The structure factor for neutron scattering from a two-state system in metals

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Abstract. We consider the dynamics of a defect tunnelling between two trap sites in a metal. The interaction with conduction electrons is shown to influence strongly the defect motion at low temperatures. We calculate the structure factor for inelastic neutron scattering. The inelastic scattering peaks found at very low temperatures are shown to merge into a single quasi-elastic peak at higher temperatures. The width of the quasi-elastic peak narrows as the temperature is increased further. This behaviour results from the damping of the defect motion through the non-adiabatic response of the screening cloud. The present paper extends our previous results for symmetric two-state systems to the asymmetric case.

1. Introduction

Recently, Kondo [1] has pointed out that conduction electrons should have a dominant influence on the quantum dynamics of defects in metals at very low temperatures. Because of the finite density of electron–hole pair excitations with arbitrarily small energies, the electronic screening cloud causes non-trivial temperature-dependent effects in a region where the influence of phonons on the defect motion can already be described by a temperature-independent renormalisation of the defect Hamiltonian. These electronic effects have led to an explanation of the anomalous increase with decreasing temperature of the muon hopping rate in aluminium and copper below 10 K [1, 2]. Another system studied in detail is hydrogen trapped by oxygen or nitrogen in niobium [3]. When the superconductivity of niobium is destroyed by a magnetic field, the electronic influence leads to a crossover between coherent clock-like hydrogen tunnelling at very low temperatures and incoherent hopping-like tunnelling above a few kelvin [4, 5]. For a comprehensive survey of these phenomena we refer to a recent article by Kondo [6].

A defect tunnelling between two trap sites in a metal is a special case of a two-state system in contact with a thermal bath. Other examples of such systems are metallic glasses [7], superconducting interference devices [8], chiral molecules interacting with the radiation field [9] and electron transfer reactions (see e.g. [10]). The two-state system has received wide attention as a representative model for studying the interplay of quantum and dissipative effects. The theoretical description in terms of a spin-boson

Hamiltonian and a functional integral technique has been expounded by Leggett *et al* [11]. Much of the theoretical work has relied on the so-called dilute bounce gas approximation to the underlying functional integral expression [11, 12]. In an earlier work [4] we have employed these methods to calculate the structure factor for a symmetric two-state system coupled to an Ohmic bath. The results were found to be in good agreement with recent experiments by Wipf *et al* [5] on hydrogen trapped by oxygen in normal-state niobium. To explore the behaviour of the structure factor at higher temperatures one needs higher defect concentrations. Then the strain field interaction between tunnelling centres will lead to asymmetric two-state systems. This has motivated the present study where we extend our earlier results to the asymmetric case.

We have chosen to use here an approach quite different from the functional integral technique. The method employed bears close resemblance to the work by Zwerger [13] and Aslangul *et al* [14] and other similar methods [15] that go under the name of 'relaxation theory'. For the symmetric case the results reduce to our earlier findings [4]. We shall take advantage of the well established correspondence between a two-state system coupled to a fermionic bath and one coupled to a bath of harmonic oscillators with appropriate spectral density and coupling strength [16]. Our treatment will be based on the spin-boson Hamiltonian. Although the calculation here is specifically motivated by the availability of neutron scattering data for H motion in Nb, the method is of general interest in the context of spectral properties of the spin-boson Hamiltonian.

The outline of the paper is as follows. In § 2.1 we formulate the problem by first introducing the basic Hamiltonian and its mapping to a spin-boson model with Ohmic dissipation. Section 2.2 bridges the gap between theory and experiment wherein we write down the structure factor in terms of a spin-correlation function of the spin-boson system. In § 2.3 we state the basic assumptions of our calculation and give an approximate expression for the equilibrium density matrix. The main theoretical results are contained in § 3 where an explicit expression for the structure factor is derived in a series of steps. Finally, in § 4 we summarise and discuss the results and present our conclusions.

2. Formulation of the problem

2.1. The Hamiltonian

As mentioned in the introduction we are concerned in this paper with the dynamics of an interstitial defect (e.g. H) in a metal at low temperatures where conduction electrons have the dominating influence on the defect motion. The Hamiltonian for this interacting system can be modelled as [1, 4]

$$H = H_0 + \sum_{q,\sigma} \varepsilon_q c^+_{q,\sigma} c_{q,\sigma} + (V_0/N) \sum_{q,q',\sigma} c^+_{q,\sigma} c_{q',\sigma} \exp[i(q - q')r] \qquad (2.1)$$

where H_0 describes the defect in a double-well potential, $c^+_{q,\sigma}$ is the creation operator for a conduction electron with wavevector q, spin σ and energy ε_q, and the last term accounts for the interaction (via the constant strength V_0) between the N-electron system and the defect at the position r.

The Hamiltonian H_0 is governed by a potential shown schematically in figure 1. The characteristic energy scales are the barrier height V_0, the quantity $\hbar\omega_0$, ω_0 being of the order of the classical small-oscillation frequencies ω_+ and ω_- in the two wells, and the asymmetry energy $\hbar\varepsilon$ between the ground states in the two wells. The gap between the
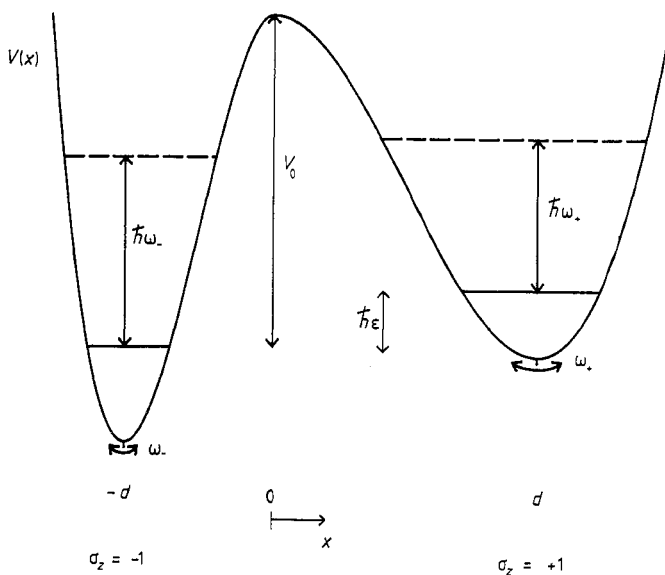
Figure 1. A double-well potential for a system in the two-state limit.

