)\sigma_0, \tag{17}$$

and
$$f(x) = [1- \exp(-4\pi/x)]\ x^2/(1+x^2), \quad x=\omega/\nu. \tag{18}$$

The parameter x depends on the temperature through (5). A plot of $f(x)$ versus x shown in figure 3 indicates why a peak was seen in the attenuation as a function of temperature by Fukase *et al* (1976). Also, as H increases, the free energy gap in figure 2b decreases (cf. TK) and one has to go to a lower temperature to keep ν fixed (see (5)). This explains why the peak position shifts towards lower temperatures with the increase of H (cf. Fukase *et al* 1976).

We are not in a position to present numerical results for the attenuation owing to inadequacy of information about barrier parameters (—incidentally, TK do not furnish these). However, once these parameters are available, the desired numbers can be obtained easily via (15). Conversely as indicated already, (15) can be used as the basis for extracting the parameters from fresh experimental measurements.

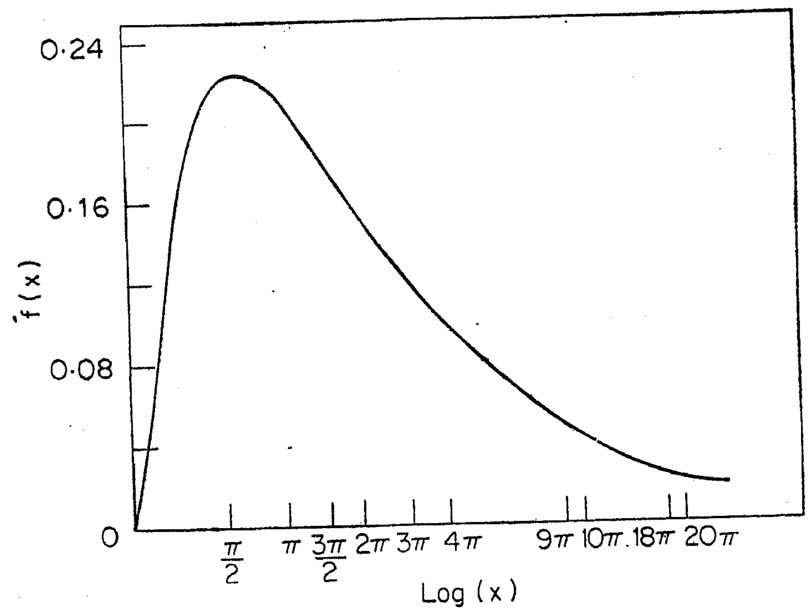

Figure 3. Plot of the factor $f(x)$ defined in (18) against $\log x$. The latter depends on the $(\text{temperature})^{-1}$ via (5). This curve demonstrates the presence of an anomalous peak in the attenuation (cf. (16)).

5. Conclusions

In this paper, we present an analysis of the anomalous ultrasonic peaks observed recently in V_3 Si at low temperatures, and in the presence of a magnetic field. The treatment is based on a free energy calculation of Tachiki and Koyama (1977) which indicates that in the mixed superconducting state, tetragonally distorted domains elongated along the magnetic field become energetically unstable. The consequent domain reorientations give rise to strain fluctuations. The contribution of the latter towards the ultrasonic attenuation is calculated with the aid of a master equation for the probability matrix whose elements give the transition probabilities from one domain configuration to another. A justification for the use of this master equation for the case in which both the magnetic field as well as the oscillatory stress are present, is given in the appendix.

One tacit assumption made in the calculations needs to be clarified here. The basic relaxation mechanism is viewed here to be connected with the decay of a metastable free energy state. A well-defined metastable state is of course an acceptable possibility for low enough magnetic fields (such as figure 2b). Tachiki and Koyama, on the other hand, present also theoretical free energy plots in which the saddle point is completely obliterated. This happens at very large magnetic fields (although, it is not clear whether these correspond to any accessible magnetic fields in the laboratory). The decay of the resultant unstable state (expected to occur very rapidly) is an altogether different kind of situation which the present formalism cannot cope with. A related point in this connection is that the rate of decay of the metastable state ν is restricted in the theory to be smaller than the rate of fluctuations in the heat bath (constituted of phonons, say) which are responsible for domain reorientations (see appendix). Once this is satisfied, there is no further restriction, however, on what ν should be vis-a-vis the probe frequency ω.

