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Glasslike low-energy excitations from pairs of interacting tunneling dipoles and quadrupoles: Exact solutions

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We consider the problem of very dilute concentrations of interacting tunneling dipoles or quadrupoles (TD's or TQ's) randomly distributed in a host matrix. We assume that the TD's and TQ's can have n equivalent directions of orientation determined by the minima in the local potential. Each TD and TQ is only allowed to tunnel to its nearest-neighbor potential wells. Starting from a microscopic Hamiltonian, we use the special properties of "circulant" matrices to obtain the *exact* energy eigenvalues for the following interacting pairs: (a) TD's or TQ's with three, four, and six orientations in a plane (tunneling clock model); (b) TD's or TQ's in three dimensions with four, six, and eight orientations. For each of the cases considered, we obtain low-energy excitations from strongly interacting tunneling units. For very low concentrations and a random distribution of TD's or TQ's in the medium, we use a virial expansion of the free energy to obtain the density of states and the heat capacity. For an r^{-3} interaction our results are in good agreement with the experimentally measured heat capacities for 340 ppm of CN^- dissolved in KBr and dilute concentrations of Li^+ in KCl. We find that the experimentally observed broadening of the Schottky specific heat arises from *strongly* interacting tunneling units.

I. INTRODUCTION

Below $T \lesssim 1$ K amorphous materials and glasses[1] exhibit distinct low-temperature anomalies[2,3] known to arise from the glassy state. The anomalies[4] are the following: the specific heat $C(T)$ is quasilinear in temperature T and has a time dependent component, the thermal conductivity $\kappa(T)$ is proportional to T^2, the absorption of sound saturates with intensity, the low-temperature sound velocity has a term proportional to $\ln T$, the dielectric susceptibility shows long relaxation times in addition to a $\ln T$ term in its real part. The anomalies are very similar for most amorphous materials and are often referred to as "universal properties of glasses."

To explain these anomalies a phenomenological model was proposed[5,6] based on the assumption that glasses contain (isolated) two-level tunneling states (TLS) with a random distribution of potential barriers separating the wells and a random distribution of asymmetry energies between the wells. An *ad hoc* assumed constant density of states explained a number of experimentally observed properties of glasses, including time dependent effects, supporting the idea of the TLS. Thus the TLS model has by now become widely accepted as the standard phenomenological model for glasses. However, in spite of its success, the TLS model gave no information on (i) what is the nature of the tunneling unit, and (ii) why is the low-energy density of states a constant? A microscopic picture for the quasi-universal properties of glasses is still missing.

Glasslike properties were also observed when electric or elastic dipoles were dissolved in alkali halide crystals.[7] For example, when Li^+ is dissolved in KCl, the Li^+ goes off center and forms an eight-orientational (8-O) tunneling dipole (TD).[8] The tunneling motion is performed between the eight potential wells provided by the crystalline environment of the surrounding medium. On the other hand, OH^- dissolved in KCl forms a 6-O TD; CN^- dissolved in KCl or KBr forms an 8-O tunneling elastic dipole, denoted here as a tunneling quadrupole (TQ).[9–11] For intermediate impurity concentrations (typically of the order of 20–70%) many of the so-called mixed crystals exhibit the same universal low-temperature properties which are also characteristic for canonical glasses.[7]

In this paper we are dealing with systems of *very dilute* concentrations of interacting TD's or TQ's randomly placed in a crystalline host matrix. Instead of treating the impurities as independent defects (the case usually treated in the literature[12]), we expand the free energy arising from our model Hamiltonian in a virial expansion[13] in the impurity concentration c, keeping only terms up to c^2. In analogy with the cluster expansions in the theory of gases, the virial coefficients involve interactions among clusters of a finite number of particles.[13] Thereby we obtain corrections to the noninteracting case (the so-called Devonshire model[12]) resulting from pair interactions. In our approach we can obtain the low-temperature thermal properties of the system *without* making use of mean-field theories which are known to be problematic in quenched systems with competing and random interactions. However, our expansion method is restricted to the very dilute concentration regime in which cooperative effects, like freezing or frustration, play no important role. Still, we obtain low-energy excitations with a constant density of states. The case of intermediate to high concentrations which has attracted much attention recently is not treated in this paper.[7,14–19]

Since the concentration of TLS in canonical glasses is believed to be dilute, we feel that a calculation of the density of low-energy states for a system of dilute interacting tunneling units from fundamental considerations is of interest. To understand the low-energy excitations from very low concentrations of TD's and TQ's, one of the authors[20] has obtained the low-T properties for 2^d-O TD's ($d = 1, 2, ...$) and 4-O TQ's (Ref. 21) using a virial expansion of the free energy up to c^2, i.e., pairs. Both systems gave glasslike excitations with a constant density of states at very low T. However, to obtain the low-energy excitations of a pair of interacting n-orientational tunneling units in general, one has to solve for the eigenvalues of a pair Hamiltonian which is an $(n^2 \times n^2)$ matrix.

In recent work[22] we have used perturbation theory to obtain the low-energy excitations for dilute interacting TD's and TQ's. We found that the low-energy excitations arise from strong interactions. However, this approach was only valid for $T \ll \Delta$ (Δ is the tunneling matrix element which is of the order of 1 K). The purpose of this paper is to develop a systematic approach to solve for the low-energy excitations of an interacting pair of TD's or TQ's exactly and to extend our previous results[22] to higher temperatures. In particular we shall consider here the following symmetries: (a) pairs of n-state clock-model TD's and TQ's with three, four, and six orientations in a plane, (b) pairs of four, six, and eight orientational TD's and TQ's in three dimensions. In each case we assume that only nearest-neighbor-well tunneling is important. The derived pair-energy spectrum is then used to evaluate the second virial coefficient $F^{(2)}$ of a system of interacting TD's or TQ's exactly. A comparison of the previous perturbation approach[22] with this work is in order: (i) Within the validity of our model Hamiltonian, our results here are now applicable for all T. (ii) The exact treatment shows that the specific heat is strongly modified near the temperature where the maximum in the Schottky specific heat occurs leading to a significant broadening of the Schottky specific heat. This could not have been seen from our perturbation calculation. (iii) The higher excitations derived in this paper, which are needed to evaluate the thermal conductivity and thermal expansion (not done in this paper), could not be obtained perturbationally.

The paper is organized as follows. In Sec. II we define our model Hamiltonian for a quenched system of interacting TD's or TQ's. In the following sections, we restrict ourselves to a pair of interacting tunneling units. We show that for the considered symmetries the pair Hamiltonian can be written as a block-circulant matrix. The important properties of circulant matrices are briefly discussed in Sec. IV. We then use their special properties to block diagonalize the pair Hamiltonian and solve for the eigenvalues of the resulting n $(n \times n)$ matrices (instead of one $n^2 \times n^2$) for the above symmetries. In Sec. VI we use these eigenvalues to calculate the specific heat for a very dilute system of randomly distributed tunneling units interacting via an r^{-3} potential considering the first two terms in a virial expansion in the impurity concentration.[20,21] Our results are compared with experimental data for 70 ppm and 150 ppm of Li^+ dissolved in KCl (8-O TD) and 340 ppm of CN^- in KBr (8-O TQ) (Refs. 8 and 10). We find good agreement between these data and our calculation.

