Thermodynamics of Phonon-Modulated Tunneling Centers

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In recent years tunneling centers have frequently been used to explain the unusual thermodynamic properties of disordered materials; in these approaches, however, the effect of the tunneling–phonon interaction is neglected. The present study considers the archetype model of phonon-assisted tunneling, which is well known from other areas of tunneling physics (quantum diffusion, etc.). It is shown that the full thermodynamic information can be rigorously extracted from a single Green function. An extended factorization procedure beyond Hartree–Fock is introduced, which is checked by sum rules as well as by exact Goldberger–Adams expansions. The phonon-modulated internal energy and specific heat are calculated for different power-law coupling setups.

KEY WORDS: Tunneling centers; glasses; amorphous materials; thermodynamic properties.

1. INTRODUCTION

In a fundamental paper Anderson *et al.*[1] have suggested an assembly of tunneling systems to explain the measured unusual thermodynamic and thermal conductivity properties of amorphous materials. Experimentally, it was found that the specific heat of glasses follows a T law[2,3] below 1 K, in contrast to the expected Debye T^3 law.[3–5] The thermal conductivity is proportional to $T.^2$ A good review of the experimental situation is given in Hunklinger and Arnold.[6] Anderson *et al.*[1] propose that the considered material contains a set of tunneling systems, the intrinsic parameters of which display a suitable distribution. In this semiphenomenological concept the single tunneling system is asymmetric and thus is characterized by two parameters, a transitive one and an asymmetric one. In their calculation they did not consider the coupling of the tunneling systems to the

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surrounding lattice excitations, such as phonons and others. From previous theoretical work on paraelectric/paraelastic centers[7-11] and from recent work on quantum diffusion[12-15] it is known that the modes of the surrounding exert a strong influence on the dynamical properties of the tunneling system.

The principal aim of the present study is the investigation of the alterations of thermodynamic properties if the interaction of the tunneling process with phonons is taken into account. A first attempt in this direction was made by de Raedt and de Raedt,[16] who preferentially considered the hierarchical situation where the Debye frequency of the bath is smaller than the tunneling splitting of the two-level system. Also, their aim was more directed toward the susceptibility calculation, paying no attention to the specific heat. We also base our analysis on the archetype model of phonon-assisted tunneling given by Holstein,[17] which has been adopted by most workers in the fields of paraelectric centers[7-11] and quantum diffusion.[12-15] This model displays spatial inversion symmetry and thus in its bare tunneling subpart is less general than the asymmetric AHV model.[1] Yet our emphasis is on the phonon influences, the study of which is considerably facilitated if symmetry arguments can be used. Moreover, this restriction may help to decide whether and to what extent asymmetry is needed in the bare tunneling subsystem.

We start with a standard perturbative calculation based on the Goldberger–Adams (GA) theorem. This yields the exact small-coupling limit of all thermodynamic quantities in the whole temperature range. In our context it is needed to have an additional check of our later approximate findings.

The central part of our study will be a Green function approach, in which the full thermodynamic information is traced back to a single Green function. For this GF we develop a factorization procedure beyond the Hartree–Fock prescription, which on one hand is suggested by an exact antiresonance condition and on the other is able to reproduce the lowest four sum rules exactly. In the final part we compute the desired thermodynamic quantities.

2. HAMILTONIAN

The generally adopted basic Hamiltonian ("archetype Hamiltonian"[17]) for mode-assisted tunneling can be written in the form

$$H = \Delta \cdot \sigma_z + \frac{1}{2} \sum_k \Omega_k (P_k^2 + Q_k^2) + \sigma_x \sum_k \Omega_k D_k Q_k \tag{1}$$

It describes a particle which can tunnel from a "left" state $|l\rangle$ to a "right" state $|r\rangle$, Δ being the tunneling matrix element. The pseudo spin operators σ_z, σ_x, and σ_y are defined as

$$\sigma_x = \frac{1}{2}\left[|l\rangle\langle l| - |r\rangle\langle r|\right] \tag{2a}$$

$$\sigma_y = \frac{1}{2i}\left[|l\rangle\langle r| - |r\rangle\langle l|\right] \tag{2b}$$

$$\sigma_z = -\frac{1}{2}\left[|l\rangle\langle r| + |r\rangle\langle l|\right] \tag{2c}$$

and satisfy commutation relations $[\sigma_x, \sigma_y]_- = i\sigma_z$ cycl. The coordinates Q_k, P_k characterize the bath modes, which may represent true oscillatory excitations, but also electronic, excitonic, or other elementary excitations, the dynamics of which is modeled by oscillators, $[Q_k, P_{k'}]_- = i\delta_{kk'}$.

The Hamiltonian (1) has been considered by many workers both in the early stages of quantum diffusion[7-9,17] as well as in the present strongly revived discussion.[13-15] One may well consider the decay problem described by the Hamiltonian (1) as the most fascinating one which has not been solved exactly. On the other hand the Hamiltonian (1) may be viewed as the phonon-modulated extension of a symmetric Anderson–Halperin–Varma (AHV) Hamiltonian.[1] To be more specific, we consider power law coupling characterized by

$$\Omega^2 D^2(\Omega)\, \rho(\Omega) = 4\alpha\Omega_D\left(\frac{\Omega}{\Omega_D}\right)^m, \qquad 0 \leqslant \Omega \leqslant \Omega_D \tag{3}$$

where $\rho(\Omega)$ is the frequency density of the oscillatory subsystem and Ω_D ("Debye" frequency) is the cutoff frequency. In recent work[12-15] mainly the particular values $m = 1$ ("Ohmic dissipation") and $m = 3$ (coupling to phonons) have been considered, but in the problem of glassy materials also other powers may become relevant. For later reference we note the identity

$$\sum_k \Omega_k D_k^2 = \frac{4\alpha}{m}\Omega_D \tag{4}$$

3. GOLDBERGER–ADAMS EXPANSIONS

Since the Hamiltonian (1) cannot be solved exactly, we want to encase our approximate evolution of thermodynamic properties as far as possible in the framework of exact limiting requirements. A straightforward check of

our approximate results is the comparison with the correct analytic form of perturbative expansions. Therefore we derive these for later reference. A standard procedure to derive weak coupling expansions of thermodynamic quantities is the application of the Goldberger–Adams (GA) theorem.[18] In our case it furnishes convergent expansions in the whole temperature range. The GA theorem reads

$$e^{-\beta(H_0 + W)} = e^{-\beta H_0} \left[1 - \int_0^\beta d\lambda \, e^{\lambda H_0} W e^{-\lambda(H_0 + W)} \right] \tag{5}$$

which yields for the partition sum $(\beta = 1/k_B T)$

$$Z = \text{tr}(e^{-\beta H}) = Z_0 \left[1 - \int_0^\beta d\lambda \, \langle e^{\lambda H_0} W e^{-\lambda H_0} \rangle_T^{H_0} \right.$$

$$\left. + \int_0^\beta d\lambda \int_0^\lambda d\lambda' \, \langle e^{\lambda H_0} W e^{-\lambda H_0} e^{\lambda' H_0} W e^{-\lambda' H_0} \rangle_T^{H_0} + O(\beta^3 W^3) \right] \tag{6}$$

where

$$Z_0 = \text{tr}(e^{-\beta H_0}) \tag{7}$$

and

$$\langle X \rangle_T^{H_0} = \frac{1}{Z_0} \text{tr}(e^{-\beta H_0} X) \tag{8}$$

Similarly, by applying relation (5), we may write the thermal expectation value of X in the form

$$\langle X \rangle_T^H = \frac{\text{tr}(e^{-\beta H} X)}{Z} = \frac{Z_0}{Z} \left[\langle X \rangle_T^{H_0} - \int_0^\beta d\lambda \, \langle e^{\lambda H_0} W e^{-\lambda H_0} X \rangle_T^{H_0} \right.$$

$$+ \int_0^\beta d\lambda \int_0^\lambda d\lambda' \, \langle e^{\lambda H_0} W e^{-\lambda H_0} e^{\lambda' H_0} W e^{-\lambda' H_0} X \rangle_T^{H_0}$$

$$\left. + O(\beta^3 W^3 X) \right] \tag{9}$$

Applying these formulas to the Hamiltonian (1), we are left with two choices for its separation into H_0 and W. We decide to choose

$$H_0 = \Delta \cdot \sigma_z + \tfrac{1}{2} \sum_k \Omega_k (P_k^2 + Q_k^2) = \Delta \cdot \sigma_z + H_{\text{bath}} \tag{10}$$

$$W = \sigma_x \sum_k D_k \Omega_k Q_k \tag{11}$$

Performing the integrations in Eq. (6), which is a lengthy but straightforward calculation, we arrive at

$$Z = Z_0 \left\{ 1 + \frac{\beta}{16} \left[\tanh \left(\frac{\beta \Delta}{2} \right) \sum_k D_k^2 \Omega_k^2 \left(\frac{1}{\Delta + \Omega_k} + \frac{1}{\Delta - \Omega_k} \right) \coth \left(\frac{\beta \Omega_k}{2} \right) \right. \right.$$

$$\left. \left. + \sum_k D_k^2 \Omega_k^2 \left(\frac{1}{\Delta + \Omega_k} + \frac{1}{\Delta - \Omega_k} \right) \right] + O(D_k^4) \right\} \tag{12}$$

where

$$Z_0 = 2 \cosh \left(\frac{\beta \Delta}{2} \right) \prod_{k=1}^{N} \frac{1}{2 \sinh(\beta \Omega_k/2)} \tag{13}$$

