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Level repulsion and the dielectric relaxation in quadrupolar glasses

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Dielectric relaxation in quadrupolar glasses is dominated at low temperatures by thermal activation over local anisotropy barriers produced by the quadrupolar freezing. The distribution of barrier height V vanishes linearly as $V \to 0$ at all temperatures due to the repulsion of levels of the random internal stress tensor. A further shift of V to higher values occurs as T decreases due to correlations. These results are compared with recent dielectric measurements in $(KBr)_{0.5}(KCN)_{0.5}$.

Very interesting recent dielectric measurements[1,2] in $(KBr)_{0.5}(KCN)_{0.5}$ have exhibited a broad distribution of dielectric relaxation times at low temperatures. The frequency and temperature dependence of the dielectric loss was explained[1] by assuming a thermal activation process over barriers whose heights V is Gaussian distributed,

$$P(V) = (\Delta V\sqrt{2\pi})^{-1} e^{-(V-V_0)^2/2(\Delta V)^2}, \quad V \geq 0 .$$

The observed values of V_0 and ΔV at low T are $V_0 = 659$ K and $\Delta V \simeq 300\ \text{K} - 1.5T$. It has been proposed[3] that the barriers arise from the local anisotropy fields produced by the freezing of the quadrupolar moments of the CN molecules. The Gaussian distribution has been explained using a mean-field argument based *on independent contributions to V from many neighboring molecules.*

The question of the distribution of V is closely related to that of the random internal magnetic fields in spin glasses.[4-6] There it is known that near the freezing temperature the distribution is (half) a Gaussian peaked at zero. However, at low temperatures a (quasi) hole develops at the origin, shifting the peak of the distribution to a positive value. Here we use mean-field theory[7] to study the distribution of the internal stress tensor $\underline{h}$ which results from the freezing of randomly interacting quadrupoles. Our main point is that since the *symmetry axes* of the local quadrupolar order fluctuate from site to site, the whole *distribution of* the random matrix $\underline{h}$ must be considered. The barrier heights to 180° rotations of the molecules correspond to the level spacing between the largest and the next largest eigenvalues of $\underline{h}$. Consequently, $P(V)$ vanishes (linearly) as $V \to 0$ *at all* T due to the well-known repulsion[8,9] of energy levels of random matrices. The effect of level repulsion should be observable mostly at intermediate temperatures where the resultant $P(V)$ has a pronounced asymmetric shape (Fig. 1). At low T, correlations shift the distribution to larger values of V (Fig. 2). The possible origin of the apparent discrepancy between these results and the available experimental data will be discussed. It should be emphasized that the present work is restricted to strongly disordered systems which do not possess long-range (ferroelastic) order. Extension of the present work to weakly disordered systems, such as $(KBr)_{1-x}(KCN)_x$ with $x > 0.6$, will be discussed elsewhere.

We study a system of N-interacting classical quadrupoles, $f_i^{mn} = \hat{n}_i^m \hat{n}_i^n - \frac{1}{3}\delta^{mn}$ $(m,n = 1,2,3)$, where $\hat{\mathbf{n}}_i$ is a three-dimensional unit vector located at the site i. As in the Edwards-Anderson model[10] of spin glasses, the fluctuations

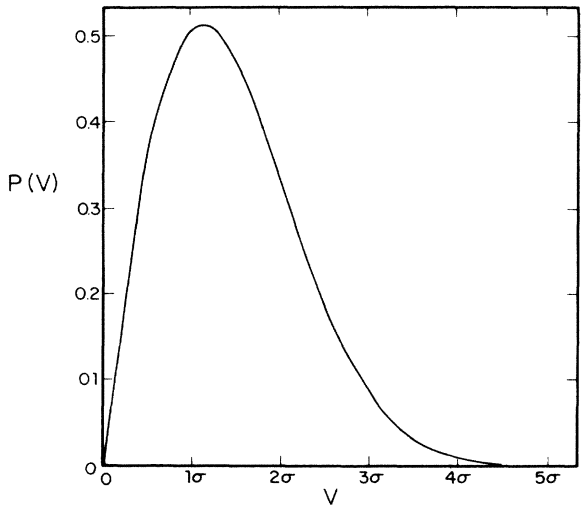

FIG. 1. Distribution of barrier heights, Eq. (7), in units of σ.