II. THE HAMILTONIAN

We consider N tunneling impurities placed at random positions $\mathbf{r}_i$ in a crystalline solid. Each impurity is assumed to have either an electric or elastic (but not both) dipole moment. The elastic moment will be denoted as a quadrupole moment. In the dilute case the possible orientations of the dipoles and quadrupoles are determined by the local potential minima in the crystalline environment around the impurity.[12,23] It was shown that electric or elastic dipoles dissolved in cubic crystals can tunnel between 6, 8, or 12 equivalent directions of orientation.[24] We assume that these directions are not changed by the dipole-dipole or quadrupole-quadrupole interaction or the dilution of the host atoms. Thus each impurity is assumed to be placed in the same crystalline environment. This approximation breaks down for higher concentrations where the dilution of the host atoms by the impurities is believed to introduce additonal static random elastic fields.[19] Furthermore, the TD's or TQ's are not treated as free rotors, but are confined to tunnel only between the different potential wells. Arrhenius type of relaxation over the potential barriers separating the wells, and excitations to higher levels within a well, will also be neglected in our model. We therefore restrict ourselves to low temperatures and dilute concentrations.

Let $\boldsymbol{\mu}^{(\alpha)}$ $(\alpha = 1, \ldots, n)$ be a unit vector at position $\mathbf{r}_i$, which can point in either one of n directions independently of site i. Let $\boldsymbol{\mu}_i$ be a vector operator at site i and $|\phi_i^{(\alpha)}\rangle$ be an eigenstate of $\boldsymbol{\mu}_i$, such that

$$\boldsymbol{\mu}_i|\phi_i^{(\alpha)}\rangle = \boldsymbol{\mu}^{(\alpha)}|\phi_i^{(\alpha)}\rangle \quad , \quad \langle\phi_i^{(\alpha)}|\phi_i^{(\beta)}\rangle = \delta_{\alpha\beta} \; , \tag{2.1}$$

where $\alpha, \beta = 1, \ldots, n$ and $\delta_{\alpha\beta}$ is the Kronecker symbol. We start with a model Hamiltonian of the form $\mathcal{H} = \mathcal{H}^L + \mathcal{H}^T$, where $\mathcal{H}^L$ describes the interaction between the impurities and $\mathcal{H}^T$ the tunneling between different directions of orientation. The interaction (longitudinal) Hamiltonian $\mathcal{H}^L$ is assumed to be of the simplified form

$$\mathcal{H}^L = -\sum_{i<j}^{N} J_{ij}(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)^k \; , \tag{2.2}$$

where $k = 1$ for TD's and $k = 2$ for TQ's.[25,26] Each site i has a tunneling Hamiltonian $\mathcal{H}_i^T$ associated with it to describe quantum mechanical tunneling. We make the simplifying assumption that the depth of the potential wells surrounding the impurity is the same for all wells. We further assume that *only* tunneling to the nearest-neighbor wells (NN wells) is important.[8,27] An example of an 8-O tunneling unit (CN^- in KBr) is shown in Fig. 1 with the possible directions of orientation (potential minima) pointing in the [111] directions. Let $\mathcal{T}$ be an $(n \times n)$ tunneling matrix with matrix elements $t_{\alpha\beta}$ given by

$$t_{\alpha\beta} = \langle \phi_i^{(\alpha)} | \mathcal{H}_i^T | \phi_i^{(\beta)} \rangle = \begin{cases} -\Delta & \text{, if } \alpha,\, \beta \text{ NN wells,} \\ 0 & \text{, otherwise ,} \end{cases} \qquad (2.3)$$

for $\alpha, \beta = 1, \ldots, n$ and an overlap energy $\Delta > 0$.[28] Note that the tunneling matrix $\mathcal{T}$, which depends only on the local crystalline environment, is defined independently of site i, i.e., each impurity finds itself in the same crystal field. Thereby we have neglected random field effects which we believe are unimportant in the case $c \rightarrow 0$. The tunneling Hamiltonian $\mathcal{H}_i^T$ can now be written as an N-fold direct product, $\mathcal{H}_i^T = \mathcal{I} \otimes \cdots \otimes \mathcal{I} \otimes \mathcal{T} \otimes \cdots \otimes \mathcal{I}$, with the tunneling matrix $\mathcal{T}$ appearing in the ith position, and $\mathcal{I}$ represents the n-dimensional identity matrix. Thus $\mathcal{H}_i^T$ is an n^N-dimensional matrix. For N tunneling units our total Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}^L + \mathcal{H}^T = -\sum_{i<j}^{N} J_{ij} (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)^k + \sum_{i=1}^{N} \mathcal{H}_i^T \ . \qquad (2.4)$$

To clarify our notation, we consider the following example. Consider the case of 2^d-orientational tunneling units in d dimensions ($d = 1, 2, \ldots$). For this special case it has been shown[29] that $\mathcal{T} = -\Delta \sum_{i=1}^{d} \sigma_i^x$ is a possible matrix representation for the tunneling matrix $\mathcal{T}$, Eq. (2.3), where σ_i^x is a d-fold direct product of the x component of the Pauli spin matrix with two-dimensional identity matrices $\mathcal{I}$, i.e., $\sigma_i^x = \mathcal{I} \otimes \cdots \otimes \sigma^x \otimes \cdots \otimes \mathcal{I}$, and σ^x appears in the ith position. This is easily be seen by inspection. Thus, in this special case we have

$$\mathcal{H}^T = \sum_{i=1}^{N} \mathcal{H}_i^T = -\Delta \sum_{i=1}^{dN} \sigma_i^x \ , \qquad (2.5)$$

where σ_i^x in Eq. (2.5) is now understood as a dN-fold direct product of two-dimensional identity matrices with σ^x, and $i = 1, \ldots, dN$ denotes the position of σ^x in the direct product. Further simplifications in the total Hamiltonian, Eq. (2.4), arise from the fact that for a 2^d-O tunneling unit, the d-dimensional unit vectors $\boldsymbol{\mu}_i^{(\alpha)}$ ($\alpha = 1, \ldots, 2^d$) are given by $(\pm 1, \pm 1, \ldots, \pm 1)^t / \sqrt{d}$ (t denotes the transposed vector). Since each coordinate of $\boldsymbol{\mu}_i^{(\alpha)}$ can be ± 1, we can replace each vector coordinate in $\boldsymbol{\mu}_i^{(\alpha)}$ by an operator $\sigma_i^z / \sqrt{d}$ ($i = 1, \ldots, dN$), where $\sigma_i^z = \mathcal{I} \otimes \cdots \otimes \sigma^z \otimes \cdots \otimes \mathcal{I}$ is a dN-fold direct product, and σ^z denotes the z component of the Pauli spin matrix. For $k = 1$ the total Hamiltonian, Eq. (2.4), for our example, denoted as $\mathcal{H}^{(2^d)}(\{J_{ij}\})$ can now be written

$$\mathcal{H}^{(2^d)}(\{J_{ij}\}) = -\sum_{i<j}^{dN} (J_{ij}/d) \sigma_i^z \sigma_j^z - \Delta \sum_{i=1}^{dN} \sigma_i^x \ . \qquad (2.6)$$

Hence for $k = 1$ and arbitrary d, the Hamiltonian, Eq. (2.6), satisfies the equation

$$\mathrm{Tr} \exp[-\beta \mathcal{H}^{(2^d)}(\{J_{ij}\})] = \Big(\mathrm{Tr} \exp[-\beta \mathcal{H}^{(2)}(\{J_{ij}/d\})] \Big)^d \ , \qquad (2.7)$$

where Tr stands for trace, $\beta = (k_B T)^{-1}$ (k_B is the Boltzmann constant), and the Hamiltonians $\mathcal{H}^{(2^d)}$ and $\mathcal{H}^{(2)}$ are defined via Eq. (2.6). Thus we have proved that the partition function of a system of 2^d-O TD's factors into a product of d Ising partition functions (with a rescaled interaction potential J_{ij}/d) in a transverse field Δ (Ref. 29).