first excited state (of the isolated well) and the ground state will be approximately $\hbar\omega_+$ ($\hbar\omega_-$) for the right-hand (left-hand) well. If the asymmetry energy $\hbar\varepsilon$ between the ground states in the two wells is small compared to V_0 and $\hbar\omega_0$, then for $k_B T \ll V_0, \hbar\omega_0$ (but $k_B T/\hbar\varepsilon$ arbitrary) the system will be effectively restricted to the two-dimensional Hilbert space spanned by the two ground states. Of course, there will be tunnelling between the states so that the projected Hamiltonian will be off-diagonal. But the tunnelling frequency Δ_0 in the WKB limit is of the order of $(\omega_0 V_0/\hbar)^{1/2} \exp(-2V_0/\hbar\omega_0)$, and hence much smaller than ω_0 itself. Therefore, in the regime $k_B T, \hbar\varepsilon, \hbar\Delta_0 \ll \hbar\omega_0$ (but $k_B T/\hbar\varepsilon$ and $k_B T/\hbar\Delta_0$ arbitrary) the dynamics of the defect in the double-well potential of figure 1 can be adequately described in terms of the two-state Hamiltonian

$$H_0 = -\tfrac{1}{2}\hbar\Delta_0\sigma_x + \tfrac{1}{2}\hbar\varepsilon\sigma_z. \tag{2.2}$$

Here, we have taken the zero of energy as the average of the ground-state energies. For a detailed discussion of this truncation approximation we refer to [11, 17].

With the mapping described above, in which the position r of the defect is essentially proportional to σ_z (see (2.12) below), the Hamiltonian H in (2.1) describes a two-state system in contact with a *fermionic* bath. But as argued by several authors [1, 4, 6, 16], the dynamics of the system at sufficiently low temperature is dominantly governed by such gross features as the density of states for low-lying excitations off the Fermi surface. These excitations can be approximately described by bosons. To the extent that we may disregard electron-assisted processes† the equilibrium thermodynamics as well as the dynamic properties of the two-state system in a fermionic bath are the same as those of a two-state system in a bosonic bath, with however a special form of the spectral function $J(\omega)$ (specified below in (2.5)), characterising the boson excitations. This form describes what has been popularised in recent years as the *Ohmic dissipation* case. Therefore, all our subsequent discussions will be based on a model essentially equivalent to the one

† The coupling constant for these events is proportional to the tunnelling frequency Δ_0 and therefore small [18]. However, these processes may become relevant at very low temperatures [19].

given in (2.1) and which has been referred to in the recent literature as the *spin-boson Hamiltonian*:

$$H = -\tfrac{1}{2}\hbar\Delta_0\sigma_x + \tfrac{1}{2}\hbar\varepsilon\sigma_z + \sigma_z \sum_j G_j(b_j^+ + b_j) + \sum_j \hbar\omega_j b_j^+ b_j + \sum_j G_j^2/\hbar\omega_j \qquad (2.3)$$

where b_j^+ is the creation operator for the jth boson of frequency ω_j and G_j is the coupling constant. The last term is a counter-term which disappears upon a unitary transformation on H (see below).

The model and its equivalence to (2.1) are however not completely established unless one specifies the spectral function $J(\omega)$. The latter, which is defined by

$$J(\omega) = (2/\hbar^2) \sum_j G_j^2 \delta(\omega - \omega_j) \qquad (2.4)$$

assumes the following specific form for Ohmic dissipation

$$J(\omega) = K\omega \exp(-\omega/D). \qquad (2.5)$$

In the above, K is a phenomenological dimensionless constant that parametrises damping which arises in the model only in the limit of an infinitely large number of bosons (as tacitly recognised by the operation in (2.4)), and D is a cut-off frequency which is of the order of $\hbar\omega_0$. The choice of the cut-off D is somewhat arbitrary. It should be noted that D and the tunnelling frequency Δ_0 are not independent, since Δ_0 contains a renormalisation due to the high-frequency environmental modes that are already eliminated adiabatically. In the final formulae D and Δ_0 appear only in a certain combination (see (3.35) below) where the arbitrariness of D drops out. See [17] for a thorough discussion of this point.

For s-wave scattering the parameter K has been calculated by Yamada *et al* [20] as

$$K = 2 \left(\frac{1}{\pi} \tan^{-1} \frac{(1 - \alpha^2)^{1/2} \tan\delta}{(1 + \alpha^2 \tan^2 \delta)^{1/2}}\right)^2 \qquad \alpha = \sin(2dk_F)/2dk_F \qquad (2.6)$$

where δ is a phase shift ($\delta < \pi/2$), k_F is the Fermi wavevector, and $2d$ is the distance between the two defect sites (figure 1). It is obvious from (2.6) that for the present problem $0 \leqslant K \leqslant 0.5$.

As alluded to earlier, the spin-boson Hamiltonian is calculationally somewhat more tractable than the Hamiltonian given in (2.1). In addition, for our later purposes, we find it convenient to make a unitary transformation on the Hamiltonian [13–15]

$$\tilde{H} = SHS^{-1} \qquad (2.7)$$

where S is a unitary operator defined by

$$S \equiv \exp\left(-\sigma_z \sum_j (G_j/\hbar\omega_j)(b_j - b_j^+)\right). \qquad (2.8)$$

One readily finds

$$\tilde{H} = -\tfrac{1}{2}\hbar\Delta_0(B_+\sigma_- + B_-\sigma_+) + \tfrac{1}{2}\hbar\varepsilon\sigma_z + \sum_j \hbar\omega_j b_j^+ b_j \qquad (2.9)$$

where $\sigma_x = \sigma_+ + \sigma_-$ and where

$$B_\pm \equiv \exp\left(\pm 2 \sum_j (G_j/\hbar\omega_j)(b_j - b_j^+)\right). \qquad (2.10)$$

This is the basis of the calculations in the sequel.

2.2. Structure factor in terms of spin-correlation functions

The experimentally measured differential cross section for neutron scattering is given in terms of the structure factor (see e.g. [21]). The latter, when the scattering is predominantly incoherent (e.g. from H), is defined by (see e.g. [22])

$$S(k, \omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle \exp[-ik \cdot r(0)] \exp[ik \cdot r(t)] \rangle \quad (2.11)$$

where k and $\hbar\omega$ are the momentum and energy transfer for the neutron during the scattering process and $r(t)$ the position of the scatterer at time t. When the scatterer tunnels between two positions $-d$ and d (see figure 1) the operator r can be mapped into a Pauli pseudo-spin:

$$r = \sigma_z d. \quad (2.12)$$

Using then a well known Pauli matrix identity we can write

$$\langle \exp[-ik \cdot r(0)] \exp[ik \cdot r(t)] \rangle = \cos^2(k \cdot d) + \sin^2(k \cdot d) \langle \sigma_z(0)\sigma_z(t) \rangle \quad (2.13)$$

which when substituted into (2.11) gives

$$S(k, \omega) = \cos^2(k \cdot d)\delta(\omega) + \sin^2(k \cdot d) \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle \sigma_z(0)\sigma_z(t) \rangle. \quad (2.14)$$