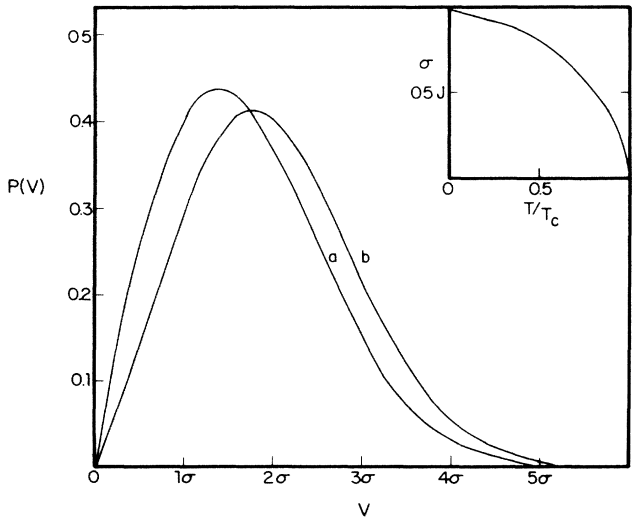

FIG. 2. Distribution of barrier height at low T. (a) Results for $T = 0.5T_g$; (b) the $T = 0$ results, Eq. (11), with $a = 1.3\sigma$. Inset shows the temperature dependence of $\sigma = J\sqrt{q}$.

in the sign and magnitude of the quadrupole-quadrupole (Q-Q) interactions due to their random locations is modeled[9] by a lattice of quadrupoles with independent random pair interactions,

$$H = -\sum_{(ij)} \sum_{\substack{m,n \\ k,l}}^{3} J_{ij}^{mnkl} f_i^{mn} f_j^{kl} \ . \tag{1}$$

The properties of the system depend on the symmetries of the tensor J_{ij}^{mnkl}. A scalar interaction

$$J_{ij}^{mnkl} = J_{ij}(\delta^{mk}\delta^{nl} + \delta^{ml}\delta^{kn})$$

corresponds to a system with full global rotational invariance. This invariance ensures that the high-temperature phase is truly disordered, i.e., that the quadrupolar-glass (QG) order parameter,

$$q = \tfrac{3}{2} \sum_{m,n=1} [\langle f_i^{mn} \rangle^2] \ , \tag{2}$$

is zero at high T. Here $\langle \cdots \rangle$ denotes a thermal average and $[\cdots]$ an average over the ensemble of J_{ij}'s. In this model, long-range ferroelastic order, represented by nonzero $[\langle f_i^{mn} \rangle]$, may develop at low T even if the mean of J_{ij} is zero. On the other hand, the elastic Q-Q interaction has large anisotropic components which are not canceled if the quadrupoles are located at random.

A more physical choice is a randomly anisotropic interaction where each of the components of the tensor J_{ij}^{mnkl} is an independent random variable with the same distribution, apart from the obvious symmetries: $J_{ij}^{mnkl} = J_{ij}^{nmkl} = J_{ij}^{mnlk}$. We will assume that $[J_{ij}^{mnkl}] = 0$, $[(J_{ij}^{mnkl})^2] = 3J^2/2z$, where z is the number of neighbors. Note that although the local environment is not invariant under global rotations, the system, on the average, is rotationally invariant. We will ignore the weak bulk crystal-field anisotropy that is present in the real system. This means that our discussion is limited to barriers which are higher than the bulk anisotropy, which is ~ 36 K in $(KBr)_{1-x}(KCN)_x$ crystals.