In our approach (Sec. VI) we shall expand the free energy arising from the Hamiltonian, Eq. (2.4), into a virial expansion in the impurity concentration c for sufficiently low c up to c^2, i.e., pairs. The evaluation of the first virial coefficient[20] involves the trace over a noninteracting Hamiltonian, i.e., the tunneling matrix $\mathcal{T}$: $\ln \mathrm{Tr} \exp(-\beta \mathcal{H}^T) = N \ln \mathrm{Tr} \exp(-\beta \mathcal{T})$, with the tunneling matrix $\mathcal{T}$ defined in Eq. (2.3). This term is easy to evaluate. The second virial coefficient involves the term $\ln \mathrm{Tr} \exp(-\beta \mathcal{H}^p)$ (Ref. 20), where $\mathcal{H}^p$ is the Hamiltonian of an interacting pair. Sections III–V are exclusively dealing with the evaluation of this term. In general it requires the diagonalization of a pair Hamiltonian $\mathcal{H}^p$ which is an $(n^2 \times n^2)$ matrix. In particular we shall be interested in the case of 8-O TQ's, i.e., CN^- in KBr, the prototype orientational glass system. Before we turn to the exact diagonalization of $\mathcal{H}^p$, we treat a simpler problem by making use of Eq. (2.7).

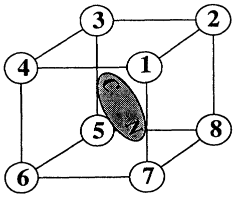

FIG. 1. Orientations for an 8-O tunneling unit. The $\boldsymbol{\mu}^{(\alpha)}$'s ($\alpha = 1, \ldots, 8$), defined in Eq. (2.1), are pointing from the center of the cube to the appropriate corner (potential well). Tunneling in our model can occur, for example, from well 1 to the nearest-neighbor wells 2, 4, and 7. The energy of a classical elastic dipole, i.e., CN^- in KBr, is invariant under 180° rotations.

III. PAIRS OF 2^d-ORIENTATIONAL TD'S

We have already shown in Eq. (2.7) that for 2^d-orientational TD's, the partition function of the total Hamiltonian, Eq. (2.4), factors into a product of d two-orientational Ising partition functions in a transverse field Δ. This holds in particular for a pair. For $d = 1$ and $N = 2$, Eq. (2.6) reduces to

$$\mathcal{H}^p = -\begin{pmatrix} J & \Delta & \Delta & 0 \\ \Delta & -J & 0 & \Delta \\ \Delta & 0 & -J & \Delta \\ 0 & \Delta & \Delta & J \end{pmatrix} . \tag{3.1}$$

Solving for the four eigenvalues E_i, one finds

$$E_{1/2} = \pm J \ , \quad E_{3/4} = \pm\sqrt{4\Delta^2 + J^2} \ , \tag{3.2}$$

and for the pair partition function $Z^{(2)}$

$$Z^{(2)}(\beta, J) = \mathrm{Tr}\exp(-\beta\mathcal{H}^p) = \sum_{i=1}^{4} \exp(-\beta E_i) \ . \tag{3.3}$$

Using Eq. (2.7) we can easily generalize this result to the case of a pair of 2^d-O TD's in d dimensions. The partition function for a pair of 2^d-O TD's, denoted as $Z^{(2^d)}(\beta, J)$, is by use of Eq. (2.7) given by

$$Z^{(2^d)}(\beta, J) = [Z^{(2)}(\beta, J/d)]^d \ , \tag{3.4}$$

with $Z^{(2)}(\beta, J)$ from Eq. (3.3). The knowledge of the pair partition function, Eq. (3.4), will be sufficient to evaluate the second virial coefficient (Sec. VI). Equation (3.4) does not apply to the TQ's nor to any other case if the number of orientations $n \neq 2^d$. In particular, for 8-O TQ's, we shall have to diagonalize the full (64×64) matrix (Sec. V B). The latter calculations involve some of the basic properties of circulant matrices, which will be presented below.

IV. CIRCULANT MATRICES

To diagonalize the pair Hamiltonian $\mathcal{H}^p$ we proceed as follows: we show that if $\mathcal{T}$, defined in Eq. (2.3), is a circulant matrix, $\mathcal{H}^p$ can be brought into block-circulant form and therefore readily be block diagonalized. The problem is then reduced to the diagonalization of n $(n \times n)$ matrices instead of one $(n^2 \times n^2)$ which greatly simplifies the algebra. We now discuss briefly some of the basic theorems on "circulants." For more details see, for example, Ref. 30.

A circulant matrix of order n is an $(n \times n)$ matrix $\mathcal{C}$ of the form

$$\mathcal{C} = \mathrm{Circ}\,(c_0, c_1, \ldots, c_{n-1}) = \begin{pmatrix} c_0 & c_1 & \cdots & c_{n-1} \\ c_{n-1} & c_0 & \cdots & c_{n-2} \\ \vdots & \vdots & \ddots & \vdots \\ c_1 & c_2 & \cdots & c_0 \end{pmatrix} , \tag{4.1}$$

where the c_ν's represent arbitrary complex numbers. The fundamental circulant matrix Π_n is defined as the n-dimensional matrix

$$\Pi_n = \mathrm{Circ}\,(0,1,0,\ldots,0) = \begin{pmatrix} 0 & 1 & 0 & 0 & \ldots & 0 \\ 0 & 0 & 1 & 0 & \ldots & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \vdots \\ 0 & 0 & 0 & \ldots & \ldots & 1 \\ 1 & 0 & 0 & \ldots & \ldots & 0 \end{pmatrix} . \tag{4.2}$$

The matrix Π_n has the very important *shift property* that when multiplied to a matrix, say $\mathcal{A}$, from the right-hand side, shifts all elements in $\mathcal{A}$ cyclically by one position to the right. For example, if $\mathcal{A}$ is an $n \times n$ matrix with elements a_{ij} $(i, j = 1, \ldots, n)$, then the matrix product $\mathcal{A}\Pi_n$ gives a matrix with elements $a_{i,j-1}$, where the subscripts are understood to be modulo n. Thus $\Pi_n^2 = \mathrm{Circ}\,(0,0,1,\ldots,0)$ and so forth. Note also that $\Pi_n^0 = \Pi_n^n = \mathcal{I}_n$ ($\mathcal{I}_n$ is the n-dimensional identity) and $\Pi_n^t = \Pi_n^{-1} = \Pi_n^{n-1}$ (t stands for transpose), where the negative exponent is understood to be modulo n. With these properties, it is now possible to express *any* circulant matrix $\mathcal{C}$, Eq. (4.1), as a polynomial in Π_n, namely,

$$\mathcal{C} = \mathrm{Circ}\,(c_0, c_1, \ldots, c_{n-1}) = \sum_{\nu=0}^{n-1} c_\nu \Pi_n^\nu \ . \tag{4.3}$$