Another point which has been made in this paper is the need for the preparation of a well-defined initial state (see comments in §§ 2 and 4). Without this, extraction of quantitative information about the parameters of the system will be difficult. We have outlined how both magnetostriction (as yet unattempted) as well as ultrasonic measurements can be suitably combined to achieve unambiguous results.

Appendix

Equation (3) of the text, in its differential form, viz.,

$$\frac{dP(t)}{dt}=P(t)W, \tag{A1}$$

is the standard master equation usually employed for describing the time-evolution of a system (from one equilibrium configuration to another, in the present situation) (see Kubo 1962, for instance). If this approach to a new state is disturbed by a time-dependent perturbation (the oscillatory stress, for the case at hand) (A1) has to be modified. A modified form of the master equation was postulated in (10), along with a further assumption embodied in (11), in the case of a *weak* time-dependent perturbation. In this Appendix, we would like to substantiate the usage of (10) and (11). Similar derivations of master equations are commonly encountered in the areas of magnetic resonance (for example Abragam 1961) and quantum optics (Agarwal 1973, for instance).

We recall that in the case under discussion, the approach to equilibrium is associated with the decay of a metastable state. This state is described in terms of a free energy, already a coarse-grained thermodynamic quantity. This is why, in our construction of the transition matrix W in (4), reverse hops from configurations in which the domains are elongated along X or Y to those in which the domains are elongated along Z, are not considered. Neither do we have to take into account 'shufflings' amongst the two *stable* free energy configurations in which the domains have their long axis perpendicular to the field ($\theta=\frac{2}{3}\pi$ and $\frac{4}{3}\pi$ in figure 2b). However, for the sake of conceptual clarity in the present discussion, we forego the free energy language and talk instead at the level of a hamiltonian. To further simplify the mathematics, we consider just a two-level problem which, nevertheless, brings out all the physical features of the problem.

We wish to study the time-variation of the population (equal initially) of a two-level system under the combined influence of a static and a time-dependent field. A two-level system can be conveniently described in terms of a pseudo spin 1/2 Hamiltonian. The population difference of the levels corresponds then to the magnetisation. It is well known that the build-up of the magentisation of a spin system proceeds via energy transfers mediated by spin-lattice interactions (Abragam 1961). Accordingly, the Hamiltonian for the system may be taken as

$$\mathcal{H}(t) = (H_0 - H\cos\omega t)\,\sigma_z + h\sigma_x + \mathcal{H}_b, \tag{A2}$$

where H_0 and H are fictitious magnetic fields, (assumed to be switched on at $t=0$), σ's, the components of the Pauli spin angular momentum, h, an operator that acts on the lattice (henceforth referred to as the heat bath) described by the Hamiltonian $\mathcal{H}_b$. The negative sign in front of H is chosen in conformity with the physics of the problem, viz., the fact that the static and oscillatory fields act in opposition, one increases the energy, the other decreases it (cf. figure 2b). The coupling term

$$V = h\sigma_x, \tag{A3}$$

is responsible for causing energy exchanges between the spin system and the heat bath and for bringing the system eventually to a magnetised state in thermal equilibrium with the lattice.

The time-development of σ_z, in the Heisenberg picture, can be written as

$$\sigma_z(t) = \exp_-\left[i\int_0^t \mathcal{H}(t')\,dt'\right]\sigma_z \exp_+\left[-i\int_0^t \mathcal{H}(t')\,dt'\right], \tag{A4}$$

where $\exp_-[\ldots.]$, for example, indicates negative time ordering, i.e., the operators with the latest time arguments stand to the right.