The randomly anisotropic model does not have long-range ferroelastic order *at any temperature*. However, the lack of any global symmetry in the Hamiltonian leads to the nonvanishing of the QG order parameter q *even at high temperatures*. This can be interpreted as resulting from internal random stress fields which are present at all T, as was noted by Harris and Meyer[11] in the context of mixed ortho-para solid H_2. Nevertheless, if the number of neighbors z is large, the high-T value of q is quite small [of $O(\beta^4 J^4/z)$] and a freezing temperature T_f may be defined loosely as the temperature around which q crosses over to a large value [of $O(1)$]. From inelastic neutron scattering,[12] T_f is estimated to be around 100 K in $(KBr)_{0.5}(KCN)_{0.5}$. Note that the elastic Q-Q interactions fall off as R^{-3} at large distances; hence the effective z may be fairly large. In the extreme mean field limit, $z = N$, the high-T value of q is zero for infinite N, leading to a sharp transition for q at T_f. The smooth increase of q (in a finite range system) does not exclude the possibility of having a sharp QG transition which marks the appearance of many degenerate QG states separated by infinitely high barriers. This transition would be similar to that which occurs in spin glasses in the presence of (uniform or random) external fields.[13,14] The most direct observation of such a transition is the appearance of glassy features such as a strong metastability and irreversibility in the response to an external stress. We will denote the temperature at which this transition occurs by T_g. Mean-field theory has $T_f = T_g = J\sqrt{2/15}$.

We now turn to discuss the dielectric relaxation in the system. We will assume that the interaction between the small electric dipoles of the molecules is small compared to the Q-Q interactions, so that no ordering of dipoles occurs *at equilibrium* in the interesting temperature regime. Nevertheless, the internal stress fields generated by the freezing of the quadrupoles creates local anisotropy barriers which slow considerably the 180° rotation of the molecules. Hence, it is reasonable to assume that the dielectric relaxation is dominated by thermal activation processes with relaxation times $\tau(V) = \tau_0 e^{V/T}$, where V is the height of the local anisotropy barrier. The distribution of relaxation times is then determined by the distribution of V which will be calculated here using mean-field theory. We will use first the "replica symmetric" theory, and will discuss later on its region of validity. Within this simple mean-field theory the effective single-ion Hamiltonian is $H_i = -\sum_{m,n} h_i^{mn} f_i^{mn}$, where the local stress tensor $\underline{h}$ is a random 3×3 symmetric matrix[15] with a Gaussian distribution,

$$P_0(\underline{h})D\underline{h} = (2\pi^2\sigma^4)^{-3/2} \prod_{\substack{m,n \\ (m \leqslant n)}} dh^{mn} \exp\left[-\frac{1}{2\sigma^2}\sum_{m,n}(h^{mn})^2\right] \ , \tag{3}$$

where $\sigma = J\sqrt{q}$.

The static and dynamic behavior of the local quadrupoles depend on the eigenvalues of the local fields h^{mn}. Let us denote the eigenvectors and eigenvalues of h_i^{mn} by $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ and h_1, h_2, h_3, where $h_1 \geqslant h_2 \geqslant h_3$. At low temperatures $\hat{\mathbf{n}}_i$ will be almost completely aligned along the direction $\mathbf{e}_1$ of the largest eigenvalue of $\underline{h}_i$. The most favorable path for a 180° flip will then be by a rotation around the axis $\mathbf{e}_3$, the energy barrier height being $V = h_1 - h_2$. Thus, *the probability distribution of the barriers for dipolar relaxations is just the distribution of the level spacing in a Gaussian ensemble of 3× 3 symmetric matrices.* The joint probability distribution of the eigenvalues $\{h_m\}$ equals[9]

$$P_0\{h_m\} = \sigma^{-6}\frac{\pi}{\sqrt{2}}(h_1-h_2)(h_1-h_3)(h_2-h_3) \times \exp\left[-\frac{1}{2\sigma^2}\sum_{m=1}^{3} h_m^2\right] \ , \tag{4}$$

from which one obtains for $P(V) = P(h_1 - h_2)$,

$$P(V) = \frac{\sigma^2}{2} e^{-V^2/3\sigma^2}\left[\sqrt{3/4\pi}\frac{V}{\sigma} + e^{V^2/12\sigma^2} \times [1 - \mathrm{erf}(V/2\sqrt{3}\sigma)]\left[\frac{3}{2} - \frac{V^2}{4\sigma^2}\right]\right] \ . \tag{5}$$

The result is plotted in Fig. 1. $P(V)$ has a clear asymmetric shape. Its maximum is at $V \simeq 1.15\sigma$, whereas the mean barrier is 1.5σ. As $V \to 0$, $P(V)$ vanishes linearly, in accord with the level repulsion property of random matrices. Note that the shape of $P(V)$ is independent of temperature (or other parameters) except for the overall scale $\sigma(T)$, which is expected to decrease with T. In mean-field theory, σ vanishes at T_f as $\sqrt{T_f - T}$, but as was stated above, in

real systems, σ will decrease to a low value as T approaches T_f. In any case, when T becomes of the order of σ, the above thermal activation picture breaks down.