Note that the second term in (12) is of order α, where α is the coupling strength [see Eq. (3)]. From (12) we can derive the internal energy $U = -\partial \ln Z/\partial \beta$,

$$U = \underbrace{\sum_k \frac{\Omega_k}{2} \coth \left(\frac{\beta \Omega_k}{2} \right)}_{U_{\text{bath}}} \underbrace{- \frac{\Delta}{2} \tanh \left(\frac{\beta \Delta}{2} \right)}_{U_{\text{spin}}} - \frac{1}{16} \left\{ \sum_k D_k^2 \Omega_k^2 \left(\frac{1}{\Delta + \Omega_k} - \frac{1}{\Delta - \Omega_k} \right) \right.$$

$$+ \left(\tanh \left(\frac{\beta \Delta}{2} \right) + \frac{\beta \Delta/2}{\cosh^2(\beta \Delta/2)} \right)$$

$$\times \sum_k D_k^2 \Omega_k^2 \left(\frac{1}{\Delta + \Omega_k} + \frac{1}{\Delta - \Omega_k} \right) \cosh \left(\frac{\beta \Omega_k}{2} \right)$$

$$\left. - \tanh \left(\frac{\beta \Delta}{2} \right) \sum_k D_k^2 \Omega_k^2 \left(\frac{1}{\Delta + \Omega_k} + \frac{1}{\Delta - \Omega_k} \right) \frac{\beta \Omega_k/2}{\sinh^2(\beta \Omega_k/2)} \right\} + O(D_k^4) \tag{14}$$

and the expression for the specific heat $C = \partial U/\partial T$. The latter expression is lengthy and is not explicitly given here.

In a completely analogous way we find the GA expansions for the two expectation values $\langle \sigma_z \rangle$ and $\sum_k D_k \Omega_k \langle \sigma_x Q_k \rangle$, which later prove to be of particular interest,

$$\langle \sigma_z \rangle_T^H = -\frac{1}{2} \tanh \left(\frac{\beta \Delta}{2} \right) \cdot \left[1 + \frac{1}{16} \sum_k D_k^2 \Omega_k^2 \left\{ \coth \frac{\beta \Omega_k}{2} \left(\frac{1}{\Delta + \Omega_k} + \frac{1}{\Delta - \Omega_k} \right) \right. \right.$$

$$\times \left(\coth \frac{\beta \Delta}{2} - \tanh \frac{\beta \Delta}{2} \right) \beta - 4 \frac{1 - e^{-\beta(\Omega_k + \Delta)}}{(1 - e^{-\beta \Omega_k})(1 - e^{-\beta \Delta})} \frac{1}{(\Delta + \Omega_k)^2}$$

$$\left. \left. + 4 \frac{e^{-\beta \Delta} - e^{-\beta \Omega_k}}{(1 - e^{-\beta \Omega_k})(1 - e^{-\beta \Delta})} \frac{1}{(\Delta - \Omega_k)^2} \right\} \right] + O(D_k^4) \tag{15}$$

$$\sum_k D_k \Omega_k \langle \sigma_x Q_k \rangle_T^H$$

$$= -\sum_k \frac{D_k^2 \Omega_k}{4} \left[1 + \frac{\Delta^2}{\Omega_k^2 - \Delta^2} - \frac{\Delta \Omega_k}{\Omega_k^2 - \Delta^2} \coth\left(\frac{\beta \Omega_k}{2}\right) \tanh\left(\frac{\beta \Delta}{2}\right) \right] + O(D_k^4)$$

$$(16)$$

4. GREEN FUNCTION THERMODYNAMICS

Since the early days of the Green function (GF) technique it has been known that for many coupled systems the full thermodynamic information is incorporated in a single GF. As regards the Hamiltonian (1), it was noted already in the instructive paper of Beck *et al.*[19] that the nine pseudospin GFs $\langle\!\langle \sigma_i | \sigma_j \rangle\!\rangle$ may be traced back to two of them and that the thermodynamic quantity $\langle \sigma_z \rangle$ is found from $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle$. It is not difficult to proceed similarly for the oscillatory GFs such that in the end the thermodynamic potentials are expressed via the single GF $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle$.

We employ Green functions of the Zubarev type[20] defined by

$$\langle\!\langle A(t) | B(t') \rangle\!\rangle^{(r,a)} = \mp i\theta(\pm(t-t'))\langle [A(t), B(t')]_- \rangle_T^H \qquad (17)$$

the Fourier transform of which, $\langle\!\langle A | B \rangle\!\rangle_E$, defines the spectral function $I_{AB}(\omega)$,

$$I_{AB}(\omega) = \frac{i}{e^{\beta\omega} - 1} [\langle\!\langle A | B \rangle\!\rangle_{\omega + i\varepsilon} - \langle\!\langle A | B \rangle\!\rangle_{\omega - i\varepsilon}], \qquad \varepsilon = 0_+ \qquad (18)$$

This function may be employed to evaluate correlation functions,

$$\langle B(0) \cdot A(t) \rangle_T^H = \int_{-\infty}^{+\infty} I_{AB}(\omega) e^{-i\omega t}\, d\omega \qquad (19)$$

Specifically, we find for thermal expectation values

$$\langle BA \rangle_T^H = \int_{-\infty}^{+\infty} I_{AB}(\omega)\, d\omega \qquad (20)$$

where $\langle X \rangle_T^H$ is defined in (6) and (9).

Since by way of Eqs. (20) and (18) thermal expectation values can be derived from Green functions, the internal energy $U = \langle H \rangle_T^H$ of the phonon-assisted tunneling problem [see Hamiltonian (1)] requires the computation of the GFs $\langle\!\langle P_k | P_k \rangle\!\rangle$, $\langle\!\langle Q_k | Q_k \rangle\!\rangle$, $\langle\!\langle Q_k | \sigma_x \rangle\!\rangle$. We show below that all these GFs can be traced back to the single GF $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle$ and

that also the remaining partial expectation value $\langle \sigma_z \rangle_T^H$ of $\langle H \rangle_T^H$ follows from $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle$.

The general equation of motion for the Zubarev GF $\langle\!\langle A | B \rangle\!\rangle_E$ (Fourier transformed, $E = \omega \pm i\varepsilon$, $\varepsilon = 0_+$) reads

$$E\langle\!\langle A | B \rangle\!\rangle_E = \frac{1}{2\pi} \langle [A, B]_- \rangle_T^H + \langle\!\langle [A, H]_- | B \rangle\!\rangle_E \tag{21}$$

or, alternatively,

$$E\langle\!\langle A | B \rangle\!\rangle_E = \frac{1}{2\pi} \langle [A, B]_- \rangle_T^H - \langle\!\langle A | [B, H]_- \rangle\!\rangle_E \tag{21'}$$

Employing Eq. (21), we get

$$E\langle\!\langle Q_k | \sigma_x \rangle\!\rangle_E = i\Omega_k \langle\!\langle P_k | \sigma_x \rangle\!\rangle_E \tag{22}$$

$$E\langle\!\langle P_k | \sigma_x \rangle\!\rangle_E = -i\Omega_k \langle\!\langle Q_k | \sigma_x \rangle\!\rangle_E - i\Omega_k D_k \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \tag{23}$$

which we combine to

$$\langle\!\langle Q_k | \sigma_x \rangle\!\rangle_E = \frac{\Omega_k^2 D_k}{E^2 - \Omega_k^2} \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E = \langle\!\langle \sigma_x | Q_k \rangle\!\rangle_E \tag{24}$$

which is one of the needed GFs. Similarly, we can find $\langle\!\langle Q_k | Q_k \rangle\!\rangle_E$,

$$E\langle\!\langle Q_k | Q_k \rangle\!\rangle_E = i\Omega_k \langle\!\langle P_k | Q_k \rangle\!\rangle_E \tag{25}$$

$$E\langle\!\langle P_k | Q_k \rangle\!\rangle_E = -\frac{i}{2\pi} - i\Omega_k \langle\!\langle Q_k | Q_k \rangle\!\rangle_E - i\Omega_k D_k \langle\!\langle \sigma_x | Q_k \rangle\!\rangle_E \tag{26}$$