In order to diagonalize $\mathcal{C}$ it is therefore sufficient to find a matrix that diagonalizes Π_n. It is easy to verify (Ref. 30), that such a matrix is given by

$$\mathcal{F}_n^* = \frac{1}{\sqrt{n}} \begin{pmatrix} 1 & 1 & 1 & \ldots & 1 \\ 1 & \omega & \omega^2 & \ldots & \omega^{n-1} \\ 1 & \omega^2 & \omega^4 & \ldots & \omega^{2(n-1)} \\ \vdots & \vdots & \vdots & & \vdots \\ 1 & \omega^{n-1} & \omega^{2(n-1)} & \ldots & \omega^{(n-1)(n-1)} \end{pmatrix} , \tag{4.4}$$

where $\mathcal{F}_n^*$ denotes the Hermitian matrix of the so-called Fourier matrix $\mathcal{F}_n$, and $\omega = \exp(2\pi i/n)$ is the nth root of unity. The Fourier matrix $\mathcal{F}_n$ is unitary, that is $\mathcal{F}_n\mathcal{F}_n^* = \mathcal{F}_n^*\mathcal{F}_n = \mathcal{I}_n$. The following important theorem holds:

$$\mathcal{F}_n^*\Pi_n\mathcal{F}_n = \Omega_n \ , \tag{4.5}$$

where Ω_n is diagonal and

$$\Omega_n = \mathrm{Diag}\,(1, \omega, \omega^2, \ldots, \omega^{n-1}) \ , \tag{4.6}$$

which is easily seen by carrying out the multiplication in Eq. (4.5). It follows from Eqs. (4.3) and (4.5) that

$$\mathcal{F}_n^*\mathcal{C}\mathcal{F}_n = \mathrm{Diag}\,(\lambda_0, \ldots, \lambda_{n-1}) \tag{4.7}$$

and

$$\lambda_j = \sum_{\nu=0}^{n-1} c_\nu \omega^{\nu j}, \quad j = 0, \ldots, n-1 \ . \tag{4.8}$$

Next we consider what happens if the c_ν's are themselves matrices, say of dimensionality m. Then instead of Eq. (4.3), we can write

$$\mathcal{C} = \mathrm{Circ}\,(\mathcal{C}_0, \mathcal{C}_1, \ldots, \mathcal{C}_{n-1}) = \sum_{\nu=0}^{n-1} \Pi_n^{\nu} \otimes \mathcal{C}_\nu \ , \tag{4.9}$$

where the $\mathcal{C}_\nu$ are now arbitrary $(m \times m)$ matrices and $\otimes$ denotes a direct product. In this case it is also very simple to show that the unitary transformation

$$(\mathcal{F}_n \otimes \mathcal{I}_m)^* \mathcal{C} (\mathcal{F}_n \otimes \mathcal{I}_m) = \begin{pmatrix} \Lambda_0 & \ldots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \ldots & \Lambda_{n-1} \end{pmatrix} \tag{4.10}$$

block diagonalizes $\mathcal{C}$. The n resulting $(m \times m)$ matrices Λ_j are

$$\Lambda_j = \sum_{\nu=0}^{n-1} \mathcal{C}_\nu \omega^{j\nu}. \tag{4.11}$$

Equations (4.10) and (4.11) will now be used to diagonalize the pair Hamiltonian $\mathcal{H}^p$.

V. DIAGONALIZATION OF $\mathcal{H}^p$

The Hamiltonian of a pair, $\mathcal{H}^p(J)$, can be expressed as

$$\mathcal{H}^p(J) = -J(\mathcal{D} \otimes \mathcal{D})^k + \mathcal{T} \otimes \mathcal{I} + \mathcal{I} \otimes \mathcal{T} \ , \tag{5.1}$$

where we have introduced the diagonal matrix $\mathcal{D}$,

$$\mathcal{D} = \mathrm{Diag}\,(\boldsymbol{\mu}^{(1)}, \boldsymbol{\mu}^{(2)}, \ldots, \boldsymbol{\mu}^{(n)}) \ . \tag{5.2}$$

This is easily seen from Eq. (2.4) by setting $N = 2$ (by the product $\boldsymbol{\mu}^{(1)}\boldsymbol{\mu}^{(2)}$ we mean the usual vector dot product). All matrices are understood to be n dimensional. The tunneling matrix $\mathcal{T}$ was defined in Eq. (2.3), $\boldsymbol{\mu}^{(\alpha)}$ in Eq. (2.1). To clarify our notation, we treat the following two-dimensional problems, before approaching the more complicated case of the 8-O TQ's.

A. Two-dimensional clock model

Consider n-orientational tunneling units in a plane with nearest-neighbor tunneling only and unit vectors

$$\boldsymbol{\mu}^{(\alpha)} = [\cos(2\pi\alpha/n), \sin(2\pi\alpha/n)]^t \ , \tag{5.3}$$

where $\alpha = 1, \ldots, n$ and t denotes the transposed vector. For convenience we measure in the following derivation all energies in units of Δ. Formally this means we set $\Delta = 1$ throughout Sec. V. Using the notation introduced in Eq. (4.1), we obtain from Eq. (2.3)

$$\mathcal{T} = -\mathrm{Circ}\,(0, 1, 0, \ldots, 0, 1) \ . \tag{5.4}$$

Hence $\mathcal{H}^T$ is a block circulant and

$$\mathcal{H}^T = \mathcal{T} \otimes \mathcal{I} + \mathcal{I} \otimes \mathcal{T} = \mathrm{Circ}\,(\mathcal{T}, -\mathcal{I}, 0, \ldots, 0, -\mathcal{I}) \ . \tag{5.5}$$

We next define the orthogonal matrix

$$\mathcal{S} = \mathrm{Diag}\,(\mathcal{I}, \Pi^{-1}, \Pi^{-2}, \ldots, \Pi^{1-n}) \ . \tag{5.6}$$

A new representation of $\mathcal{H}^p$ is obtained from the similarity transformation

$$\mathcal{S}^t \mathcal{H}^p \mathcal{S} = \mathrm{Circ}\,(-J\mathcal{B}^k + \mathcal{T}, -\Pi^{-1}, 0, \ldots, 0, -\Pi^{1-n}) \ , \tag{5.7}$$

where use has been made of Eqs. (5.1) and (5.6), and we have introduced the diagonal matrix

$$\mathcal{B} = \mathrm{Diag}\,(\boldsymbol{\mu}^{(1)}\boldsymbol{\mu}^{(1)}, \ldots, \boldsymbol{\mu}^{(1)}\boldsymbol{\mu}^{(n)}) \ . \tag{5.8}$$

Since Eq. (5.7) is of block circulant form, we can block diagonalize it by making use of Eqs. (4.10) and (4.11). The so-obtained n blocks Λ_j are given by

$$\Lambda_j = -J\mathcal{B}^k - (1 + \omega^{-j})\,\Pi - [(1 + \omega^{-j})\,\Pi]^* \ , \tag{5.9}$$

where $j = 0, \ldots, n-1$ and $*$ means Hermitian. For our special choice for the $\boldsymbol{\mu}^{(\alpha)}$'s in Eq. (5.3), Eq. (5.8) yields $\mathcal{B} = (\Omega + \Omega^*)/2$, where Ω was defined previously in Eq. (4.6).