It is convenient for calculational purposes to introduce a symmetrised correlation function

$$C(t) \equiv \tfrac{1}{2}[\langle \sigma_z(0)\sigma_z(t) \rangle + \langle \sigma_z(t)\sigma_z(0) \rangle]. \quad (2.15)$$

The structure factor can then be expressed as

$$S(k, \omega) = \cos^2(k \cdot d)\delta(\omega) + \sin^2(k \cdot d) \frac{1}{1 + \exp(\beta\hbar\omega)} \frac{1}{\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) C(t). \quad (2.16)$$

Noting that $C(t) = C(-t)$, the above result can also be rewritten in terms of the real part of a Laplace transform:

$$S(k, \omega) = \cos^2(k \cdot d)\delta(\omega) + \frac{\sin^2(k \cdot d)}{1 + \exp(\beta\hbar\omega)} \mathrm{Re} \left(\frac{2}{\pi} \lim_{\delta \to 0} \hat{C}(z) \right) \quad (2.17)$$

where $\beta = (k_B T)^{-1}$, $z = i\omega + \delta$ and

$$\hat{C}(z) = \int_0^{\infty} dt \exp(-zt)C(t). \quad (2.18)$$

The first term in the structure factor represents an elastic peak, which is a consequence of restricted diffusion of the scatterer [22].

In order to make direct comparison with experiments it may be useful to perform an isotropic average over the direction of the vector d (with its length d fixed) with respect to the wavevector k. The result is

$$S(k, \omega) = \tfrac{1}{2}\left(1 + \frac{\sin(2kd)}{2kd}\right)\delta(\omega) + \frac{1}{\pi}\left(1 - \frac{\sin(2kd)}{2kd}\right)\frac{1}{1 + \exp(\beta\hbar\omega)}$$
$$\times \operatorname{Re}\left(\operatorname*{Lim}_{\delta\to 0} \hat{C}(z)\right). \tag{2.19}$$

For $kd \ll 2\pi$, such an isotropic average is also appropriate to single-crystal metals with cubic crystal symmetry, as is the case with niobium.

2.3. Factorisation approximation of the equilibrium density matrix

It is evident from (2.16) that the calculation for the structure factor boils down to evaluating the correlation function $C(t)$. This requires the calculation of averages such as

$$\langle\sigma_z(0)\sigma_z(t)\rangle = \operatorname{Tr}[\rho_E\sigma_z(0)\exp(iHt/\hbar)\sigma_z(0)\exp(-iHt/\hbar)] \tag{2.20}$$

where ρ_E, the density matrix in equilibrium, is given by

$$\rho_E = (1/Z)\exp(-\beta H) \tag{2.21}$$

Z being the partition function. Using the unitary transformation (2.8), the cyclic property of the trace, and the fact that $[\sigma_z, S] = 0$, it is easy to show that

$$\langle\sigma_z(0)\sigma_z(t)\rangle = \operatorname{Tr}[\tilde{\rho}_E\sigma_z(0)\exp(i\tilde{H}t/\hbar)\sigma_z(0)\exp(-i\tilde{H}t/\hbar)] \tag{2.22}$$

where $\tilde{\rho}_E$ is obtained from (2.21) upon replacing H by $\tilde{H}$. So far (2.22) is exact. We now write

$$\tilde{H} = H_S + H_I + H_B \tag{2.23}$$

where

$$H_S = \tfrac{1}{2}\hbar\varepsilon\sigma_z \tag{2.24}$$

$$H_I = -\tfrac{1}{2}\hbar\Delta_0(B_+\sigma_- + B_-\sigma_+) \tag{2.25}$$

$$H_B = \sum_j \hbar\omega_j b_j^+ b_j. \tag{2.26}$$

Here H_S and H_B represent pure spin and bath Hamiltonians respectively whereas H_I describes the spin–bath interaction.

The main assumption made in the sequel is that we can describe the system in terms of a perturbative expansion in H_I. In a first approximation we neglect the interaction and put

$$\exp(-\beta\tilde{H}) \simeq \exp(-\tfrac{1}{2}\hbar\beta\varepsilon\sigma_z)\exp\left(-\hbar\beta\sum_j\omega_j b_j^+ b_j\right) \tag{2.27}$$

which leads to a factorising equilibrium density matrix

$$\tilde{\rho}_E^0 = \tfrac{1}{2}[1 - \tanh(\tfrac{1}{2}\hbar\beta\varepsilon)\sigma_z]\rho_B \tag{2.28}$$

where

$$\rho_B = Z_B^{-1} \exp\left(-\hbar\beta \sum_j \omega_j b_j^+ b_j\right) \tag{2.29}$$

and Z_B is the partition function associated with the purely bath Hamiltonian H_B. The thermal expectation value of σ_z obtained from (2.28) is

$$\langle \sigma_z \rangle_0 = -\tanh(\tfrac{1}{2}\hbar\beta\varepsilon). \tag{2.30}$$

This disregards the effects of tunnelling on the equilibrium state. Naturally, the interaction H_I will modify the equilibrium density matrix. A more general *ansatz* for $\tilde{\rho}_E$ reads

$$\tilde{\rho}_E = \tfrac{1}{2}[1 + \langle \sigma_z \rangle \sigma_z + \langle \sigma_x \rangle \sigma_x + \langle \sigma_y \rangle \sigma_y]\rho_B. \tag{2.31}$$

While this density matrix is still of a factorising form, we may insert more accurate expressions for the spin expectation values. We shall make use of this approximate form of $\tilde{\rho}_E$ below and return to a discussion of its validity at the end of § 3.

3. Calculation of the spin-correlation function

3.1. *The Liouvillian and the bath-averaged time-development operator*

The symmetrised correlation function can be written from (2.15) and (2.22) as

$$C(t) = \tfrac{1}{2}\mathrm{Tr}\{[\tilde{\rho}_E \sigma_z(0) + \sigma_z(0)\tilde{\rho}_E]\tilde{\sigma}_z(t)\} \tag{3.1}$$

where we have introduced

$$\tilde{\sigma}_z(t) \equiv \exp(i\tilde{H}/\hbar)\sigma_z(0)\exp(-i\tilde{H}t/\hbar), \tag{3.2}$$

and applied the cyclic property of the trace. Employing then a density matrix of the form (2.28) or (2.31) in (3.1) and the fact that $\sigma_z^2 = 1$ and $\sigma_{x,y}\sigma_z + \sigma_z\sigma_{x,y} = 0$, the expression simplifies considerably (exemplifying the advantage of using the symmetrised form in $C(t)$):

$$C(t) = \tfrac{1}{2}\mathrm{Tr}_B\{\rho_B[\sigma_z(0) + \langle \sigma_z \rangle]\tilde{\sigma}_z(t)\}. \tag{3.3}$$