Combining these two equations and inserting (24), we have

$$\langle\!\langle Q_k | Q_k \rangle\!\rangle_E = \frac{\Omega_k}{2\pi(E^2 - \Omega_k^2)} + \frac{(\Omega_k^2 D_k)^2}{(E^2 - \Omega_k^2)^2} \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \tag{27}$$

Finally, we evaluate $\langle\!\langle P_k | P_k \rangle\!\rangle_E$ by proceeding from Eq. (22) via the second equation of motion (21'),

$$E\langle\!\langle P_k | Q_k \rangle\!\rangle_E = -\frac{i}{2\pi} - i\Omega_k \langle\!\langle P_k | P_k \rangle\!\rangle_E \tag{28}$$

which we insert in Eq. (25),

$$E^2 \langle\!\langle Q_k | Q_k \rangle\!\rangle_E = \frac{\Omega_k}{2\pi} + \Omega_k^2 \langle\!\langle P_k | P_k \rangle\!\rangle_E \tag{29}$$

and using Eq. (27), we find

$$\langle\!\langle P_k | P_k \rangle\!\rangle = \frac{\Omega_k}{2\pi(E^2 - \Omega_k^2)} + \frac{E^2 \Omega_k^2 D_k^2}{(E^2 - \Omega_k^2)^2} \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \qquad (30)$$

In this manner we have succeeded, as already mentioned above, to trace back all partial expectation values of $\langle H \rangle_T^H$ (apart from $\langle \sigma_z \rangle_T^H$) to the GF $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle$. The $\langle \sigma_z \rangle_T^H$ will be found also in the process of calculating $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle$. Collecting results, we have

$$\frac{1}{2}\sum_k \Omega_k (\langle\!\langle P_k | P_k \rangle\!\rangle_E + \langle\!\langle Q_k | Q_k \rangle\!\rangle_E)$$

$$= \frac{1}{2\pi}\sum_k \frac{\Omega_k^2}{E^2 - \Omega_k^2} + \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \sum_k \frac{D_k^2 \Omega_k^3}{4}\left[\frac{1}{(E - \Omega_k)^2} + \frac{1}{(E + \Omega_k)^2}\right] \quad (31)$$

5. FACTORIZATION BEYOND HARTREE–FOCK

We now want to find a solution for the GF $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E$ itself. To this end we establish the hierarchy of equations of motion for $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E$,

$$E\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E = -i\varDelta\langle\!\langle \sigma_y | \sigma_x \rangle\!\rangle_E \qquad (32)$$

$$E\langle\!\langle \sigma_y | \sigma_x \rangle\!\rangle_E = -\frac{i}{2\pi}\langle \sigma_z \rangle_T^H + i\varDelta\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E$$

$$-i\sum_k \Omega_k D_k \langle\!\langle \sigma_z Q_k | \sigma_x \rangle\!\rangle_E \qquad (33)$$

At this stage of hierarchy we earlier introduced a Hartree–Fock factorization[15]

$$\langle\!\langle \sigma_z Q_k | \sigma_x \rangle\!\rangle_E \approx \langle \sigma_z \rangle_T^H \langle\!\langle Q_k | \sigma_x \rangle\!\rangle_E \qquad (34)$$

By this approximation the set of equations of motion for $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E$ can be closed. However, although this kind of factorization is very frequently used in the literature, it is inappropriate if it violates basic sum rules. In point of fact, when checking the sum rules of the factorization (34) itself as well as the sum rules of the GF $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E$ derived from it, we have found that even the lower sum rules are not conserved.

We therefore introduce an improved factorization procedure by requiring that the lower sum rules of the factorization itself *as well as* those of the GF in question be preserved. The first option in this direction is the factorization

$$\langle\!\langle \sigma_z Q_k | \sigma_x \rangle\!\rangle_E = \eta\langle\!\langle Q_k | \sigma_x \rangle\!\rangle_E + \zeta\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \qquad (35)$$

which, with respect to the spectral function $I_{\sigma_z Q_k; \sigma_x}$, amounts to the factorization

$$I_{\sigma_z Q_k; \sigma_x}(\omega) = \eta I_{Q_k; \sigma_x}(\omega) + \zeta I_{\sigma_x; \sigma_x}(\omega) \tag{36}$$

This constitutes already a considerable improvement beyond the HF factorization (34). The two open parameters η and ζ are determined by sum rules.

In our analysis we resort to the sum rules for the spectral function I_{AB},

$$
\begin{aligned}
M^{(n)} &= \int_{-\infty}^{+\infty} I_{AB}(\omega) \omega^n \, d\omega \\
&= \langle B[\ldots[[A, H]_-, H]_-, \ldots H]_-\rangle \\
&= \langle [H, \ldots [H, [H, B]_-]_- A \rangle
\end{aligned}
\tag{37}
$$

Applying this rule to the spectral functions of Eq. (36), we find

$$M_0: \quad -\frac{i}{2} \langle \sigma_y Q_k \rangle_T^H = \eta \langle \sigma_x Q_k \rangle_T^H + \frac{1}{4} \zeta \tag{38}$$

$$M_1: \quad \frac{i}{2} \langle \sigma_x Q_k \rangle_T^H = \eta \langle \sigma_y Q_k \rangle_T^H - \frac{i}{2} \zeta \langle \sigma_z \rangle_T^H \tag{39}$$

We now apply the identity

$$\langle [A, H]_- \rangle_T^H \equiv 0 \tag{40}$$

which often is a useful aid in calculating thermal expectation values. Specifically, it yields

$$\langle \sigma_y Q_k \rangle_T^H = 0 \tag{41}$$

Employing this, we get from Eqs. (38) and (39) that $\eta = 1/(4\langle \sigma_z \rangle_T^H)$ and $\zeta = -\langle \sigma_x Q_k \rangle_T^H / \langle \sigma_z \rangle_T^H$ and thus from (35)

$$\langle\!\langle \sigma_z Q_k | \sigma_x \rangle\!\rangle_E = \frac{1}{4 \langle \sigma_z \rangle_T^H} \langle\!\langle Q_k | \sigma_x \rangle\!\rangle_E + \frac{\langle \sigma_x Q_k \rangle_T^H}{\langle -\sigma_z \rangle_T^H} \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \tag{42}$$

The most striking feature of this formula is the fact that $\langle \sigma_z \rangle_T^H$ appears in the denominator now, which is the inverse behavior to the Hartree–Fock factorization (34). Consequently, the thermal behavior of physical properties such as the damping or the tunneling frequency of the diffusion process is quite different, not to say contrary, to the results based on Eq. (34).

Inserting (42) and (24) in Eqs. (32)–(33), we have

$$
E^2 \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E = -\frac{\Delta}{2\pi} \langle \sigma_z \rangle + \Delta^2 \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E
$$

$$
- \Delta \sum_k \Omega_k D_k \left[\frac{1}{4\langle \sigma_z \rangle} \frac{\Omega_k^2 D_k}{E^2 - \Omega_k^2} + \frac{\langle \sigma_x Q_k \rangle}{\langle -\sigma_z \rangle} \right] \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E
$$

$$(43)$$

whence we finally arrive at

$$
\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E = \frac{\Delta \langle -\sigma_z \rangle}{\Omega_s} \frac{\Omega_s}{2\pi} \left[E^2 - \Omega_s^2 - \sum_k \frac{\Omega_k \Omega_s V_k^2}{E^2 - \Omega_k^2} \right]^{-1} \tag{44}
$$

with abbreviations

$$
\Omega_s^2 = \Delta^2 + \Delta \sum_k \Omega_k D_k \frac{\langle \sigma_x Q_k \rangle}{\langle \sigma_z \rangle}, \qquad V_k^2 = \frac{\Delta \Omega_k^2 D_k^2}{4\Omega_s \langle -\sigma_z \rangle} \tag{45}
$$

In passing we mention another way of arriving at (44)–(45). Combining the equations of motion for the GFs $\langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E$, $\langle\!\langle \sigma_y | \sigma_x \rangle\!\rangle_E$, $\langle\!\langle \sigma_z Q_k | \sigma_x \rangle\!\rangle_E$, etc., one gets

$$
(E^2 - \Delta^2) \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E
$$

$$
= -\frac{\Delta}{2\pi} \langle \sigma_z \rangle + \frac{\Delta^2}{E^2 - \Delta^2} \left\{ \sum_{k,k'} \Omega_k D_k \Omega_{k'} D_{k'} \langle\!\langle \sigma_z Q_k | \sigma_z Q_{k'} \rangle\!\rangle_E \right.
$$

$$
\left. - \frac{1}{2\pi} \sum_k \Omega_k D_k \langle \sigma_x Q_k \rangle \right\} \tag{46}
$$

which is still an exact relation. An antiresonant ansatz for $\{\cdots\}$ finally leads to (44)–(45).