Finally we have to diagonalize the Λ_j's in Eq. (5.9). We consider here only the following symmetries in a plane: directions of orientation (local potential minima) lying along the corners of a triangle (3-O), square (4-O), hexagon (6-O). The calculations involve the diagonalization of n $(n \times n)$ matrices [Λ_j in Eq. (5.9)], where $n = 3$, 4, and 6 is the dimensionality of the matrices $\mathcal{B}$ and Π; $k = 1$ for TD's and $k = 2$ for TQ's. For the examples considered this presents no difficulties, however, the algebra involved is somewhat tedious. The final results for the energy eigenvalues E_i $(i = 1, \ldots, n^2)$ are summarized in Tables I–IV for TD's and TQ's. The eigenvalues as a function of J and Δ are obtained by changing $E_i \rightarrow E_i/\Delta$ and $J \rightarrow J/\Delta$ in the tables.

Provided that the tunneling matrix $\mathcal{T}$ is a circulant, we can easily generalize Eq. (5.7). Assuming the tunneling matrix $\mathcal{T}$ is of the more general form $\mathcal{T} = -\mathrm{Circ}\,(0, \Delta_1, \ldots, \Delta_{n-1})$, we obtain from Eqs. (5.1) and (5.6)

$$\mathcal{S}^t \mathcal{H}^p \mathcal{S} = \mathrm{Circ}\,(-J\mathcal{B}^k + \mathcal{T}, -\Delta_1\Pi^{-1}, -\Delta_2\Pi^{-2}, \ldots, -\Delta_{n-1}\Pi^{1-n}) \ . \tag{5.10}$$

Using Eqs. (4.10) and (4.11) we can still block diagonalize Eq. (5.10). The resulting n blocks are

TABLE I. Energy eigenvalues E_i for 3-O TD's and TQ's in a plane. For TD's let $K = 3J/4$ and $E_i = \lambda_i - J/4$. For TQ's set $K = 3J/8$ and $E_i = \lambda_i - 5J/8$. All energies are measured in units of Δ.

Eigenvalue	Energy	Degeneracy
λ_1	$K - 2$	1
λ_2	$K + 1$	2
$\lambda_{3,4}$	$1 \pm \sqrt{9 + 2K + K^2}$	1
$\lambda_{5,6}$	$(-1 \pm \sqrt{9 - 4K + 4K^2})/2$	2

TABLE II. Energies for 4-O TQ's in a plane. The TD case has been treated in Sec. III.

Eigenvalue	Energy	Degeneracy
E_1	0	3
E_2	$-J$	3
$E_{3,4}$	$(-J \pm \sqrt{64+J^2})/2$	1
$E_{5,6}$	$(-J \pm \sqrt{16+J^2})/2$	4

$$\Lambda_j = -J\mathcal{B}^k - \sum_{\nu=1}^{n-1} \Delta_\nu (\omega^{j\nu}\Pi^{-\nu} + \Pi^\nu) , \tag{5.11}$$

with $j = 0, \ldots, n-1$. For simplicity we consider in the following only cases in which the overlap energies Δ_ν between nearest-neighbor wells are the same, as was assumed in Eq. (2.3). This approximation, that each particle finds itself in the same crystalline environment, would break down for higher concentrations, when the local crystal field becomes strongly disturbed by static random elastic fields introduced by the host-impurity disorder.[19]

B. Three-dimensional problems

As applications of Eqs. (5.10) and (5.11), we consider the following two problems.

(i) For 4-O TD's and TQ's with potential wells lying along the corners of a tetrahedron, the tunneling matrix is given by $\mathcal{T} = -\mathrm{Circ}\,(0,1,1,1)$ (in units of Δ). Once the order of the states, $|\phi_i^{(\alpha)}\rangle$ in Eq. (2.1), is chosen, $\mathcal{B}$ can be readily found from Eq. (5.8). In this case $\mathcal{B} = \mathrm{Diag}\,(1,-1/3,-1/3,-1/3)$. The eigenvalues are obtained by diagonalizing the four (4×4) matrices Λ_j in Eq. (5.11) for $k = 1, 2$ and $\Delta_1 = \Delta_2 = \Delta_3 = 1$. The final result is given in Table V.

(ii) For 6-O TD's and TQ's with potential minima in the [100] directions, we can choose $\mathcal{T} = -\mathrm{Circ}\,(0,1,1,0,1,1)$ and $\mathcal{B} = \mathrm{Diag}\,(1,0,0,-1,0,0)$. In the quadrupole case this leads to Table VI and for the dipoles to Table VII.

TABLE III. Energies for 6-O TQ's in a plane. $R = \sqrt{27+4K^2}$, $\cos\Phi = -8K^3/R^3$, $K = 3J/8$, $E_i = \lambda_i - 5J/8$.

Eigenvalue	Energy	Degeneracy
λ_1	$-K$	2
λ_2	K	4
$\lambda_{3,4}$	$\pm 2 + K$	1
$\lambda_{5,6}$	$\pm 1 + K$	2
$\lambda_{7,8}$	$1 \pm \sqrt{9+2K+K^2}$	1
$\lambda_{9,10}$	$-1 \pm \sqrt{9-2K+K^2}$	1
$\lambda_{11,12}$	$(-1 \pm \sqrt{9-4K+4K^2})/2$	2
$\lambda_{13,14}$	$(1 \pm \sqrt{9+4K+4K^2})/2$	2
λ_{15}	$(K + 2R\cos[\Phi/3])/3$	4
λ_{16}	$(K + 2R\cos[(\Phi+2\pi)/3])/3$	4
λ_{17}	$(K + 2R\cos[(\Phi+4\pi)/3])/3$	4

TABLE IV. Energies for 6-O TD's in a plane. $R = \sqrt{108+7J^2}$, $\cos\Phi = [2J(5J^2-162)]/R^3$.

Eigenvalue	Energy	Degn.
$E_{1,2}$	$\pm J$	1
$E_{3,4}$	$\pm J/2$	2
$E_{5,6}$	$\pm\sqrt{4+J^2}/2$	2
$E_{7,8}$	$\pm\sqrt{16+J^2}/2$	1
$E_{9,10,11,12}$	$\pm\sqrt{80+5J^2 \pm \sqrt{2304+1056J^2+9J^4}}/\sqrt{8}$	1
$E_{13,14,15,16}$	$\pm\sqrt{20+5J^2 \pm \sqrt{144+264J^2+9J^4}}/\sqrt{8}$	2
$E_{17,18}$	$\pm(-J + R\cos[\Phi/3])/3$	2
$E_{19,20}$	$\pm(-J + R\cos[(\Phi+2\pi)/3])/3$	2
$E_{20,21}$	$\pm(-J + R\cos[(\Phi+4\pi)/3])/3$	2