It is well known that the replica symmetric theory upon which the results (3)–(5) are based is unstable below T_g. In the correct mean-field theory the contributions from the neighbors to the local fields are correlated and this leads to a modification of their distributions. Simulations of the internal fields in short-range spin glasses also exhibit deviations from a Gaussian distribution.[6] Nevertheless, in both the mean-field theory[16] and in the simulations[6] the deviations are substantial only at low temperatures. Thus, the above results may be a reasonable approximation for $T \lesssim T_g < T_f$. On the other hand, at very low temperatures, modifications of the Gaussian distribution (3) are expected.

Calculation of the *exact* mean-field theory involves evaluation of an order function $q(x)$ and is impossible to carry out at low T even in an Ising spin glass. We will use here an approximation theory[7] in which $q(x)=0$ for $0<x<\bar{x}$ and $q(x)=q$ for $\bar{x}<x<1$. Although the phase with a single-step function is not stable at low T, it is, in the case of the QG, a good approximation to the correct solution at all temperatures.[7] Let us define the effective single-ion partition function,

$$Z(\underline{h}_i)=\int d\hat{\mathbf{n}}_i \exp\left(\beta \sum_{m,n} h_i^{m,n}\hat{n}_i^m \hat{n}_i^n\right) .$$

Within the above mentioned mean-field theory, the distribution of $\underline{h}$ is found to be

$$P(\underline{h})=A^{-1}P_0(\underline{h})[Z(\underline{h})]^{\bar{x}} , \tag{6}$$

where $P_0(\underline{h})$ is the Gaussian distribution, Eq. (3), and A is the normalization constant.

$$A=\int D\underline{h} P_0(\underline{h})[Z(\underline{h})]^{\bar{x}} . \tag{7}$$

The parameters q (which appears via $\sigma=J\sqrt{q}$) and $\bar{x}$ are determined by the saddle-point equations $\partial f/\partial q=\partial f/\bar{x}=0$, where the replica free-energy f per ion is given by [17]

$$f(q,\bar{x})=\frac{\beta J^2}{6}(1-q)^2-\frac{\bar{x}\beta J^2}{6}q(1+q)+(\beta\bar{x})^{-1}\ln A . \tag{8}$$

We first present in some detail the *zero-temperature limit* of the theory. Assuming $\beta J\to\infty$, one obtains $q\to 1$ (i.e., $\sigma\to J$) and $\bar{x}\to 0$ such that $a\equiv\bar{x}\beta\sigma^2$ remains finite. Also at low T, $\hat{\mathbf{n}}_i$ is oriented along the direction $\mathbf{e}_1$ of the maximum eigenvalue h_1 of $\underline{h}$, so that $Z^{\bar{x}}\to e^{\beta\bar{x}h_1}=e^{ah_1/\sigma^2}$, and hence by Eq. (6)

$$P(\underline{h})=A^{-1}P_0(\underline{h})e^{ah_1/\sigma^2} . \tag{9}$$

This result implies rather complicated correlations among the elements of $\underline{h}$. Nevertheless, the ensemble of $\underline{h}$ is still rotationally invariant, i.e., $P(\underline{h})$ depends explicitly only on the eigenvalue $\{h_m\}$. Consequently, a generalization of the level repulsion result (4) to an arbitrary rotationally invariant ensembles leads to the following distribution of the eigenvalues:

$$P\{h_m\}=C(h_1-h_2)(h_1-h_3)(h_2-h_3)\times\exp\left(-\frac{1}{2\sigma^2}(h_1-a)^2-\frac{1}{2\sigma^2}(h_2^2+h_3^2)\right) , \tag{10}$$

where $C=A^{-1}\sigma^{-6}\sqrt{2}/\pi\exp(a^2/2\sigma^2)$.