We may now perform a partial trace over the spin states yielding

$$C(t) = \tfrac{1}{2}\mathrm{Tr}_B\{\rho_B([\langle +|\tilde{\sigma}_z(t)|+\rangle - \langle -|\tilde{\sigma}_z(t)|-\rangle] + \langle \sigma_z \rangle[\langle +|\tilde{\sigma}_z(t)|+\rangle$$
$$+ \langle -|\tilde{\sigma}_z(t)|-\rangle])\} \tag{3.4}$$

where the subscript in Tr_B implies a trace over the bath variables alone. It is convenient at this stage to write the time development of σ_z in (3.2) in terms of the Liouvillian $\tilde{L}$ [22]:

$$\tilde{\sigma}_z(t) = \exp(i\tilde{L}t)\sigma_z(0) \tag{3.5}$$

where $\tilde{L}$ is defined by

$$\tilde{L}A \equiv (1/\hbar)[\tilde{H}, A] \tag{3.6}$$

for an arbitrary operator A. The notation can be simplified further by writing

$$\tilde{\sigma}_z(t) = U(t)\sigma_z(0) \tag{3.7}$$

where

$$U(t) \equiv \exp(i\tilde{L}t) \tag{3.8}$$

is the so-called time-development operator. Evidently in (3.4) we require terms of the form[†]

$$\sum_n \langle n|\rho_B|n\rangle \langle \mu n|U(t)\sigma_z(0)|\mu n\rangle$$

$$= \sum_{nn'} \sum_{\mu'} \langle n|\rho_B|n\rangle (\mu n \mu n|U(t)|\mu'n'\mu'n')\langle \mu'|\sigma_z|\mu'\rangle$$

$$= \sum_{\mu'} \mu'(\mu\mu|[U(t)]_{av}|\mu'\mu'). \tag{3.9}$$

Here $|\mu\rangle$ with $\mu = \pm 1$ refers to the spin states, $|n\rangle$ denotes the occupation-number states for bosons, and $[U(t)]_{av}$ is the bath-averaged time-development operator denoted by [22]

$$[U(t)]_{av} = \sum_{nn'} \langle n|\rho_B|n\rangle (nn|U(t)|n'n'). \tag{3.10}$$

Substitution in (3.4) leads to a more compact expression for the correlation function as

$$C(t) = \tfrac{1}{2} \sum_{\mu\mu'} (\mu + \langle\sigma_z\rangle)\mu'(\mu\mu|[U(t)]_{av}|\mu'\mu'). \tag{3.11}$$

The remaining task is clearly then to evaluate the bath-averaged time-development operator.

3.2. Resolvent operator method

It is evident from the above discussion that what one needs in the structure factor calculation (cf. (2.17)) is the Laplace transform of the time-development operator (i.e. its resolvent)

$$\hat{U}(z) \equiv \int_0^\infty dt \exp(-zt)U(t) = 1/(z - i\tilde{L}). \tag{3.12}$$

This is a lucky situation because one can now employ certain powerful methods directly in the z-space [22].

Recall that the Hamiltonian $\tilde{H}$ can be split as in (2.23). The corresponding Liouville operator may be similarly decomposed as

$$\tilde{L} = L_S + L_I + L_B. \tag{3.13}$$

Developing L_I as perturbation in the resolvent and suitably rearranging terms up to second order in L_I we can show [22]

$$[\hat{U}(z)]_{av} \simeq \{z - iL_S + [L_I(z - iL_S - iL_B)^{-1}L_I]_{av}\}^{-1} \tag{3.14}$$

where $[\ldots]_{av}$ has been defined in (3.10). The second-order result (3.14) holds for interactions H_I that vanish when averaged over the bath density matrix ρ_B, as is the case for the interaction (2.25) in the Ohmic dissipation case (2.4), (2.5). Note that the strategy has been to group all terms representing the influence of the heat bath in the resolvent itself. Further the truncated series in (3.14), although of order L_I^2 (and hence Δ_0^2),

[†] For superoperators S (like $\tilde{L}$ and $U(t)$) we use the notation $\langle \mu n|[S(|\nu m\rangle\langle\nu'm'|)]|\mu'n'\rangle = (\mu n \mu'n'|S|\nu m \nu'm')$.

already contains terms of arbitrary orders in the original coupling constants G_j in view of the exponentiation in (2.10). While it is straightforward to go beyond $O(L_I^2)$ in (3.14), the theory is already quite rich in structure, yielding results equivalent to those obtained by the dilute bounce gas approximation (see below).

As we need the matrix elements of $[\check{U}(z)]_{av}$ amongst the spin states (cf. (3.11)) it is convenient first to tabulate the matrix elements of the *self-energy* in (3.14). The latter, upon repeated application of the properties of the Liouvillian, turn out to be

$$(\mu\nu|[L_I(z - iL_S - iL_B)^{-1}L_I]_{av}|\mu'\nu')$$

$$= \frac{1}{\hbar^2} \sum_{nn'} \langle n|\rho_B|n\rangle \left(\delta_{\nu\nu'} \sum_{\eta} \frac{\langle \mu n|H_I|\eta n'\rangle\langle \eta n'|H_I|\mu'n\rangle}{z - i(E_{n'} - E_n)/\hbar - (i\varepsilon/2)(\eta - \nu)} \right.$$

$$+ \delta_{\mu\mu'} \sum_{\eta} \frac{\langle \nu'n|H_I|\eta n'\rangle\langle \eta n'|H_I|\nu n\rangle}{z - i(E_n - E_{n'})/\hbar - (i\varepsilon/2)(\mu - \eta)}$$

$$- \frac{\langle \mu n|H_I|\mu'n'\rangle\langle \nu'n'|H_I|\nu n\rangle}{z - i(E_{n'} - E_n)/\hbar - (i\varepsilon/2)(\mu' - \nu)}$$

$$\left. - \frac{\langle \mu n|H_I|\mu'n'\rangle\langle \nu'n'|H_I|\nu n\rangle}{z - i(E_n - E_{n'})/\hbar - (i\varepsilon/2)(\mu - \nu')} \right) \tag{3.15}$$

where

$$E_n \equiv \langle n|H_B|n\rangle. \tag{3.16}$$

The next strategy is to plug in the explicit form of H_I (cf. (2.25)), rewrite the denominators back in the form of integrals over t and express the sum over the bath states (n, n', etc) as correlation functions for bath operators. We find for the matrix of $[L_I(z - iL_S - iL_B)^{-1}L_I]_{av}$:

$$\begin{pmatrix} [\hat{\Phi}_{-+}(z_+) + \hat{\Phi}'_{-+}(z_-)] & -[\hat{\Phi}_{-+}(z_+) + \hat{\Phi}'_{-+}(z_-)] & 0 & 0 \\ -[\hat{\Phi}_{+-}(z_-) + \hat{\Phi}'_{+-}(z_+)] & [\hat{\Phi}_{+-}(z_-) + \hat{\Phi}'_{+-}(z_+)] & 0 & 0 \\ 0 & 0 & [\hat{\Phi}_{-+}(z) + \hat{\Phi}'_{+-}(z)] & -[\hat{\Phi}_{--}(z) + \hat{\Phi}'_{--}(z)] \\ 0 & 0 & -[\hat{\Phi}_{++}(z) + \hat{\Phi}'_{++}(z)] & [\hat{\Phi}_{+-}(z) + \hat{\Phi}'_{-+}(z)] \end{pmatrix}$$

$$\tag{3.17}$$

where the rows and columns are labelled by $++$, $--$, $+-$ and $-+$ respectively,

$$z_\pm = z \pm i\varepsilon \tag{3.18}$$

and

$$\Phi_{+-}(t) = (\Delta_0^2/4)\langle B_+(0)B_-(t)\rangle$$

$$\Phi_{-+}(t) = (\Delta_0^2/4)\langle B_-(0)B_+(t)\rangle$$

$$\Phi_{++}(t) = (\Delta_0^2/4)\langle B_+(0)B_+(t)\rangle \tag{3.19}$$

$$\Phi_{--}(t) = (\Delta_0^2/4)\langle B_-(0)B_-(t)\rangle.$$

Further, all primed quantities are obtained by replacing the argument t by $-t$, and the hat denotes the Laplace transform. It may be stressed again that the angular brackets in (3.19) denote thermal averages governed by ρ_B and the time development of $B_\pm(t)$ is dictated by H_B alone.

The matrix in (3.17) has to be combined with that of $z - iL_S$ (cf. (3.14)) and then inverted. However, for our purposes we need focus only on the upper left block in (3.17) (see (3.11)), and thus we find (displaying only the upper left block) for the matrix of $[U(z)]_{av}$:

$$\frac{1}{\text{Det}} \begin{pmatrix} z + [\hat{\Phi}_{+-}(z_-) + \hat{\Phi}'_{+-}(z_+)] & [\hat{\Phi}_{-+}(z_+) + \hat{\Phi}'_{-+}(z_-)] \\ [\hat{\Phi}_{+-}(z_-) + \hat{\Phi}'_{+-}(z_+)] & z + [\hat{\Phi}_{-+}(z_+) + \hat{\Phi}'_{-+}(z_-)] \end{pmatrix}$$

(3.20)

where the determinant Det is given by

$$\text{Det} = z\{z + [\hat{\Phi}_{+-}(z_-) + \hat{\Phi}'_{+-}(z_+)] + [\hat{\Phi}_{-+}(z_+) + \hat{\Phi}'_{-+}(z_-)]\}.$$

(3.21)

The relevant matrix elements of $[\hat{U}(z)]_{av}$ can be read out from (3.20) and substituted in (3.11) for the purpose of evaluating $\hat{C}(z)$. It may be remarked that in calculating correlation functions other than $\langle \sigma_z(0)\sigma_z(t) \rangle$ (which may be relevant in a different context) the full 4×4 matrix in (3.17) may have to be analysed.

3.3. The bath correlations

The method given in § 3.2 is independent of the specific nature of the heat bath. However, in order to make explicit calculations for the correlation functions enumerated in (3.19) one has to spell out the exact form of the bath variables. Adopting then the bosonic model (cf. (2.25) and (2.26)) and using certain well known properties of a harmonic oscillator system we find

$$\Phi_{-+}(t) = \Phi_{-+}(t) \equiv \Phi(t)$$

$$= \frac{\Delta_0^2}{4} \exp \left\{ - \sum_j \frac{4G_j^2}{\hbar^2 \omega_j^2} \left[\coth \left(\frac{\beta\hbar\omega_j}{2} \right) [1 - \cos(\omega_j t)] - i \sin(\omega_j t) \right] \right\}$$

(3.22)

$$\Phi'_{+-}(t) = \Phi'_{-+}(t) \equiv \Phi'(t) = \Phi(-t).$$

(3.23)

(The expressions for $\Phi_{++}(t)$ and $\Phi_{--}(t)$ are not listed here since they are not relevant for our present purpose.)

The stage is now set to go to a continuum set of bath oscillators, i.e. to replace the summation over j in (3.22) by an integral over ω with the aid of an appropriate spectral function. Using in addition the Ohmic dissipation model (cf. (2.4) and (2.5)) we find

$$\Phi(t) = \frac{\Delta_0^2}{4} \exp \left\{ -2K \int_0^\infty \frac{d\omega}{\omega} \exp \left(\frac{-\omega}{D} \right) \left[\coth \left(\frac{\beta\hbar\omega}{2} \right) [1 - \cos(\omega t) - i \sin(\omega t)] \right] \right\}.$$

(3.24)

For $\beta\hbar D \gg 1$ the integral in (3.24) yields

$$\Phi(t) = \frac{\Delta_0^2}{4} \exp[i\pi K \, \text{sgn}(t)] \left(\frac{\pi}{\hbar\beta D} \right)^{2K} \frac{1}{[\sinh(\pi|t|/\hbar\beta)]^{2K}}.$$

(3.25)

Finally, the Laplace transform of (3.25) is given by

$$\hat{\Phi}(z) = \frac{\Delta_0^2}{4D} \exp(i\pi K) \left(\frac{2\pi}{\hbar\beta D} \right)^{2K-1} \frac{\Gamma(1 - 2K)\Gamma(K + z\hbar\beta/2\pi)}{\Gamma(1 - K + z\hbar\beta/2\pi)}$$

(3.26)

where $\Gamma(z)$ is the gamma function of argument z. Similarly,

$$\hat{\Phi}'(z) = \frac{\Delta_0^2}{4D} \exp(-i\pi K) \left(\frac{2\pi}{\hbar\beta D}\right)^{2K-1} \frac{\Gamma(1-2K)\Gamma(K+z\hbar\beta/2\pi)}{\Gamma(1-K+z\hbar\beta/2\pi)}. \tag{3.27}$$

3.4. The spin-correlation function

Combining (3.11) and (3.20) we derive

$$\hat{C}(z) = (1/\mathrm{Det})\{z - \langle\sigma_z\rangle([\hat{\Phi}(z_+) - \hat{\Phi}'(z_+)] - [\hat{\Phi}(z_-) - \hat{\Phi}'(z_-)])\} \tag{3.28}$$

where now Det is given by

$$\mathrm{Det} = z\{z + ([\hat{\Phi}(z_+) + \hat{\Phi}'(z_+)] + [\hat{\Phi}(z_-) + \hat{\Phi}'(z_-)])\}. \tag{3.29}$$