For the 8-O TQ problem the potential minima lie in the [111] directions (Fig. 1). It is easy to show that in this case the tunneling matrix cannot be brought into circulant form. Instead it is possible to write $\mathcal{T}$ as a block circulant with circulant blocks, namely $\mathcal{T}_8 = -\mathcal{I}_2 \otimes \mathcal{T}^{(1)} - \Pi_2 \otimes \mathcal{T}^{(2)}$, where $\mathcal{T}^{(1)} = \Pi_4 + \Pi_4^3$ and $\mathcal{T}^{(2)} = \Pi_4^2$. We have used subscripts to show the dimensionality of the single matrices. Figure 1 shows the order of the potential minima 1–8 leading to this special representation of $\mathcal{T}$. Defining the orthogonal matrix

$$\mathcal{S} = \mathrm{Diag}\,(\mathcal{I}_2 \otimes \mathcal{I}_4, \mathcal{I}_2 \otimes \Pi_4^{-1}, \mathcal{I}_2 \otimes \Pi_4^{-2}, \mathcal{I}_2 \otimes \Pi_4^{-3}, \\ \Pi_2 \otimes \mathcal{I}_4, \Pi_2 \otimes \Pi_4^{-1}, \Pi_2 \otimes \Pi_4^{-2}, \Pi_2 \otimes \Pi_4^{-3}) , \tag{5.12}$$

it is easy to show that

$$\mathcal{S}^t \mathcal{H}^p \mathcal{S} = \mathcal{I}_8 \otimes (-J\mathcal{B}_8^k + \mathcal{T}_8) - \mathcal{I}_2 \otimes \Pi_4 \otimes \mathcal{I}_2 \otimes \Pi_4^3 \\ -\mathcal{I}_2 \otimes \Pi_4^3 \otimes \mathcal{I}_2 \otimes \Pi_4 - \Pi_2 \otimes \Pi_4^2 \otimes \Pi_2 \otimes \Pi_4^2 , \tag{5.13}$$

and $\mathcal{B}_8 = \mathrm{Diag}\,(1, 1/3, -1/3, 1/3, -1, -1/3, 1/3, -1/3)$. By use of the transformation

$$(\mathcal{F}_2 \otimes \mathcal{F}_4 \otimes \mathcal{I}_8)^* \, \mathcal{H}^p (\mathcal{F}_2 \otimes \mathcal{F}_4 \otimes \mathcal{I}_8) , \tag{5.14}$$

we can block diagonalize Eq. (5.13). The result for the eight blocks is

$$\Lambda_{pq} = -J\mathcal{B}_8^k - [1 + (-1)^{(p+q)}]\, \Pi_2 \otimes \Pi_4^2 \\ - [1 + (-i)^q]\, \mathcal{I}_2 \otimes \Pi_4 - (1 + i^q)\, \mathcal{I}_2 \otimes \Pi_4^3 , \tag{5.15}$$

with $p = 0, 1$ and $q = 0, 1, 2, 3$. Again the problem is reduced to the diagonalization of eight (8×8) matrices. We are only interested in the quadrupole case $k = 2$ ($k = 1$ was discussed in Sec. III). Defining

TABLE V. Energies for 4-O TQ's and TD's in three dimensions. For TQ's $K = 4J/9$ and $E_i = \lambda_i - 5J/9$; for TD's $K = 2J/3$ and $E_i = \lambda_i - J/3$.

Eigenvalue	Energy	Degeneracy
λ_1	$-2 + K$	5
$\lambda_{2,3}$	$2 \pm \sqrt{16+4K+K^2}$	1
$\lambda_{4,5}$	$\pm\sqrt{4+K^2}$	3
λ_6	$2 + K$	1

TABLE VI. Energies for 6-O TQ's in three dimensions.

Eigenvalue	Energy	Degeneracy
$E_{1,2}$	$(-J+4\pm\sqrt{J^2+8J+144})/2$	1
$E_{3,4}$	$(-J-2\pm\sqrt{J^2-4J+36})/2$	2
$E_{5,6}$	$(-J+2\pm\sqrt{J^2+4J+36})/2$	6
E_7	$-J$	3
E_8	-4	1
E_9	-2	6
E_{10}	0	6
E_{11}	2	2

$\mathcal{A}_4 = \mathrm{Diag}\,(1, 1/9, 1/9, 1/9)$ and replacing $\mathcal{B}_8^2$ by $\mathcal{I}_2 \otimes \mathcal{A}_4$ in Eq. (5.15), the transformation $(\mathcal{F}_2 \otimes \mathcal{I}_2)^* \Lambda_{pq} (\mathcal{F}_2 \otimes \mathcal{I}_2)$ yields some further simplifications. We obtain for the resulting 16 (4 × 4) matrices

$$\Lambda_{pq}^{\pm} = -J\mathcal{A}_4 - [1+(-i)^q]\,\Pi_4 - \{[1+(-i)^q]\,\Pi_4\}^* \pm [1+(-1)^{(p+q)}]\,\Pi_4^2 \; . \tag{5.16}$$

The evaluation of Eq. (5.16) for $p = 0, 1$ and $q = 0, 1, 2, 3$ is easy, and the eigenvalues are listed in Table VIII.

It was mentioned in Ref. 25 that the full quadrupole-quadrupole interaction is a tensor. In general the interaction potential V_{ij} between two quadrupoles is of the form $V_{ij} = V(\boldsymbol{\mu}_i, \boldsymbol{\mu}_j, \mathbf{r})$, where $\mathbf{r}$ is the vector connecting the two quadrupoles at site i and j ($\mathbf{r}$ is considered to be random, but fixed in a quenched system). Provided the tunneling matrix $\mathcal{T}$ is a circulant or block circulant, we could easily rederive Eqs. (5.11) and (5.15) for a more general potential V_{ij} with the only change that $-J\mathcal{B}^k$ in our previous derivation had to be replaced by

$$\mathcal{V}_n = \mathrm{Diag}\,(V_{11}, V_{12}, \ldots, V_{1n}) \; . \tag{5.17}$$

Furthermore the quadrupole-quadrupole interaction is invariant under the inversion of $\boldsymbol{\mu}_i$ (Ref. 26). For even n, we can then define a matrix $\mathcal{U}_{n/2}$ with the property $\mathcal{I}_2 \otimes \mathcal{U}_{n/2} = \mathcal{V}_n$. Thus in the most general case we only have to replace $-J\mathcal{A}_4$ in Eq. (5.16) by $\mathcal{U}_4 = \mathrm{Diag}\,(V_{11}, V_{12}, V_{13}, V_{14})$, where the V_{1j}'s are some functions of $\mathbf{r}$ which are easily obtained from the full tensor.[26] Again the problem is reduced to the diagonalization of 16 (4 × 4) matrices, which can always be solved analytically. However, we are not going to pursue this problem here any further and continue with our simplified Hamiltonian[25] in Eq. (2.4). The result in Table VIII concludes our discussion of the pair Hamiltonian.

TABLE VII. Energies for 6-O TD's in three dimensions. $R = \sqrt{28+3J^2}$, $\cos\Phi = (18J^2-80)/R^3$, $S = \sqrt{112+3J^2}$, $\cos\Psi = (640-36J^2)/S^3$.

Eigenvalue	Energy	Degeneracy
$E_{1,2}$	$(J+2\pm\sqrt{J^2-4J+36})/2$	3
$E_{3,4}$	$(-J+2\pm\sqrt{J^2+4J+36})/2$	3
E_5	2	2
E_6	-4	1
E_7	-2	6
E_8	0	6
E_9	$2(-1+R\cos[\Phi/3])/3$	2
E_{10}	$2(-1+R\cos[(\Phi+2\pi)/3])/3$	2
E_{11}	$2(-1+R\cos[(\Phi+4\pi)/3])/3$	2
E_{12}	$2(2+S\cos[\Psi/3])/3$	1
E_{13}	$2(2+S\cos[(\Psi+2\pi)/3])/3$	1
E_{14}	$2(2+S\cos[(\Psi+4\pi)/3])/3$	1

TABLE VIII. Energies for 8-O TQ's in three dimensions in units of Δ. $R = \sqrt{12+K^2}$, $\cos\Phi = [K(9-K^2)]/R^3$, $K = 4J/9$, $E_i = \lambda_i - 5J/9$.