The result (10) is physically plausible. The effect of the low-T correlations is to enhance the stability of the state by shifting the distribution of the maximum eigenvalue of the local stress field to larger values. Using Eq. (10) to evaluate the probability distribution of h_1-h_2, we obtain

$$P(V)\propto Ve^{-(V-a)^2/3\sigma^2}\left\{\frac{1}{2\sigma}\sqrt{3/\pi}(V+a)+e^{(V-a)^2/12\sigma^2}\left[1-\mathrm{erf}\left(\frac{V-a}{2\sqrt{3}\sigma}\right)\right]\left[\frac{3}{2}-\frac{V^2}{4\sigma^2}+\frac{a^2}{4\sigma^2}\right]\right\} , \tag{11}$$

where, at $T=0$, σ is simply J. The parameter a is determined by a variation of the zero-T limit of Eq. (8),

$$E/J=-(a/3J)+(J/a)\ln A , \tag{12}$$

where $A=\int\pi\, dh_m\, P_0\{h_m\}e^{ah_1/J^2}$. Solving $\partial E/\partial a=0$ numerically yields $a\simeq 1.3J$. The zero-T result, Eq. (11), with $a=1.3J$ is plotted in Fig. 2(b). We have also evaluated numerically $P(V)$ at all $T<T_g$, using the above replica theory, Eqs. (6)–(8). The result for $T=0.5T_g$ is plotted in Fig. 2(a). We also present in Fig. 2 the temperature dependence of $\sigma=J\sqrt{q}$ which sets the "scale" of V. The results of Figs. 1 and 2 show that at all temperatures $P(V)$ vanish linearly with V at the origin. Decreasing T has the effect of shifting the bulk of the distribution to larger values.

The present theory predicts significant deviations of $P(V)$ from the Gaussian form, which has been deduced from the dielectric measurements of Ref. 1. Also, the predicted ratio between the maximum barrier and the width of $P(V)$, $V_0/\Delta V\sim 1.8$ (at $T=0$) is smaller than the observed value $V_0/\Delta V\sim 3.1$. These discrepancies may point to the inadequacies of the mean-field approximation. In particular, the observed barriers in $(KBr)_{0.5}(KCN)_{0.5}$ may be associated with a correlated motion of a *group* of quadrupoles rather than an isolated 180° flips of a single molecule. Also, the small but non-negligible dipole-dipole interactions may play an important role in the dipolar relaxation. In the above mean-field description, these interactions do not contribute to the local static fields as long as the dipoles do not undergo a *static* freezing. Finally, it is also possible that at a concentration of $x=0.5$ there is still substantial short-range ferroelastic order, which leads to strong correlations between the local principal axes of the quadrupoles. Further dielectric measurements on wider ranges of frequencies, temperatures, and concentrations will be helpful in clarifying these issues.

Finally, we comment on the low-temperature thermal properties of these crystals. It has been proposed[3] that, with the addition of weak dipole-dipole coupling, the 180° rotations of the CN molecules form a two-level system (TLS) which is the microscopic origin of the time-dependent, linear specific heat observed below ~ 0.1 K. The logarithmic time dependence ($C_v\sim\ln t$) is explained in the

standard TLS theory[18] by assuming a high density of low barrier heights [$P(V) \propto V^{-1/2}$]. Assuming a Gaussian distribution, i.e., $P(V) \approx \text{const}$ leads to $C_v \sim (\ln t - \ln t_0)$.[2,19] If, as we have argued, the distribution of barriers to 180° rotations goes as $P(V) \sim V$, the result would be $C_v \sim (\ln t - \ln t_0)^4$, whereas the observed time dependence in $(KBr)_{0.5}(KCN)_{0.5}$ fits $C_v \sim \ln t$ quite well. This suggests that the origin of the TLS in $(KBr)_{1-x}(KCN)_x$ crystals is not the 180° rotations of the individual CN molecules, but other more complicated degrees of freedom just as in glasses or spin glasses.

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