Finally, it is instructive to glance at the GF procedure used by Zwerger[21] for the dissipative dynamics of the Hamiltonian (1). In that paper the second step of the GF hierarchy is chosen in an alternative manner to our Eq. (33),

$$
E \langle\!\langle \sigma_y | \sigma_x \rangle\!\rangle_E = -\frac{i}{2\pi} \langle \sigma_z \rangle + i\Delta \langle\!\langle \sigma_y | \sigma_y \rangle\!\rangle_E \tag{47}
$$

and the hierarchy is terminated at this step. The unknown GF $\langle\!\langle \sigma_y | \sigma_y \rangle\!\rangle$ then is transcribed via a displacive unitary transformation and factorized in an appropriate way. For details we refer to the original paper. In the end the lowest sum rule is employed as a self-consistency requirement, whereas

higher sum rules are not considered. In our calculation the GF hierarchy is terminated after the fourth step; two sum rules are used as self-consistency requirements and the two further sum rules are satisfied automatically (see Section 7).

6. EXACTLY SOLVABLE SISTER PROBLEM (OSCILLATOR–BATH)

For computational economy it is highly advantageous at this stage to glance at the sister problem to our spin–bath setup, which is the oscillator–bath problem characterized by the Hamiltonian

$$H_{\text{ob}} = \tfrac{1}{2}\Omega_s(P_s^2 + Q_s^2) + \tfrac{1}{2}\sum_k \Omega_k(P_k^2 + Q_k^2) + Q_s\sum_k V_k Q_k \qquad (48)$$

The decay problem $\langle Q_s(0) Q_s(t)\rangle$ pertinent to this Hamiltonian is one of the very few exactly solvable models in statistical physics and has been handled by Ullersma[22] and Louisell and Walker[23] and more recently Wagner.[24] The GF $\langle\!\langle Q_s | Q_s\rangle\!\rangle_E$ reads

$$\langle\!\langle Q_s | Q_s\rangle\!\rangle_E = \frac{\Omega_s}{2\pi}\left[E^2 - \Omega_s^2 - \sum_k \frac{\Omega_k \Omega_s V_k^2}{E^2 - \Omega_k^2}\right]^{-1} \qquad (49)$$

and thus is seen to be just of the form found for $\langle\!\langle \sigma_x | \sigma_x\rangle\!\rangle_E$ [see Eq. (44)]

$$\langle\!\langle \sigma_x | \sigma_x\rangle\!\rangle_E = \frac{\Delta\langle -\sigma_z\rangle}{\Omega_s}\langle\!\langle Q_s | Q_s\rangle\!\rangle_E \qquad (50)$$

if we use the identification (45). In this manner our factorization has traced back the tunneling problem to the exactly solvable oscillator–bath problem. We have to keep in mind, however, that the effective quantities Ω_s and V_k [see (45)] now are temperature dependent.

In our context the great efficacy of returning to the oscillator–bath problem lies in the fact that the odd sum rules for $I_{Q_sQ_s}(\omega)$ are of a particularly simple nature. Generally we have

$$M_{Q_sQ_s}^{(2n+1)} = \Omega_s \int_0^{\Omega_D} S(\Omega)\cdot(-1)\cdot\Omega^{2n+1}\,d\Omega \qquad (51)$$

$$M_{Q_sQ_s}^{(2n)} = \Omega_s \int_0^{\Omega_D} S(\Omega)\coth\left(\frac{\beta\Omega}{2}\right)\Omega^{2n}\,d\Omega \qquad (52)$$

where

$$S(\Omega) = \frac{1}{\pi} \frac{\Gamma(\Omega)}{[\Omega^2 - \Omega_s^2 - \Pi(\Omega)]^2 + \Gamma^2(\Omega)} \tag{53}$$

$$\Gamma(\Omega) = \frac{\pi}{2} \Omega_s V^2(\Omega) \rho(\Omega), \qquad \Pi(\Omega) = \frac{2}{\pi} P \int_0^{\Omega_D} \frac{\Omega' \Gamma(\Omega')}{\Omega^2 - \Omega'^2} d\Omega' \tag{54}$$

Here we have replaced $\sum_k \cdots$ by an integral, where $\rho(\omega)$ is the frequency density of the bath. Specifically, this yields

$$M^{(1)}_{Q_s Q_s} = -\frac{\Omega_s}{2} \tag{55a}$$

$$M^{(3)}_{Q_s Q_s} = -\frac{\Omega_s^3}{2} \tag{55b}$$

$$M^{(5)}_{Q_s Q_s} = -\frac{\Omega_s}{2} \left[\Omega_s^4 + \sum_k V_k^4 \right] \tag{55c}$$

We will employ these relations to evaluate the sum rules of the spectral function $I_{\sigma_x \sigma_x}$ belonging to the tunneling problem. From Eq. (50) we have

$$M^{(n)}_{\sigma_x \sigma_x} = \frac{\Delta \langle -\sigma_z \rangle}{\Omega_s} M^{(n)}_{Q_s Q_s} \tag{56}$$

7. RIGOROUS COUNTERCHECKS AND SELF-CONSISTENCY PROCEDURE

Our extended factorization prescription [Eq. (42)] has the virtue of not involving free parameters. But it involves the thermal expectation values $\langle \sigma_z \rangle$ and $\langle \sigma_x Q_k \rangle$, which have to be determined in a self-consistent way. We achieve this aim by considering the exact sum rules of the spectral function $I_{\sigma_x \sigma_x}(\omega)$, which we calculate by way of Eq. (37). We find

$$M^{(0)}_{\sigma_x \sigma_x} = \frac{1}{4} \tag{57a}$$

$$M^{(1)}_{\sigma_x \sigma_x} = \frac{\Delta}{2} \langle \sigma_z \rangle \tag{57b}$$

$$M^{(2)}_{\sigma_x \sigma_x} = \frac{\Delta^2}{4} \tag{57c}$$

$$M^{(3)}_{\sigma_x \sigma_x} = \frac{\Delta}{2} \left(\Delta^2 \langle \sigma_z \rangle + \Delta \sum_k \Omega_k D_k \langle \sigma_x Q_k \rangle \right) \tag{57d}$$

$$M^{(4)}_{\sigma_x \sigma_x} = \frac{\Delta^2}{4} \left(\Delta^2 + \sum_{k,k'} D_k D_{k'} \Omega_k \Omega_{k'} \langle Q_k Q_{k'} \rangle \right) \tag{57e}$$

This sequence of moments constitutes another rigorous frame for checking our approximate spectral function $I_{\sigma_x\sigma_x}$, the moments of which we may calculate from Eqs. (56). Using the definition (45) of Ω_s and Eqs. (55a) and (55b), we make the remarkable observation that the first and third moments [see Eqs. (57b) and (57d)] of our approximate spectral function *automatically display their exact values*. This offers us the possibility to employ the zeroth and second sum rules as self-consistency conditions to determine the unknown expectation values $\langle\sigma_z\rangle$ and $\sum_k\Omega_kD_k\langle\sigma_xQ_x\rangle$. From Eqs. (57a), (57c), (56), and (52) we arrive at

$$\Delta\langle-\sigma_z\rangle\int_0^{\Omega_D}S(\Omega)\coth\left(\frac{\beta\Omega}{2}\right)d\Omega=\frac{1}{4}\tag{58}$$

$$\Delta\langle-\sigma_z\rangle\int_0^{\Omega_D}S(\Omega)\,\Omega^2\coth\left(\frac{\beta\Omega}{2}\right)d\Omega=\frac{\Delta^2}{4}\tag{59}$$

Since

$$\sum_k\Omega_kD_k\langle\sigma_xQ_k\rangle_T^H\to\frac{-\alpha\Omega_D}{m}\qquad\text{for}\quad\Delta\to0$$

[see Eq. (4)], it proves useful to introduce a quantity B by means of the definition

$$\sum_k\Omega_kD_k\langle\sigma_xQ_k\rangle_T^H=-\frac{\alpha\Omega_D}{m}(1-B)\tag{60}$$

The self-consistently determined B turns out to be a small quantity ($B\ll1$) for all cases of practical interest. We now consider again the power law coupling setups of Eq. (3) and further introduce the abbreviations

$$x_s=\frac{\Delta}{\Omega_D},\qquad x=\frac{\Omega}{\Omega_D},\qquad\xi=\frac{\alpha}{\langle-\sigma_z\rangle}\tag{61}$$

Then the self-consistency equations for $\langle-\sigma_z\rangle$ and B read ($m=1$ or 3)

$$\langle-\sigma_z\rangle\int_0^1\xi x_s^2x^m\coth\left(\frac{\beta\Omega_D}{2}x\right)$$

$$\left\{\left[x^2\left(1+x_s\xi\frac{m-1}{2}\right)-x_s^2\left(1-\frac{B\xi}{mx_s}\right)\right.\right.$$

$$\left.\left.-\frac{x_s\xi}{2}x^m\ln\left|\frac{1+x}{1-x}\right|\right]^2+\left[\frac{\pi}{2}x_s\xi x^m\right]^2\right\}^{-1}dx=\frac{1}{2}\tag{62}$$

$$\langle -\sigma_z \rangle \int_0^1 \xi x^{m+2} \coth\left(\frac{\beta \Omega_D}{2} x\right)$$

$$\left\{ \left[x^2 \left(1 + x_s \xi \frac{m-1}{2}\right) - x_s^2 \left(1 - \frac{B\xi}{mx_s}\right) \right. \right.$$

$$\left. \left. - \frac{x_s \xi}{2} x^m \ln\left|\frac{1+x}{1-x}\right| \right]^2 + \left[\frac{\pi}{2} x_s \xi x^m\right]^2 \right\}^{-1} dx = \frac{1}{2} \qquad (63)$$

So for any given values of the coupling strength α and of the temperature the corresponding values of $\langle -\sigma_z \rangle$ and B can be calculated numerically. The result for $\langle -\sigma_z \rangle$ is illustrated in Fig. 1 for $m=1$ (Ohmic dissipation). For other powers ($m=2$, $m=3$) the qualitative behavior is similar.