From (A2)–(A4), we have

$$\sigma_z(t) = \exp_-\left[i\int_0^t V(t')dt'\right]\sigma_z \exp_+\left[-i\int_0^t V(t')dt'\right], \tag{A5}$$

where
$$V(t) = \exp\left[i\int_0^t \mathcal{H}_1(t')\,dt'\right]V\exp\left[-i\int_0^t \mathcal{H}_1(t')\,dt'\right], \tag{A6}$$

and
$$\mathcal{H}_1(t) = (H_0 - H\cos\omega t)\,\sigma_z + \mathcal{H}_b. \tag{A7}$$

In writing (A5) we have made use of the fact that

$$[\mathcal{H}_1(t), \mathcal{H}_1(t')] = 0, \text{ even for } t \neq t',$$

since
$$[\sigma_z, \mathcal{H}_b] = 0. \tag{A8}$$

Using (A8) and the properties of the Pauli spin matrices, one can easily show that

$$V(t) = \tfrac{1}{2}h(t)\,\{\sigma_+\exp[2i\phi(t)] + \sigma_-\exp[-2i\phi(t)]\}, \tag{A9}$$

where
$$h(t) = \exp(i\,\mathcal{H}_b\,t)\,h\exp(-i\,\mathcal{H}_b\,t), \tag{A10}$$

and
$$\phi(t) = H_0 t - (H/\omega)\sin\omega t. \tag{A11}$$

We wish to write (A5) as

$$\sigma_z(t) = \left(\exp_-\left[i\int_0^t V^\times(t')\,dt'\right]\right)\sigma_z, \tag{A12}$$

where $V^\times$ is the Liouville operator associated with V (for instance, Kubo 1962). The time development operator can therefore be denoted as

$$U(t) = \exp_-\left[i\int_0^t V^\times(t')\,dt'\right]. \tag{A13}$$

The probability matrix $P'(t)$, introduced in the text, is the time evolution operator for the sub-system alone (here, the spin system) obtained from (A13) by averaging $U(t)$ over the degrees of freedom of the heat bath:

$$P'(t) = \mathrm{Tr}_b[\rho_b U(t)] \equiv \langle U(t)\rangle_b, \tag{A14}$$

where the subscript b stands for bath, while ρ_b is the density matrix defined by

$$\rho_b = \exp(-\mathcal{H}_b/KT)/\mathrm{Tr}_b\,[\rho_b\exp(-\mathcal{H}_b/KT)]. \tag{A15}$$

In the above, it is assumed that the bath remains always at a constant temperature T.

To evaluate $\langle U(t)\rangle_b$, we make use of the cumulant expansion theorem (Kubo 1962) and write from (A13),

$$\langle U(t)\rangle_b \approx \exp_-\{i\int_0^t \langle V^\times(t_1)\rangle_b\, dt_1 + i^2\int_0^t dt_1\int_0^{t_1} dt_2\, [\langle V^\times(t_2)\, V^\times(t_1)\rangle_b - \langle V^\times(t_2)\rangle_b \langle V^\times(t_1)\rangle_b]\}. \quad (A16)$$

Note that (A16) is an approximate equation in which cumulants of order higher than the second (i.e. terms of $O(V^3)$) are ignored. In stochastic theories in which $V(t)$ defined by (A6) is assumed to be a random function of time, (A16) is exact if the underlying stochastic process is a Gaussian-Markovian one.