For the sake of completeness we tabulate:

$$\hat{\Phi}(z_+) + \hat{\Phi}'(z_+) = \frac{\Delta_0^2}{2D} \cos(\pi K) \left(\frac{2\pi}{\hbar\beta D}\right)^{2K-1} \frac{\Gamma(1-2K)\Gamma(K+z_+\hbar\beta/2\pi)}{\Gamma(1-K+z_+\hbar\beta/2\pi)} \tag{3.30}$$

$$\hat{\Phi}(z_+) - \hat{\Phi}'(z_+) = i\frac{\Delta_0^2}{2D} \sin(\pi K) \left(\frac{2\pi}{\hbar\beta D}\right)^{2K-1} \frac{\Gamma(1-2K)\Gamma(K+z_+\hbar\beta/2\pi)}{\Gamma(1-K+z_+\hbar\beta/2\pi)}. \tag{3.31}$$

The other necessary expressions are obtained by replacing z_+ by z_-. Introducing

$$J(z) = \frac{\Delta_0^2}{2D} \left(\frac{2\pi}{\hbar\beta D}\right)^{2K-1} \frac{\Gamma(1-2K)\Gamma(K+z\hbar\beta/2\pi)}{\Gamma(1-K+z\hbar\beta/2\pi)} \tag{3.32}$$

and recalling $z_\pm = z \pm i\varepsilon$ (cf. (3.18)), the expression (3.28) may be written in the compact form

$$\hat{C}(z) = \frac{z - i\langle\sigma_z\rangle \sin(\pi K)[J(z+i\varepsilon) - J(z-i\varepsilon)]}{z\{z + \cos(\pi K)[J(z+i\varepsilon) + J(z-i\varepsilon)]\}}. \tag{3.33}$$

Equation (3.33) is deceptively similar to the result derived by Grabert and Weiss [23] and Fisher and Dorsey [23] for the Laplace transform of the occupation probability of an initially localised state within the dilute bounce gas approximation. The expression (3.33) for the correlation function is however also crucially different by the presence of the factor $\langle\sigma_z\rangle$ in the numerator.

For further discussion it is convenient to introduce the effective tunnelling frequency [4, 24]

$$\Delta = [\cos(\pi K)\Gamma(1-2K)]^{1/(2-2K)} \Delta_0 \left(\frac{\Delta_0}{D}\right)^{K/(1-K)} \tag{3.34}$$

in terms of which $J(z)$ may be written as

$$J(z) = \frac{\Delta}{2} \left(\frac{\hbar\beta\Delta}{2\pi}\right)^{1-2K} \frac{\Gamma(K+z\hbar\beta/2\pi)}{\cos(\pi K)\Gamma(1-K+z\hbar\beta/2\pi)}. \tag{3.35}$$

In this expression the cut-off D does not appear any longer. The tunnel splitting Δ is related to the tunnel frequency observed in neutron scattering experiments [4]. In the *symmetrical case* ($\varepsilon = 0$) the formula (3.33) simplifies to read

$$\hat{C}(z) = [z + 2\cos(\pi K)J(z)]^{-1} \tag{3.36}$$

which is identical to the answer obtained by us earlier in the dilute bounce gas approximation [4]. In the *zero-damping limit* $(K = 0)$ we have

$$J(z) = \Delta^2/2z \qquad \Delta = \Delta_0 \tag{3.37}$$

and (3.33) gives

$$\hat{C}(z) = \frac{z^2 + \varepsilon^2}{z(z^2 + \varepsilon^2 + \Delta^2)} \tag{3.38}$$

a result that can easily be checked by an independent calculation. In the general case, we obtain from (3.33)

$$\lim_{z \to 0} z\hat{C}(z) = \langle \sigma_z \rangle \tan(\pi K) \operatorname{Im}[J(\mathrm{i}\varepsilon)]/\operatorname{Re}[J(\mathrm{i}\varepsilon)]. \tag{3.39}$$

Now, from (3.35) we have

$$\operatorname{Im}[J(\mathrm{i}\varepsilon)]/\operatorname{Re}[J(\mathrm{i}\varepsilon)] = -\cot(\pi K) \tanh(\hbar\beta\varepsilon/2) \tag{3.40}$$

which gives

$$\lim_{z \to 0} z\hat{C}(z) = \langle \sigma_z \rangle [-\tanh(\hbar\beta\varepsilon/2]. \tag{3.41}$$

Since

$$\lim_{z \to 0} z\hat{C}(z) = \lim_{t \to \infty} C(t) = \langle \sigma_z \rangle^2 \tag{3.42}$$

we find an internally consistent result only when $\langle \sigma_z \rangle$ is approximated by (2.30). Hence, the approximations made so far are quite similar to those inherent in the dilute bounce gas approximation which also leads to an equilibrium average of $\langle \sigma_z \rangle$ given by (2.30) [11, 12, 23]. The true equilibrium value of $\langle \sigma_z \rangle$ will deviate from (2.30) for finite asymmetry and low temperatures. In this region the result (3.33) will not be reliable for small values of z where the precise long-time behaviour of $C(t)$ matters. As will be seen from the results in the following section, for systems with small K the dominant features of the low-temperature structure factor for inelastic neutron scattering depend on the behaviour of $\hat{C}(z)$ for frequencies of order Δ or larger. Only at higher temperatures, where the scattering is quasi-elastic, does the low-frequency behaviour of $\hat{C}(z)$ become important. In this latter region, however, the thermal average $\langle \sigma_z \rangle$ is well approximated by (2.30). We therefore expect that for systems with small K the theory gives a reasonable approximation for the structure factor in the entire range of temperatures. Furthermore, our results become basically exact in the region of quasi-elastic scattering at higher temperatures (see below). It is precisely in this region where our results on asymmetric systems are particularly important, since for experiments at higher temperatures larger defect concentrations are needed to distinguish the quasi-elastic peak from the background.

4. Discussion and conclusions

4.1. The structure factor

In this section we summarise our main results. The natural frequency scale of the problem is set by the effective tunnelling frequency Δ characterising the renormalised

tunnel splitting of a symmetric two-state system at zero temperature. It is convenient to introduce a dimensionless frequency

$$\nu = \omega/\Delta \tag{4.1}$$

a dimensionless asymmetry

$$\sigma = \varepsilon/\Delta \tag{4.2}$$

where $\hbar\varepsilon$ is the asymmetry energy, and a dimensionless temperature

$$\tau = k_B T/\hbar\Delta. \tag{4.3}$$

The structure factor (2.19) may then be written as

$$S(k, \omega) = \frac{1}{2}\left(1 + \frac{\sin(2kd)}{2kd}\right)\delta(\omega) + \frac{1}{2}\left(1 - \frac{\sin(2kd)}{2kd}\right)\frac{1}{\pi\Delta}j(\omega/\Delta) \tag{4.4}$$

where

$$j(\nu) = \frac{2}{1 + \exp(\nu/\tau)}\,\Delta\,\mathrm{Re}(\hat{C}(i\nu\Delta)) \tag{4.5}$$

is a dimensionless function characterising the inelastic part of the structure factor. Combining (4.5) with (2.30), (3.33) and (3.35) we find

$$j(\nu) = \frac{2}{1 + \exp(\nu/\tau)}\,\mathrm{Re}\left(\frac{\nu + \frac{1}{2}\tan(\pi K)\tanh(\sigma/2\tau)[f(\nu + \sigma) - f(\nu - \sigma)]}{\nu\{i\nu + \frac{1}{2}[f(\nu + \sigma) + f(\nu - \sigma)]\}}\right) \tag{4.6}$$

where

$$f(\nu) = (2\pi\tau)^{2K-1}\frac{\Gamma(K + i\nu/2\pi\tau)}{\Gamma(1 - K + i\nu/2\pi\tau)}. \tag{4.7}$$