Beyond the virtue that our spectral function $I_{\sigma_x \sigma_x}$ satisfies the lowest *four sum rules*, we have the additional option of checking the self-consistency requirements themselves by exact Goldberger–Adams expansions. Since both for the self-consistency requirements (58) and (59) as well as for the GA results (15) and (16) it is not feasible to write down general analytic expressions, we confine ourselves to deriving simplified expressions for three different temperature regions. For very high temperatures ($k_B T \gg \Omega_D$) the self-consistency equations (62) and (63) yield

$$\langle \sigma_z \rangle = -\frac{1}{2} \tanh\left(\frac{\beta \Delta}{2}\right) + \frac{\alpha \beta^2 \Delta \Omega_D}{12m} + O(\alpha^2) \qquad \text{for} \quad m = 1, 3 \qquad (64)$$

$$\sum_k D_k \Omega_k \langle \sigma_x Q_k \rangle = -\frac{\alpha \Omega_D}{m}\left(1 - \frac{(\beta \Delta)^2}{12}\right) + O(\alpha^2) \qquad \text{for} \quad m = 1, 3 \qquad (65)$$
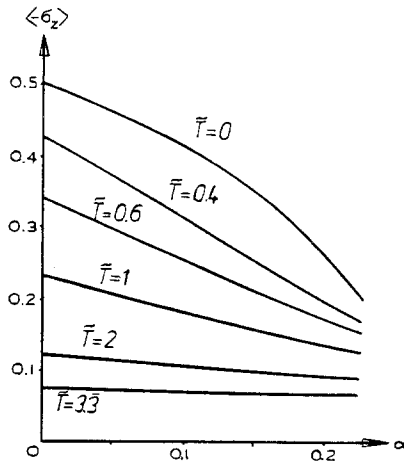

Fig. 1.   Plot of $\langle -\sigma_z \rangle$ as a function of temperature and coupling strength for $m=1$ ("Ohmic dissipation"), $\tilde{T} = k_B T/\Delta$, and $x_s = \Delta/\Omega_D = 0.1$.

For very low temperatures ($k_B T \ll \Delta$) we have

$$\langle \sigma_z \rangle =$$

$$\begin{cases} -\dfrac{1}{2}\left\{1-\alpha\left[\left(\ln\dfrac{1}{x_s}-1+2x_s\right)+\dfrac{(k_B T)^2}{\Delta^2}\dfrac{\pi^2}{3}\right]\right\}+O(\alpha^2) & \text{for } m=1 \\ & \qquad\qquad (66a) \\ -\dfrac{1}{2}\left\{1-\alpha\left[\left(\dfrac{1}{2}-2x_s+3x_s^2\ln\dfrac{1}{x_s}\right)+\dfrac{(k_B T)^4}{\Delta^2\Omega_D^2}\dfrac{2\pi^4}{15}\right]\right\}+O(\alpha^2) & \text{for } m=3 \\ & \qquad\qquad (66b) \end{cases}$$

$$\sum_k D_k \Omega_k \langle \sigma_x Q_k \rangle$$

$$= -\dfrac{\alpha\Omega_D}{m}\begin{cases}\left[\left(1-x_s\ln\dfrac{1}{x_s}-x_s^2\right)+\dfrac{(k_B T)^2}{\Delta\Omega_D}\dfrac{\pi^2}{3}+O(\alpha)\right] & \text{for } m=1 \\ & \qquad (67a) \\ \left[\left(1-\dfrac{3}{2}x_s+3x_s^2\right)+\dfrac{(k_B T)^4}{\Delta\Omega_D^3}\dfrac{2\pi^4}{5}+O(\alpha)\right] & \text{for } m=3 \\ & \qquad (67b)\end{cases}$$

Finally, in the intermediate temperature regime ($\Delta \ll k_B T \ll \Omega_D$) we obtain

$$\langle \sigma_z \rangle = \begin{cases} -\dfrac{\beta\Delta}{4}\left[1-2\alpha\left(\ln\dfrac{\beta\Omega_D}{2}+\dfrac{2}{\beta\Omega_D}-\dfrac{2}{3}\right)\right]+O(\alpha^2) & \text{for } m=1 \\ & \qquad (68a) \\ -\dfrac{\beta\Delta}{4}\left[1-2\alpha\left(\dfrac{1}{2}-\dfrac{2}{\beta\Omega_D}\right)\right]+O(\alpha^2) & \text{for } m=3 \\ & \qquad (68b)\end{cases}$$

$$\sum_k D_k \Omega_k \langle \sigma_x Q_k \rangle$$

$$= -\dfrac{\alpha\Omega_D}{m}\begin{cases}\left[1-\dfrac{x_s(\beta\Delta)}{2}\left(\ln\dfrac{\beta\Omega_D}{2}-\dfrac{2}{3}+\dfrac{2}{\beta\Omega_D}\right)+O(\alpha)\right] & \text{for } m=1 \\ & \qquad (69a) \\ \left[1-\dfrac{3x_s(\beta\Delta)}{4}\left(1-\dfrac{4}{\beta\Omega_D}+\dfrac{80}{9}\dfrac{1}{(\beta\Omega_D)^2}\right)+O(\alpha)\right] & \text{for } m=3 \\ & \qquad (69b)\end{cases}$$

All these expressions coincide with those found from the GA equations (15) and (16) up the leading coupling term.

8. THERMODYNAMIC PROPERTIES DERIVED FROM GREEN FUNCTIONS

We now come back to the calculation of the thermodynamic potential $U = \langle H \rangle_T^H$ (see Section 4). Using relations (20), (18), and (31), we find

$$U = \langle H \rangle$$

$$= \Delta \langle \sigma_z \rangle + \sum_k D_k \Omega_k \langle \sigma_x \Omega_k \rangle$$

$$+ \frac{1}{2} \sum_k \Omega_k \int_{-\infty}^{+\infty} \left[I_{p_k p_k}(\omega) + I_{Q_k Q_k}(\omega) \right] d\omega$$

$$= \Delta \langle \sigma_z \rangle + \sum_k D_k \Omega_k \langle \sigma_x Q_k \rangle + \frac{1}{2} \sum_k \Omega_k \coth \left(\frac{\beta \Omega_k}{2} \right)$$

$$+ \int_{-\infty}^{+\infty} \left[\sum_k \frac{D_k^2 \Omega_k^3}{4} \left(\frac{1}{(E - \Omega_k)^2} + \frac{1}{(E + \Omega_k)^2} \right) \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \bigg|_{E = \omega + i\varepsilon} \right.$$

$$\left. - \sum_k \frac{D_k^2 \Omega_k^3}{4} \left(\frac{1}{(E - \Omega_k)^2} + \frac{1}{(E + \Omega_k)^2} \right) \langle\!\langle \sigma_x | \sigma_x \rangle\!\rangle_E \bigg|_{E = \omega - i\varepsilon} \right] \frac{i \, d\omega}{e^{\beta\omega} - 1}$$

$$\tag{70}$$

The last term in Eq. (70) is handled in Appendix A. Using the result (A2), we are finally left with

$$U = 2\Delta \langle \sigma_z \rangle + U_{\text{bath}} - \frac{\alpha \Omega_D}{2m} (1 - B)$$

$$+ \langle \sigma_z \rangle^2 \Omega_D \left(\coth \frac{\beta \Omega_D}{2} + \frac{2}{\beta \Omega_D} - \frac{2}{\pi} \right.$$

$$\times \int_0^1 \arctan \left[\frac{x^2 (1 \mp \xi x_s) - x_s (x_s - B\xi/m)}{x_s \xi \pi x^m / 2} \right]$$

$$\left. \times \left[\coth \left(\frac{\beta \Omega_D x}{2} \right) - \frac{\beta \Omega_D x/2}{\sinh^2 (\beta \Omega_D x/2)} \right] dx \right) \tag{71}$$

where

$$U_{\text{bath}} = \sum_k \frac{\Omega_k}{2} \coth \left(\frac{\beta \Omega_k}{2} \right) \tag{72}$$

and where in the integrand the minus sign has to be taken for $m = 1$ and the plus sign for $m = 2, 3$.