Eigenvalue	Energy	Degeneracy
λ_1	$-K$	2
λ_2	K	12
$\lambda_{3/4}$	$\pm 2+K$	8
$\lambda_{5/6}$	$\pm\sqrt{4+K^2}$	6
$\lambda_{7/8}$	$2\pm\sqrt{16+4K+K^2}$	1
$\lambda_{9/10}$	$-2\pm\sqrt{16-4K+K^2}$	1
λ_{11}	$(K+4R\cos[\Phi/3])/3$	6
λ_{12}	$(K+4R\cos[(\Phi+2\pi)/3])/3$	6
λ_{13}	$(K+4R\cos[(\Phi+4\pi)/3])/3$	6

VI. HEAT CAPACITY FOR DILUTE CONCENTRATIONS OF INTERACTING TD'S AND TQ'S

We consider a quenched system of randomly distributed tunneling units. We further assume an interaction potential of the form $J_{ij} = \pm b\,r_{ij}^{-3}$, where r_{ij} is the distance between two impurities and b is a positive constant. The ± indicates that the interaction is competing with the same probability for being negative or positive.[25] Starting from our model Hamiltonian in Eq. (2.4), we expand the free energy into a virial expansion in the impurity concentration c for sufficiently low c keeping only terms up to c^2. Following Ref. 20, the contributions to the free energy $F = F^{(1)} + F^{(2)}$ from the first and second virial coefficients are given by

$$-\beta F^{(1)} = \ln \mathrm{Tr}\, e^{-\beta\mathcal{H}^T} = cN_0 \ln \mathrm{Tr}\, e^{-\beta\mathcal{T}} \; , \tag{6.1a}$$

$$-\beta F^{(2)} = \frac{\pi c^2 N_0 b}{3v} \int_{-J_0}^{J_0} \left(\ln \mathrm{Tr}\, e^{-\beta\mathcal{H}^p(J)} - \ln \mathrm{Tr}\, e^{-\beta\mathcal{H}^p(0)} \right) \times \frac{dJ}{J^2} \; . \tag{6.1b}$$

N_0 is the number of sites available to the impurities in the crystal, $c = N/N_0$ is the concentration and N the number of impurities, $v = V/N_0$ is the volume per site, $J_0 = b\,r_0^{-3}$ is the near-neighbor interaction, i.e., the maximum strength of the interaction. The operators $\mathcal{T}$ and $\mathcal{H}^p(J)$ have been defined in Eq. (2.3) and Eq. (5.1), respectively, and the trace (Tr) in Eqs. (6.1a) and (6.1b) is over their eigenvalues.[31] The specific heat, $C(T)$, is calculated from $C(T) = C^{(1)} + C^{(2)}$ with $C^{(i)} = k_B\beta^2(\partial^2/\partial\beta^2)(-\beta F^{(i)})$.

As our first application, we calculate $C(T)$ for a system of 8-O TD's. The 2^d-O tunneling Hamiltonian is given in Eq. (2.5). Thus we obtain from Eq. (6.1a) that $\ln \mathrm{Tr} \exp(-\beta \mathcal{H}^T) = 3N \ln[2\cosh(\Delta\beta)]$ and

$$C^{(1)} = 3cN_0k_B\,[\Delta\beta \operatorname{sech}(\Delta\beta)]^2\ . \tag{6.2}$$

Equation (6.2) is the Schottky specific heat. $C^{(2)}$ has to be evaluated numerically by use of Eqs. (6.1b) and (3.4). The result of this simple integration for two different concentrations of $^6\mathrm{Li}^+$ in KCl is shown in Fig. 2, together with the experimental data from Ref. 8. There are two adjustable parameters entering in our calculation: the tunneling matrix element Δ and the maximum strength of the interaction J_0. These parameters are readily determined from the experimental specific heat. For both of our graphs we have used the same values $\Delta/k_B = 0.9$ K (Ref. 32) and $J_0/k_B = 550$ K. This choice is in agreement with previous results (Refs. 20–22) and experiment (Ref. 8).

For the 8-O TQ's we have to evaluate $C^{(2)}$ from Eq. (6.1b) using the energy eigenvalues provided in Table VIII. The total specific heat is again obtained by adding $C^{(2)}$ and the Schottky contribution $C^{(1)}$ from Eq. (6.2). Our result for 340 ppm of CN^- in KBr is shown in Fig. 3. The solid line shows our predicted specific heat assuming $\Delta/k_B = 0.65$ K and $J_0/k_B = 450$ K. These values were chosen in agreement with Ref. 10. Our result improved remarkably in comparison with experiment, if two slightly different values[33] for Δ in $C^{(1)}$ and $C^{(2)}$ were used (see caption to Fig. 3).

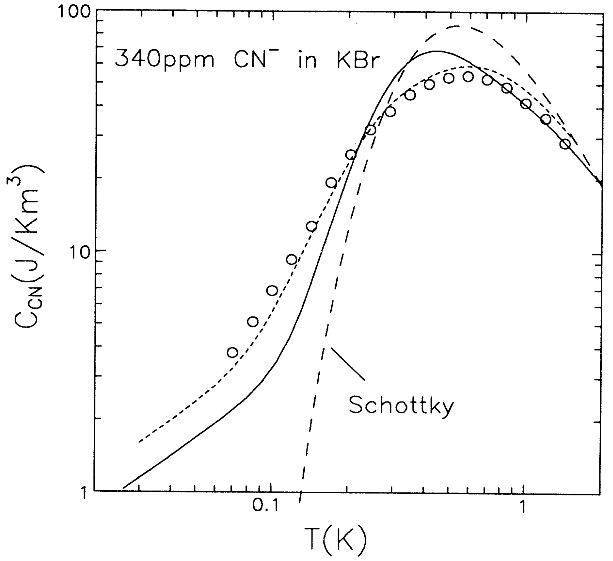

FIG. 3. Specific heat for 340 ppm CN^- in KBr (8-O TQ). The open circles show the experimental data from Ref. 10. The long dashes show the Schottky specific heat $C^{(1)}$ without the corrections from the second virial coefficient. The solid line is the total specific heat predicted from our calculation assuming $\Delta/k = 0.65$ K and $J_0/k = 450$ K (Ref. 10). An improvement was made (short dashes) with values $c = 320$ ppm and a $\Delta_1/k = 0.65$ K for the noninteracting part $[C^{(1)}(\Delta_1)]$ and a slightly different $\Delta_2/k = 0.55$ K for the interacting part $[C^{(2)}(\Delta_2)]$ (Ref. 33).