As mentioned earlier, for low temperatures the spectral function (4.6) is not expected to be accurate at low frequencies. In fact, the result (4.6) becomes negative for $\sigma \neq 0$ and small τ and ν. This shortcoming of the perturbative calculation can be removed for systems with small values of K, as is the case for H in Nb where K is near $1/20$ [5]. In the limit $K \ll 1$ the function $f(\nu)$ may be approximated by

$$f(\nu) = \frac{1}{\nu^2 + (2\pi\tau K)^2}\left\{\pi K\nu\coth\left(\frac{\nu}{2\tau}\right) - i\nu\left(1 + 2K\,\mathrm{Re}\left[\Psi\left(i\frac{\nu}{2\pi\tau}\right)\right] + 2K\ln(2\pi\tau)\right)\right\} \tag{4.8}$$

where $\Psi(z)$ is the logarithmic derivative of the complex gamma function.

When the approximation (4.8) is inserted into (4.6) the expression can be simplified considerably. At low temperatures the structure factor has two narrow resonances near $\nu \simeq \pm(1 + \sigma^2)^{1/2}$ which stay away from the parameter region where the result (4.6) is not reliable. Near these resonances the function $j(\nu)$ takes the form

$$j(\nu) = \frac{1}{1 + \exp(\nu/\tau)}\frac{1}{1 + \sigma^2}\frac{4\nu_0^2\gamma}{(\nu^2 - \nu_0^2)^2 + 4\nu_0^2\gamma^2} \tag{4.9}$$

for $K \ll 1$, $2\pi\tau K \ll 1$, where

$$\nu_0^2 = 1 + \sigma^2 + 2K[R_+ - \sigma R_-/w + \ln(2\pi\tau)] \tag{4.10}$$

defines the dimensionless resonance frequency ν_0 with

$$R_\pm = \tfrac{1}{2}\mathrm{Re}\left[\Psi\left(\mathrm{i}\,\frac{w + \sigma}{2\pi\tau}\right)\right] \pm \tfrac{1}{2}\mathrm{Re}\left[\Psi\left(\mathrm{i}\,\frac{w - \sigma}{2\pi\tau}\right)\right] \qquad w = (1 + \sigma^2)^{1/2}. \tag{4.11}$$

The result (4.9) describes two inelastic scattering peaks. The relative intensity of these peaks is determined by a detailed balance factor. From (4.10) we see that the peak positions are shifted by the asymmetry energy in the usual way and there is a further temperature-dependent shift due to the damping. In the asymmetric case the total intensity of the peaks is reduced by the factor $1 + \sigma^2$. Hence, only systems with moderate asymmetry contribute to the inelastic scattering. The dimensionless parameter γ reads

$$\gamma = \pi K[C_+ - \sigma C_-/w]/2w \tag{4.12}$$

with

$$C_\pm = \tfrac{1}{2}\coth\left(\frac{w + \sigma}{2\tau}\right) \pm \tfrac{1}{2}\coth\left(\frac{w - \sigma}{2\tau}\right) \tag{4.13}$$

and it determines the linewidth Γ of the scattering peaks through $\Gamma = 2\gamma\Delta$. In figure 2 the temperature dependences of ν_0 and γ are depicted for $K = 0.05$ and various values of $\sigma = \varepsilon/\Delta$. Frequently, σ will be distributed statistically. Then, the σ dependence of ν_0 causes an inhomogeneous broadening of the lines and Γ gives the homogeneous linewidth.

At increased temperatures higher-order terms in K become important which shift the resonances towards the origin. At a characteristic crossover temperature the scattering peaks merge into a single quasi-elastic peak. For hydrogen trapped by oxygen in niobium this occurs for temperatures near 11 K [5]. In the region of quasi-elastic scattering $k_B T \gg \hbar\Delta$, i.e. $\tau \gg 1$, we may replace $f(\nu \pm \sigma)$ by $f(\pm\sigma)$. This gives for the dimensionless structure factor

$$j(\nu) = \frac{1}{1 + \exp(\nu/\tau)}\,\frac{1}{\cosh^2(\sigma/2\tau)}\,\frac{2\gamma_{qe}}{\nu^2 + \gamma_{qe}^2} \qquad \tau \gg 1 \tag{4.14}$$

where

$$\gamma_{qe} = \mathrm{Re}[f(\sigma)] = (2\pi\tau)^{2K-1}\,\frac{\sin(\pi K)}{\pi}\cosh\left(\frac{\sigma}{2\tau}\right)\left|\Gamma\left(K + \frac{\mathrm{i}\sigma}{2\pi\tau}\right)\right|^2. \tag{4.15}$$

The spectral function (4.14) describes a quasi-elastic peak of linewidth $\Gamma = 2\gamma_{qe}\Delta$. For small K the dimensionless linewidth (4.15) can be approximated by