Equation (71) allows us to calculate $U_e \equiv U - U_{\text{bath}} - \alpha \Omega_D / 2m$ and the specific heat $C_e = \partial U_e / \partial T = C - C_{\text{bath}}$ numerically for any given values of temperature and of the coupling strength α, since $\langle \sigma_z \rangle_T^H$ and B can be obtained by self-consistency. The results for U_e and C_e are illustrated in Figs. 2–4 for $m = 1, 2, 3$. We recognize that the typical peak characterizing
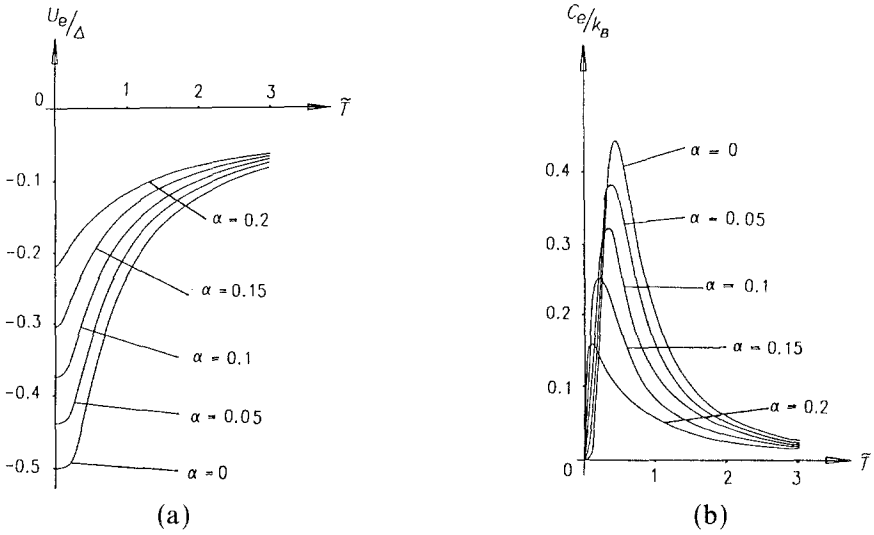
Fig. 2. (a) Excess internal energy $U_e = U - U_{\text{bath}} - \alpha\Omega_D/2m$ and (b) specific heat C_e $(= C - C_{\text{bath}})$ of tunneling centers for different coupling strengths α $(m = 1, \ x_s = \Delta/\Omega_D = 0.1, \ \tilde{T} = k_B T/\Delta)$.
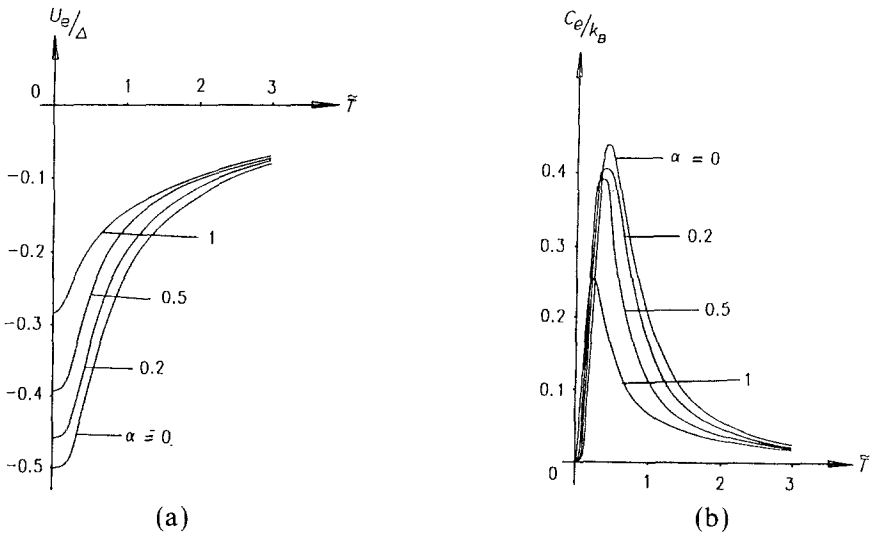

Fig. 3. (a) Excess internal energy $U_e = U - U_{\text{bath}} - \alpha\Omega_D/2m$ and (b) specific heat C_e $(= C - C_{\text{bath}})$ of tunneling centers for different coupling strengths α $(m = 3, \ x_s = \Delta/\Omega_D = 0.1, \ \tilde{T} = k_B T/\Delta)$.
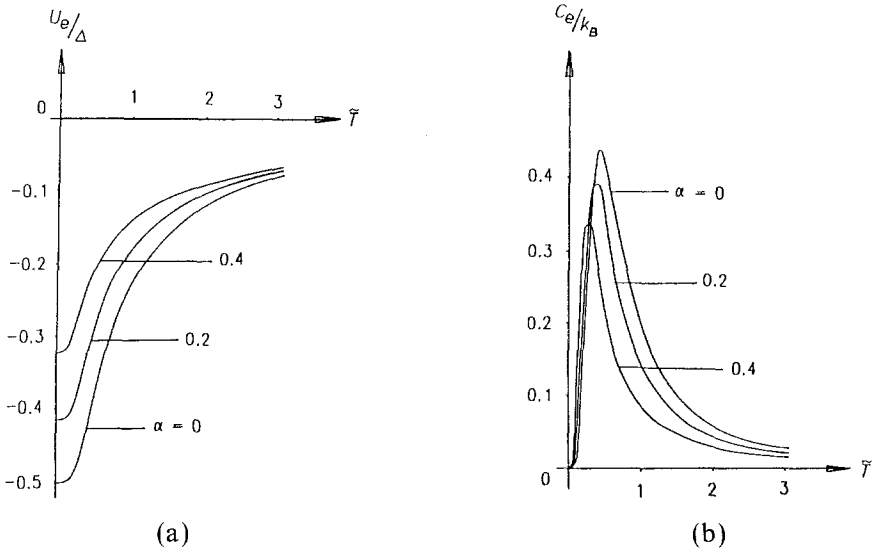
Fig. 4. (a) Excess internal energy $U_e = U - U_{\text{bath}} - \alpha\Omega_D/2m$ and (b) specific heat C_e ($= C - C_{\text{bath}}$) of tunneling centers for different coupling strengths α ($m = 2$, $x_s = \Delta/\Omega_D = 0.1$, $\tilde{T} = k_B T/\Delta$).

the specific heat of the pure spin system is diminished by the coupling and that the peak position is shifted to lower temperature.

It is desirable to obtain also some simple analytic forms of the results in Figs. 2–4. This can be achieved only for the selected temperature regions considered earlier, and for small values of α. The results then are obtained by a lengthy but elementary series expansion analysis of the arctan integral in (71). We refrain from giving the details of this straightforward calculation. We use the abbreviations C_{bath} and C_{spin} describing the specific heat of the pure oscillatory and spin subsystems,

$$C_{\text{bath}} = \frac{\partial}{\partial T} U_{\text{bath}} = k_B \sum_k \left(\frac{\beta\Omega_k}{2}\right)^2 \frac{1}{\sinh^2(\beta\Omega_k/2)} \tag{73}$$

$$C_{\text{spin}} = \frac{\partial}{\partial T} U_{\text{spin}} = k_B \left(\frac{\beta\Delta}{2}\right)^2 \frac{1}{\cosh^2(\beta\Delta_k/2)} \tag{74}$$

Then for very high temperatures ($k_B T \gg \Omega_D$) we get

$$C = C_{\text{bath}} + k_B \left(\frac{\beta\Delta}{2}\right)^2 \left(1 - \frac{\alpha\beta\Omega_D}{m}\right) + O(\beta^4\Delta^4 k_B) \qquad \text{for} \quad m = 1, 2, 3 \tag{75}$$

For very low temperatures $(k_B T \ll \Delta)$ we have

$$C = C_{\text{bath}} + C_{\text{spin}} + \alpha m(m+1)(m!)\, \zeta(m+1)\, \frac{(k_B T)^m}{\Omega_D^{m-1}\Delta} \quad \text{for } m = 1, 2, 3 \quad (76)$$

where the zeta function $\zeta(m+1)$ can be simplified to [compare Eqs. (66a) and (66b)]

$$\zeta(m+1) = \begin{cases} \pi^2/6 & \text{for} \quad m = 1 \\ \pi^4/90 & \text{for} \quad m = 3 \end{cases} \quad (77)$$

In the intermediate temperature regime $\Delta \ll k_B T \ll \Omega_D$ we are left with

$$C = C_{\text{bath}} + k_B \left(\frac{\beta\Delta}{2}\right)^2 \begin{cases} \left(\dfrac{\beta\Omega_D}{2}\right)^{-2\alpha}(1-\alpha)\,e^{-9\alpha/10} & \text{for} \quad m = 1 \quad (78a) \\[3mm] \left(e^{-2\alpha} + \dfrac{2\alpha}{\beta\Omega_D}\right) & \text{for} \quad m = 2 \quad (78b) \\[3mm] e^{-\alpha} & \text{for} \quad m = 3 \quad (78c) \end{cases}$$

Comparing the expansions (76), (75), and (78) with the corresponding ones derived from the Goldberger–Adams result (14), it is very satisfactory to note that for each temperature region there is a complete coincidence up to the leading coupling term inclusive.