Equation (A16) can be simplified further by constructing the coupling term V to be such that

$$\langle h(t)\rangle_b = 0. \quad (A17)$$

In that case,

$$\langle U(t)\rangle_b \approx \exp_-\{-\int_0^t dt_1\int_0^{t_1} dt_2\, \langle V^\times(t_2)\, V^\times(t_1)\rangle_b\}. \quad (A18)$$

Bearing in mind the fact that the time ordering in (A18) is maintained in the expansion of the exponential function, we obtain, by differentiating (A18) and making use of the definition (A14),

$$dP'(t)/dt = P'(t)\, W'(t), \quad (A19)$$

$$\text{where } W'(t) \equiv -\int_0^t dt'\, \langle V^\times(t')\, V^\times(t)\rangle_b. \quad (A20)$$

It may be pointed out that W' is a Liouville operator for the spin system alone, the bath variables having been averaged over in (A20). Recalling the fact that we are interested in the time evolution of a *diagonal* operator (cf. (A12)), the only relevant matrix elements that enter into the calculation are of the type $(\mu\mu \mid W' \mid \nu\nu)$. Here the 'states' of a Liouville operator are defined in the usual manner by

$$\mid \mu\nu) = \mid \mu\rangle \langle \nu \mid, \quad (A21)$$

where $\mid \mu\rangle$ can be either $\mid +\rangle$ or $\mid -\rangle$, the spin-up or spin-down eigenstates of σ_z. In the rate-theory language (the language used in the text), W' is a 2×2 matrix, and if we identify the level number 1 with the spin-up state, and level number 2 with the spin-down state, then

$$W'_{11} = (+ + \mid W' \mid + +),\ W'_{12} = (+ + \mid W' \mid - -), \text{ etc.} \quad (A22)$$

Using $$(\mu\nu|V^{\times}|\mu'\nu') = \langle\mu|V|\mu'\rangle\,\delta_{\nu\nu'} - \langle\nu'|V|\nu\rangle\,\delta_{\mu\mu'}, \tag{A23}$$

which expresses the matrix elements of a Liouville operator in terms of those of the associated ordinary operator, we can show from (A20) and (A22) that

$$W'_{12}(t) = -W'_{11}(t) = \int_0^t dt' \{\langle h(t-t')\,h(0)\rangle_b \exp[2i(\phi(t)-\phi(t'))]$$

$$+\langle h(0)\,h(t-t')\rangle_b \exp[-2i(\phi(t)-\phi(t'))]\}. \tag{A24}$$

Similarly,

$$W'_{21}(t) = -W'_{22}(t) = \int_0^t dt' \{\langle h(t-t')\,h(0)\rangle_b \exp[-2i(\phi(t)-\phi(t'))]$$

$$+\langle h(0)\,h(t-t')\rangle_b \exp[2i(\phi(t)-\phi(t'))]\} \tag{A25}$$

Recalling that $\phi(t)$ is defined by (A11), we have, for a weak oscillatory field (linear response considered),

$$\exp[2i(\phi(t)-\phi(t'))] \approx \exp[2i\,H_0(t-t')]$$

$$\times\left[1-\frac{2i\,H}{\omega}(\sin\omega t-\sin\omega t')\right]. \tag{A26}$$

Substituting (A26) into (A24), we obtain

$$W'_{12}(t) = \int_0^t d\tau\,[\langle h(\tau)\,h(0)\rangle_b \exp(2i\,H_0\tau)+\langle h(0)\,h(\tau)\rangle_b \exp(-2i\,H_0\tau)]$$

$$-\frac{2i\,H}{\omega}\int_0^t d\tau\,[\langle h(\tau)\,h(0)\rangle_b \exp(2i\,H_0\tau)-\langle h(0)\,h(\tau)\rangle_b \exp(-2i\,H_0)\tau]$$

$$\times[\sin\omega t-\sin\omega(t-\tau)]. \tag{A27}$$

At this stage we make the important assumption (common to all rate theories) that the fluctuations in the heat bath are very much shortlived. In other words, the correlation time associated with the correlation function, say $\langle h(\tau)\,h(0)\rangle_b$ is much smaller than the other time scales (e.g. H_0^{-1}, H^{-1}, ω^{-1}, in the present case). This implies that the upper limit in the integrals in (A27) can be extended to ∞. The shortness of the correlation time of the bath variables enables us further to write (A27) approximately as