$$\gamma_{qe} = (2\pi\tau)^{2K-1}\,\frac{K}{K^2 + (\sigma/2\pi\tau)^2}\,\frac{\sigma}{2\tau}\coth\left(\frac{\sigma}{2\tau}\right) \qquad K \ll 1 \tag{4.16}$$
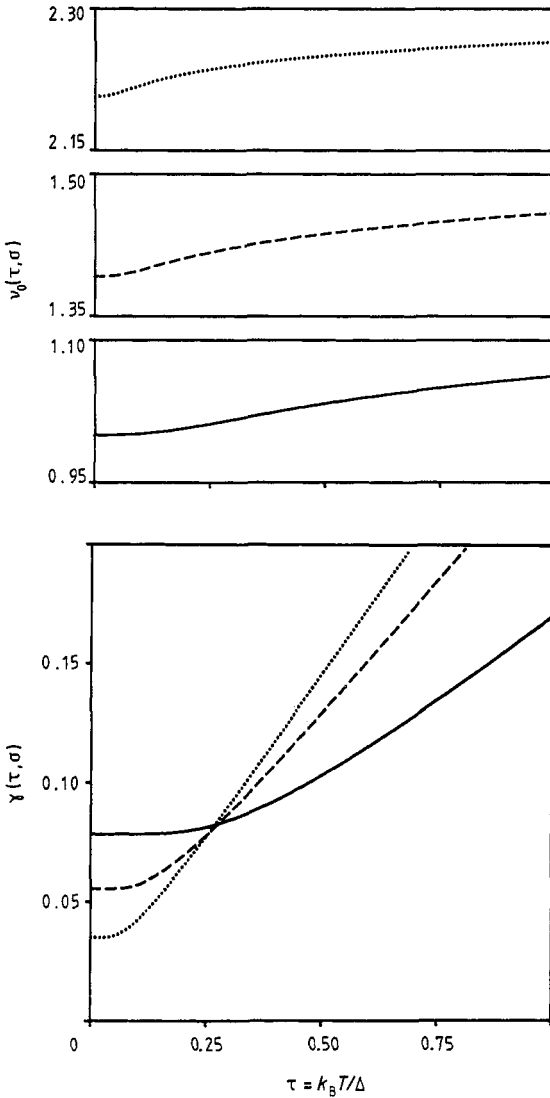
Figure 2. For a system with dimensionless coupling constant $K = 0.05$ the dimensionless resonance frequency ν_0 and linewidth γ of the inelastic scattering peaks are shown as functions of temperature for various values of $\sigma = \varepsilon/\Delta$: —— $\sigma = 0$; ----- $\sigma = 1$; ····· $\sigma = 2$.

which shows that asymmetric tunnelling systems have their linewidth reduced roughly by the factor $1 + (\sigma/2\pi\tau K)^2$. As the temperature increases, systems with stronger asymmetry become relevant.

From these considerations we see that the spectral function $j(\nu)$, equation (4.6), changes its form in a characteristic way when the temperature is increased. At low temperatures the tunnelling system has a well defined tunnelling frequency and neutron scattering shows corresponding inelastic scattering peaks. At higher temperatures these peaks merge into a quasi-elastic peak and the system is now characterised by an incoherent tunnelling rate. This changeover is also seen from figure 3 where $j(\nu)$ is

depicted for two temperatures well below and well above the crossover temperature between coherent and incoherent tunnelling. The characteristic temperature dependence of the scattering function arises from the destruction of the coherent clock-like tunnelling of the two-state system by the thermally excited electron-hole pairs. As the temperature is increased further, the quasi-elastic peak narrows. This corresponds to the region of the anomalous temperature dependence proportional to T^{2K-1} observed for the muon hopping rate [1, 2]. Equation (4.16) shows that the simple power-law behaviour is modified for asymmetric systems. For defects in metals the peak will widen again at higher temperatures because of phonon effects [6, 25] which are disregarded here.
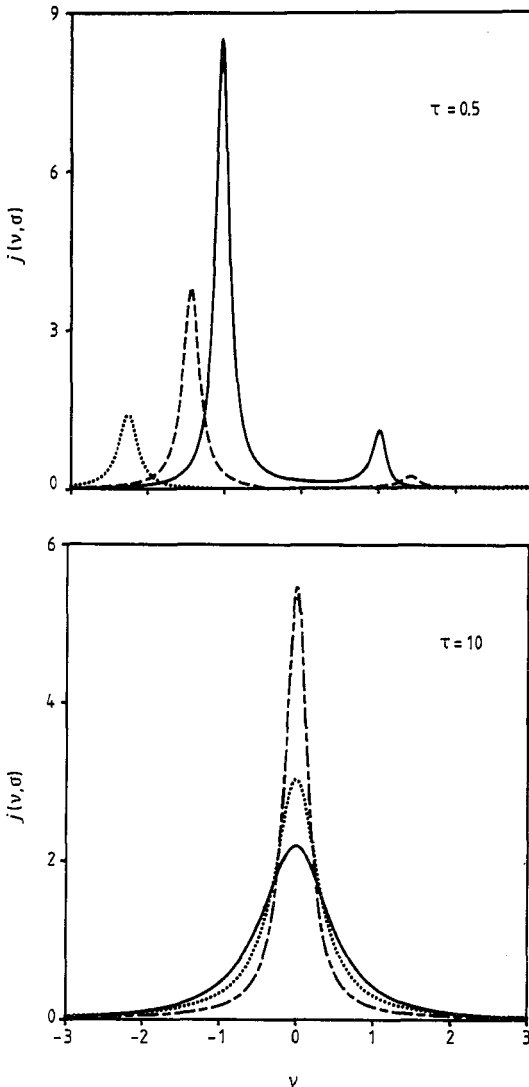

Figure 3. For a system with $K = 0.05$ the dimensionless structure factor $j(\nu)$ is shown for two temperatures and various values of σ: —— $\sigma = 0$; - - - - $\sigma = 1$; $\cdots\cdots$ $\sigma = 2$, ———— $\sigma = 4$.

4.2. Conclusions

We have examined the low-temperature behaviour of the structure factor for neutron scattering from a defect tunnelling between two trap sites in a metal. At very low temperatures the inelastic scattering shows peaks near the tunnelling frequency of the system with a finite width due to the interaction with the conduction electrons. As the temperature increases, thermally excited electron–hole pairs destroy the coherence of tunnelling, and the structure factor becomes that of a system hopping incoherently between two sites. The width of the inelastic peak decreases with increasing temperature until phonon effects set in and enhance the hopping rate. This specific temperature dependence of the structure factor is characteristic for the Ohmic dissipation model.

The most promising system for an experimental observation of this behaviour seems to be hydrogen trapped by oxygen (or nitrogen) in normal-state niobium [3]. When the defect concentration is low, the tunnelling systems are almost symmetric. For such samples the changeover from inelastic to quasi-elastic scattering was observed by Wipf *et al* [5]. More recent data [26] are also indicative of a narrowing of the quasi-elastic peak with increasing temperature until a minimum is reached around 70 K. These experiments require higher defect concentrations, making the tunnelling systems asymmetric.

To determine the structure factor for asymmetric two-state systems we have used quantum relaxation theory. The self-energy was evaluated in second-order perturbation theory in the tunnel splitting. This is equivalent to a calculation employing the functional integral method [11, 12] in the dilute bounce gas approximation. We have pointed out the shortcomings of this approximation but have argued that our results become essentially exact in the region of quasi-elastic scattering. It is just in this region where they are most important, since higher defect concentrations are needed to observe the scattered neutrons against the background. We have further argued that for systems with $K \ll 1$ the essential features of the scattering intensity in the low-temperature region should also be described reasonably well by our results, since the intensity peaks at finite frequencies. However, a more accurate calculation would be very desirable.

Acknowledgments

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