9. SUMMARY AND REMARKS

In this study we have investigated the thermodynamic aspects of a Hamiltonian which during the past 30 years has been taken as the archetype Hamiltonian for mode-assisted tunneling processes ("soft tunneling"). The main purpose of our investigation has been twofold. On one hand we sought to derive an exact and explicit representation of the thermodynamic potentials in terms of the specific Green function which also governs the tunneling evolution. This has been fully achieved by means of a Zubarev Green function technique. On the other hand, our aim has been to establish in an alternative way exact and explicit series expansions for the thermodynamic behavior, which can be exploited to check the Green function result. This has been achieved by an appropriate application of the Goldberger–Adams theorem, by means of which we were able to give series expansions in the whole temperature range.

By a factorization beyond the HF procedure we have derived an approximate spectral function $I_{\sigma_x\sigma_x}$ of the tunneling problem, which can be traced back to an effective oscillator–bath problem with temperature-

dependent intrinsic parameters. Our factorization procedure constitutes a considerable improvement beyond the generally used Hartree–Fock factorization, since it displays the flexibility to satisfy sum rules. It may be extended by adding further basic Green functions such that step by step higher sum rules could be reproduced. The version used in this paper already establishes a serious alteration of the qualitative features found within the HF scheme. We also note that our factorization procedure does not invoke adjustable parameters, but the weight of the single GF contributions is determined by consistency requirements, which themselves are based on sum rules. The spectral function $I_{\sigma_x \sigma_x}$ found in this manner automatically conserves two of the lower sum rules by its analytical form, and materializes two others by self-consistency requirements, whence in total the four lowest sum rules are correctly given in the whole temperature range. Further, our spectral function also matches the thermodynamics up to the dominant coupling term inclusive in the whole temperature range, as shown by comparison with the exact Goldberger–Adams calculation.

In the intermediate temperature range $\Delta \ll k_B T \ll \Omega_D$ the excess specific heat C_e follows a $T^{-2+2\alpha}$ law in the case of Ohmic dissipation, whereas for $m = 3$ the T^{-2} law of the uncoupled tunneling system is preserved, the only effect of the coupling being a reduction factor depending on α. In the very low temperature region we get a T^m law ($m = 1, 2, 3$) for C_e. Having a view of the whole temperature range, we notice that the coupling to the surrounding bath modifies the thermodynamic properties of a two-level system quite considerably; it suppresses the typical peak of the specific heat and obviously shifts its position to lower temperatures.

With regard to the glass problem, the most interesting result is the T^m law of the excessive specific heat C_e at low temperatures. In metallic material it is believed[12] that in the low-frequency regime the role of the phonons is less important than that of electronic excitations across the Fermi level. These excitations theoretically also may be described as oscillatory ones, which is a standard assumption in quantum diffusion.[12] If this is done, a coupling law with $m = 1$ would be effective. Then one arrives at a first power law for C_e already for the single symmetric tunneling center of our study. Whether this suffices to explain quantitatively the behavior of metallic glasses must be left to future work.

For nonmetallic material many different types of coupling laws have been proposed in the context of tunneling centers. Most often the $m = 3$ law has been chosen.[7, 8] We should keep in mind, however, that the power very sensibly depends on the assumption of how the tunneling system is built into the lattice. If one ascribes the peculiar C_e behavior of nonmetallic glasses to the interaction of tunneling systems with phonons, the required power law $m = 1$ would supply a useful hint to the nature of the tunneling

objects, which presently still are not known; e.g., one could think of objects having a finite linear extension instead of point centers. However, this remark is of a very speculative nature and careful analysis remains to be done. In the present stage it cannot be decided whether the observed T behavior of thermodynamic properties is predominately due to a distribution of bare asymmetric tunneling centers or to (possibly not pointlike) tunneling systems coupled to phonons with a specific coupling law $m = 1$. Further progress can only be made if realistic models for such a coupling are established. It would seem appropriate to treat this question before studying the interaction of tunneling centers mediated by phonons.

APPENDIX A. THERMAL EXPECTATION VALUE OF THE
$$\text{GF} \sum_k \tfrac{1}{4} D_k^2 \Omega_k^3 [(E - \Omega_k)^{-2} + (E + \Omega_k)^{-2}] \langle\langle \sigma_x | \sigma_x \rangle\rangle_E$$

Using (44), (45), and (54), we can rewrite the GF:

$$\sum_k \frac{D_k^2 \Omega_k^3}{4} \left(\frac{1}{(E-\Omega_k)^2} + \frac{1}{(E+\Omega_k)^2} \right) \langle\langle \sigma_x | \sigma_x \rangle\rangle_E \bigg|_{E = \omega \pm i\varepsilon}$$

$$= \left[\sum_k \frac{\langle -\sigma_z \rangle}{\Delta} \Omega_s \Omega_k V_k^2 \left(-\frac{\partial}{\partial E} \right) \left(\frac{1}{E-\Omega_k} + \frac{1}{E+\Omega_k} \right) \right] \frac{\Delta \langle -\sigma_z \rangle}{2\pi}$$

$$\times \left(E^2 - \Omega_s^2 - \sum_k \frac{\Omega_k \Omega_s V_k^2}{E^2 - \Omega_k^2} \right)^{-1} \bigg|_{E = \omega \pm i\varepsilon}$$

$$= \left\{ -\frac{\partial}{\partial \omega} \frac{2 \langle -\sigma_z \rangle}{\Delta} \omega [\Pi(\omega) \mp i\Gamma(\omega)] \right\} \frac{\Delta \langle -\sigma_z \rangle}{2\pi}$$

$$\times \frac{[\omega^2 - \Omega_s^2 - \Pi(\omega)] \mp i\Gamma(\omega)}{[\omega^2 - \Omega_s^2 - \Pi(\omega)]^2 + \Gamma^2(\omega)} \tag{A1}$$

A straightforward calculation then yields

$$\int_{-\infty}^{+\infty} \frac{i \, d\omega}{e^{\beta\omega} - 1} \left[\sum_k \frac{D_k^2 \Omega_k^3}{4} \left(\frac{1}{(E-\Omega_k)^2} + \frac{1}{(E+\Omega_k)^2} \right) \langle\langle \sigma_x | \sigma_x \rangle\rangle_E \bigg|_{E = \omega + i\varepsilon} \right.$$

$$\left. - \sum_k \frac{D_k^2 \Omega_k^3}{4} \left(\frac{1}{(E-\Omega_k)^2} + \frac{1}{(E+\Omega_k)^2} \right) \langle\langle \sigma_x | \sigma_x \rangle\rangle_E \bigg|_{E = \omega - i\varepsilon} \right]$$

$$= -\frac{4 \langle -\sigma_z \rangle}{\Delta} \frac{\Delta \langle -\sigma_z \rangle}{2\pi}$$

$$\times \int_{-\infty}^{+\infty} \frac{[(\partial/\partial\omega)\omega\Pi(\omega)] \, \Gamma(\omega) + [(\partial/\partial\omega) \, \omega\Gamma(\omega)][\omega^2 - \Omega_s^2 - \Pi(\omega)]}{[\omega^2 - \Omega_s^2 - \Pi(\omega)]^2 + \Gamma^2(\omega)}$$

$$\times \frac{1}{e^{\beta\omega} - 1} \, d\omega$$

$$
= \frac{2\langle -\sigma_z \rangle}{\Delta} \int_{-\infty}^{+\infty} I_{\sigma_x \sigma_x}(\omega)(\Omega_s^2 - 3\omega^2)\, d\omega
$$

$$
+ \frac{2}{\pi} \langle -\sigma_z \rangle^2 \int_0^\infty \left(\omega \coth \frac{\beta\omega}{2} \right) \left(\frac{d}{d\omega} \arctan \left[\frac{\omega^2 - \Omega_s^2 - \Pi(\omega)}{\Gamma(\omega)} \right] \right) d\omega
$$

$$
= \frac{2\langle -\sigma_z \rangle}{\Delta} \frac{1}{4} (\Omega_s^2 - 3\Delta^2) + \frac{2}{\pi} \langle -\sigma_z \rangle^2 \left[\left(\frac{\pi}{2} \Omega_D \coth \frac{\beta\Omega_D}{2} + \frac{\pi}{2} \frac{2}{\beta} \right) \right.
$$

$$
\left. - \int_0^{\Omega_D} \arctan \left[\frac{\omega^2(1 \mp \xi x_s) - \Omega_s^2 + \Delta\Omega_D \xi/m}{\Delta \xi \Omega_D \pi (\omega/\Omega_D)^m/2} \right] \left[\frac{d}{d\omega} \left(\omega \coth \frac{\beta\omega}{2} \right) \right] d\omega \right]
$$

$$
\tag{A2}
$$

where Eqs. (57a)–(57c) and the expansion $\ln[(1+x)/(1-x)] \approx 2x$ for small x have been used. In the integrand the minus sign has to be taken for $m = 1$ and the plus sign for $m = 2, 3$.