$$W'_{12}(t) \approx W_{12} - 2i\,H\cos\omega t\int_0^\infty \tau d\tau$$

$$\times[\langle h(\tau)h(0)\rangle_b \exp(2iH_0\tau) - \langle h(0)h(\tau)\rangle_b \exp(-2iH_0\tau)], \tag{A28}$$

where the time-independent part is given by

$$W_{12} = \int_0^\infty d\tau \, [\langle h(\tau)h(0)\rangle_b \exp(2iH_0\tau) + \langle h(0)h(\tau)\rangle_b \exp(-2iH_0\tau)]$$

$$= \int_{-\infty}^{\infty} d\tau \, \langle h(\tau)h(0)\rangle_b \exp(-2iH_0\tau). \tag{A29}$$

Note that had the H-field been static instead of being oscillatory, the resultant transition matrix would be time-independent and would be obtained from (A29) on replacing H_0 by (H_0-H). Furthermore, since we are interested only in linear response to H, we would have from (A29),

$$W'_{12} \approx W_{12} - 2iH \int_0^\infty d\tau\tau [\langle h(\tau)h(0)\rangle_b \exp(2iH_0\tau)$$

$$- \langle h(0)h(\tau)\rangle_b \exp(-2iH_0\tau)] \equiv W_{12} + (\mathscr{L}_0)_{12}, \tag{A30}$$

where $(\mathscr{L}_0)_{12}$ is the contribution to the transition matrix arising from the small field H.
Combining (A28) and (A30), we have

$$W'_{12}(t) = W_{12} + (\mathscr{L}_0)_{12} \cos \omega t. \tag{A31}$$

We can similarly show from (A25),

$$W'_{21}(t) = W_{21} (\mathscr{L}_0)_{21} \cos \omega t, \tag{A32}$$

where $$W_{21} = \int_{-\infty}^{\infty} d\tau \, \langle h(\tau)\, h(0)\rangle_b \exp(-2iH_0\, \tau), \tag{A33}$$

$$(\mathscr{L}_0)_{21} = 2iH \int_0^\infty \tau d\tau \, [\langle h(\tau)\, h(0)\rangle_b \exp(-2iH_0\, \tau)$$

$$-\langle h(0)\, h(\tau)\rangle_b \exp(2iH_0\, \tau). \tag{A34}$$

Equations (A31) and (A32), in conjunction with (A19), constitute the completion of the task we have set ourselves in this appendix, viz. establishing the validity of (10) and (11) used in the text. Before concluding, we make one other observation. From (A29) and (A33), it can be shown after standard manipulations (Kubo 1957) that

$$W_{12}/W_{21} = \exp(2H_0/KT) \tag{A35}$$

Recalling the fact that $2H_0$ represents the energy-difference of the two levels in a static field H_0, (cf. (A2)), (A35) expresses the detailed balance of transitions at finite temperatures. Incidentally, (A29) and (A33) indicate also how the rate constants, appearing in a phenomenological rate theory, are related to Fourier transforms of some basic correlations involving bath variables. Consistent with the detailed balance relation, one may set

$$W_{12} = \xi \exp(H_0/KT), \; W_{21} = \xi \exp(-H_0/KT), \tag{A36}$$

where ξ may be taken to be independent of H_0, in view of the assumption stated earlier that the correlation time of the bath variables is much smaller than the time associated with H_0^{-1} (white noise approximation). From (A29) and (A30) then, we can write

$$(\mathscr{L}_0)_{12} = -H\frac{d}{dH_0}W_{12} = -\frac{H}{KT}W_{12}. \tag{A37}$$

Equation (A37) justifies the use of (13) in the text.

Finally, we remark that the master equation (A19), albeit derived here in the context of a simple two-level problem, is expected to be applicable to a variety of physical situations in which one is interested in investigating the response of a time-evolving system to a weak time-dependent probe.

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