Figure 3 also shows that the Schottky term $C^{(1)}$ alone (long dashes) exceeds the experimental data by about 50% at the maximum, whereas for T below 0.2 K, $C^{(1)}$ vanishes exponentially. Both of these findings are in disagreement with experiment. A model of isolated defects thus seems to be inappropriate to explain the experimental data. This discrepancy between theory and experiment is usually explained in terms of a *broad* distribution function of overlap energies Δ which has its origin in static random elastic fields. The existence of these random fields seems to be well established in the intermediate to high concentration range.[7,17,19,34] However, we feel that no justification for such a distribution function exists in the very dilute limit, as $c \to 0$. Furthermore it has been estimated[8] that the random strain fields needed to explain the observed broadening of the Schottky specific heat would be unphysically large. A similar question has been discussed previously elsewhere.[35]

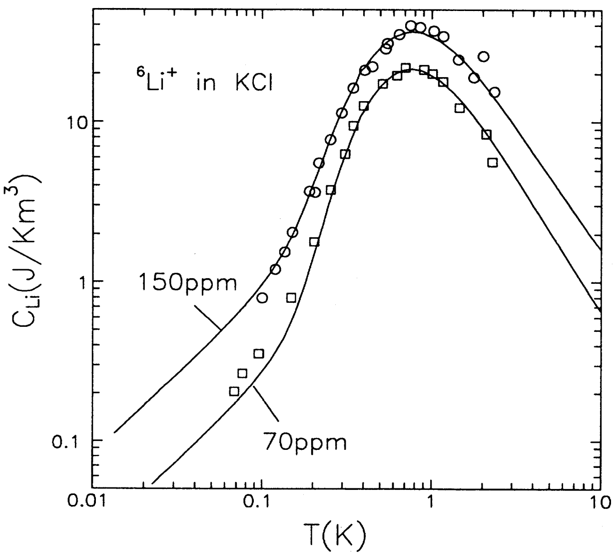

FIG. 2. Specific heat for two different concentrations of $^6\mathrm{Li}^+$ in KCl (8-O TD's). The upper graph shows our result for $c = 150$ ppm, the lower graph for $c = 70$ ppm. The experimental data (circles, squares) were taken from Ref. 8. In both calculations (solid lines) we have used $\Delta/k = 0.90$ K (Ref. 32) and $J_0/k = 550$ K.

Figure 4 shows the specific heats arising from the first and second virial coefficients in our model separately. For $T \lesssim 0.2$ K, $C^{(2)}$ greatly exceeds the Schottky contribution and therefore $C \approx C^{(2)}$. The maximum strength of the interaction J_0 is then obtained by fitting $C^{(2)}$ to experiment.[22] $C^{(2)}$ reaches its minimum approximately where $C^{(1)}$ has its maximum at $T_m \approx 0.83\Delta/k_B$. Thus the net specific heat is predicted to be significantly reduced compared to $C^{(1)}$ at $T \approx T_m$, and the Schottky peak appears to be broadened, as is observed in experiment. As c is increased beyond $\sim$ 500 ppm a dip begins to show up in the predicted CN^- specific heat (not shown). The resulting two peaks in the specific heat arise in our model from the sum of the first and sec-

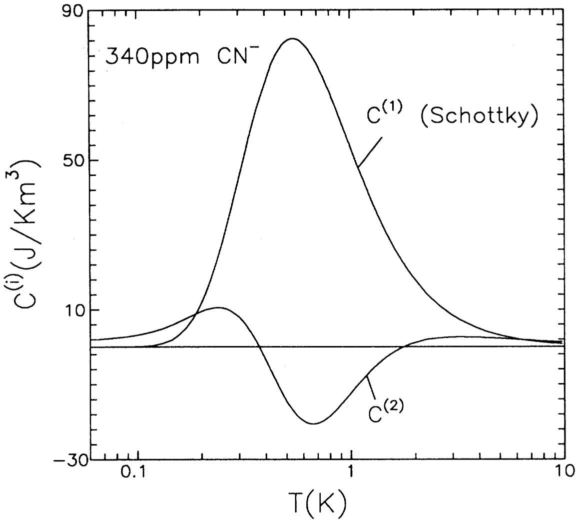

FIG. 4. Specific heats $C^{(1)}$ and $C^{(2)}$ arising from the first and second virial coefficients, respectively.

ond virial coefficients $C^{(1)}$ and $C^{(2)}$: since $C^{(2)}$ scales with c^2, a second peak in the specific heat will show up as c is increased, where $C^{(2)}$ has its maximum at about 0.25 K (Fig. 4). The double peak, which is also observed experimentally,[11,12] is usually explained by assuming a small perturbation on the crystal field potential, which has otherwise perfect octahedral symmetry (Ref. 12). Here it is a direct consequence of the interaction.

The very low-T behavior of $C(T)$ and the density of states in our model is determined by the lowest excitation energies which result from strong interactions. This seemingly contradictory result has been discussed in length in a previous paper[22] and is most easily understood using perturbation theory. In short, consider an interacting pair of classical dipoles or quadrupoles. If the ground state energy of the pair is degenerate and the interaction J between a pair is assumed to be large, the tunneling part of the Hamiltonian, Eq. (5.1), can be treated as a perturbation. If the particles are only allowed to tunnel between the n directions provided by the crystalline environment, it is easy to show that the degeneracy is not lifted in first order.[22] Thus the tunnel splittings (low-energy excitations) will be of the order $\Delta^{\alpha+1}/|J|^{\alpha}$, where $\alpha \geq 1$ and $|J| \gg \Delta$. A calculation of the very low-T thermal properties and density of states therefore requires an asymptotic expansion of the energy eigenvalues given in Tables I–VIII for large J. We give here only the final results, because the identical result can be obtained in a simpler way from perturbation theory.[22] However, this perturbation approach was restricted to the very low-temperature range $T \ll \Delta/k_B$.

For all symmetries treated in this paper, except the 8-O TQ, the calculated specific heat is linear in T below 0.1 K, and the density of states is a constant for small energies.[22] For 340 ppm of CN$^-$ in KBr (8-O TQ), we find that as T is lowered below 0.1 K the specific heat is proportional to T^{α}, where $\alpha \approx 0.8$. As T is further lowered (below $T \approx 10$ mK), $C(T)$ is predicted to be proportional to $T^{1/2}$. The density of states $P(E)$ for CN$^-$ goes over from being approximately constant below 0.1 K to $P(E) \sim E^{-1/2}$ for T less then 10 mK.[22] Below 1 mK there are no more energy states because of the finite cutoff at the near-neighbor J_0 which is of the order $k_B\,500$ K, and the specific heat is expected to vanish exponentially. This is so because the smallest excitation energies arise from the largest interaction.

VII. CONCLUSION

We have used the special properties of “circulant” matrices to obtain the exact energy spectrum for pairs of interacting tunneling dipoles (TD’s) and tunneling quadrupoles (TQ’s) for the various symmetries listed in the text. We found low-energy excitations in all of the considered cases from *strong* interactions in agreement with previous results. Starting from a microscopic Hamiltonian, we have used these excitation energies to derive the free energy of a very dilute system of interacting TD’s or TQ’s *without* making use of mean-field theory known to be very problematic in systems with random and competing interactions. The low-temperature specific heat and density of states were calculated. In particular we derived the specific heat for eight-orientational TD’s (^{6}Li$^+$ in KCl) and eight-orientational TQ’s (340 ppm of CN$^-$ in KBr). We found good agreement with experimental results supporting the idea that it is strongly interacting tunneling units that give the anomalous low-T thermal properties and density of states observed in dilute (orientational) glasses. Since we deal here with very low concentrations, our work does not apply to the concentrated mixed crystals discussed by Sethna and co-workers.[14–16]

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