APPENDIX B. OSCILLATOR–BATH PROBLEM

We apply the Green function problem described in Section 4 to evaluate the thermodynamics of the oscillator–bath problem with Hamiltonian (48). The formulas corresponding to (24), (27), (29), and (30) are

$$
\langle\!\langle Q_k | Q_s \rangle\!\rangle_E = \frac{\Omega_k V_k}{E^2 - \Omega_k^2} \langle\!\langle Q_s | Q_s \rangle\!\rangle_E \tag{B1a}
$$

$$
\langle\!\langle Q_k | Q_k \rangle\!\rangle_E = \frac{\Omega_k}{2\pi(E^2 - \Omega_k^2)} + \frac{\Omega_k^2 V_k^2}{(E^2 - \Omega_k^2)^2} \langle\!\langle Q_s | Q_s \rangle\!\rangle_E \tag{B1b}
$$

$$
\langle\!\langle P_k | P_k \rangle\!\rangle_E = \frac{\Omega_k}{2\pi(E^2 - \Omega_k^2)} + \frac{E^2 V_k^2}{(E^2 - \Omega_k^2)^2} \langle\!\langle Q_s | Q_s \rangle\!\rangle_E \tag{B1c}
$$

$$
\langle\!\langle P_s | P_s \rangle\!\rangle_E = -\frac{1}{2\pi\Omega_s} + \frac{E^2}{\Omega_s^2} \langle\!\langle Q_s | Q_s \rangle\!\rangle_E \tag{B1d}
$$

and the fundamental GF $\langle\!\langle Q_s | Q_s \rangle\!\rangle_E$ is given by Eq. (49).

Note that (49) is an exact result: in contrast to the tunneling problem, there is no need for factorization. The internal energy is then given as

$$
U = \langle H \rangle = \frac{1}{2} \Omega_s (\langle P_s^2 \rangle + \langle Q_s^2 \rangle) + \tfrac{1}{2} \sum_k \Omega_k (\langle P_k^2 \rangle + \langle Q_k^2 \rangle) + \sum_k V_k \langle Q_k Q_s \rangle
$$

$$
\tag{B2}
$$

where [see Eq. (52)]

$$\frac{1}{2}\Omega_s(\langle P_s^2\rangle + \langle Q_s^2\rangle) = \int_{-\infty}^{+\infty} \frac{1}{2\Omega_s}(\omega^2 + \Omega_s^2)\, I_{Q_sQ_s}(\omega)\, d\omega$$

$$= \frac{1}{2}\int_0^{\Omega_D}(\omega^2 + \Omega_s^2)\, S(\omega)\coth\left(\frac{\beta\omega}{2}\right) d\omega \qquad \text{(B3)}$$

$$\sum_k V_k\langle Q_k Q_s\rangle = \int_{-\infty}^{+\infty} \frac{i}{e^{\beta\omega}-1}\left(\frac{1}{2\Omega_s}\right)\left[\sum_k \frac{\Omega_k\Omega_s V_k^2}{E^2 - \Omega_k^2}\langle\!\langle Q_s | Q_s\rangle\!\rangle_E\Big|_{E=\omega+i\varepsilon}\right.$$

$$\left.- \sum_k \frac{\Omega_k\Omega_s V_k^2}{E^2 - \Omega_k^2}\langle\!\langle Q_s | Q_s\rangle\!\rangle_E\Big|_{E=\omega-i\varepsilon}\right]$$

$$= \int_0^{\Omega_D}(\omega^2 - \Omega_s^2)\, S(\omega)\coth\frac{\beta\omega}{2}\, d\omega \qquad \text{(B4)}$$

In a similar manner as in Appendix A, we can calculate the bath part in (B2):

$$\frac{1}{2}\sum_k \Omega_k(\langle P_k^2\rangle + \langle Q_k^2\rangle)$$

$$= \sum_k \frac{\Omega_k}{2}\coth\frac{\beta\Omega_k}{2} - \frac{1}{2}\int_0^{\Omega_D} S(\omega)\coth\frac{\beta\omega}{2}(3\omega^2 - \Omega_s^2)\, d\omega$$

$$+ \frac{1}{2\pi}\int_0^{\Omega_D} \omega\coth\frac{\beta\omega}{2}\left(\frac{d}{d\omega}\arctan\left[\frac{\omega^2 - \Omega_s^2 - \mathbb{T}(\omega)}{\Gamma(\omega)}\right]\right) d\omega \qquad \text{(B5)}$$

Collecting the results (B2)–(B5), we are left with

$$U = \underbrace{\sum_k \frac{\Omega_k}{2}\coth\left(\frac{\beta\Omega_k}{2}\right)}_{U_{\text{bath}}} + \frac{\Omega_D}{4}\left\{\coth\frac{\beta\Omega_D}{2} + \frac{2}{\beta\Omega_D} - \frac{2}{\pi}\int_0^1\left[\frac{d}{dx}\left(x\coth\frac{\beta\Omega_D}{2}x\right)\right]\right.$$

$$\left.\times \arctan\left(\frac{x^2 - x_s^2 - 4\alpha x_s/m \mp x^2\cdot 4\alpha x_s}{(\pi/2)\, 4\alpha x_s x^m}\right) dx\right\} \qquad \text{(B6)}$$

where the minus sign has to be taken for $m = 1$ and the plus sign for $m = 2, 3$. Note that we have supposed a power law coupling of the form

$$V^2(\Omega)\, \rho(\Omega) = 4\alpha\Omega_D\left(\frac{\Omega}{\Omega_D}\right)^m \qquad \text{(B7)}$$

Expression (B6) can be rewritten as

$$U = \sum_k \frac{\Omega_k}{2} \coth \frac{\beta\Omega_k}{2} + \frac{\Omega_D}{4} \left\{ 2\tilde{x}_s \coth\left(\frac{\beta\Omega_D}{2} \tilde{x}_s \right) + 4\alpha x_s \int_0^1 \frac{x^m}{x^2 - \tilde{x}_s^2} \right.$$
$$\left. \times \left[\coth\left(\frac{\beta\Omega_D}{2} x \right) - \frac{x\beta\Omega_D/2}{\sinh^2(\beta\Omega_D x/2)} \right] dx \right\} \tag{B8}$$

where

$$\tilde{x}_s^2 = x_s \left(x_s - \frac{4\alpha}{m} \pm 4\alpha x_s^2 \right) \quad \text{with } x_s = \frac{\Omega_s}{\Omega_D} \quad (+ \text{ for } m = 1; \ - \text{ for } m = 2, 3) \tag{B9}$$

For $\alpha \to 0$ we get the result for the uncoupled system:

$$U = U_{\text{bath}} + \frac{\Omega_s}{2} \coth\left(\frac{\beta\Omega_s}{2} \right) \tag{B10}$$

In the very high temperature regime an evaluation of the coth and sinh terms yields

$$U = \sum_k \frac{\Omega_k}{2} \coth \frac{\beta\Omega_k}{2} + \frac{\Omega_s}{2} \frac{\tilde{x}_s}{x_s} \coth\left(\frac{\beta\Omega_s}{2} \frac{\tilde{x}_s}{x_s} \right) + \alpha\Omega_s \frac{\beta\Omega_D}{3} \left(\frac{1}{m} \mp \tilde{x}_s^2 \right) \tag{B11}$$

For very low temperatures $(T \to 0)$ the specific heat follows a T^m law:

$$C = C_{\text{bath}} + k_B \left(\frac{\beta\Omega_s \tilde{x}_s}{2x_s} \right)^2 \frac{1}{\sinh^2(\beta\Omega_s \tilde{x}_s/2x_s)}$$
$$+ 2k_B \frac{\alpha m(m+1)(m!) \, \zeta(m+1)}{1 - 4\alpha/mx_s \pm 4\alpha x_s} \frac{(k_B T)^m}{\Omega_s \Omega_D^{m-1}} \tag{B12}$$

NOTE ADDED IN PROOF

In the meantime another paper on the subject has appeared (R. Görlich and U. Weiss, *Phys. Rev. B* **38**:5245 (1988)), in which a different method has been employed. These results support our findings.

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