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Low-frequency dynamics of orientational glasses

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We provide a unified explanation of the low-frequency relaxation and the low-temperature specific heat of the orientational-glass phase of solid ortho-para hydrogen mixtures. The analysis is based on Fisher's and Huse's recent picture of the short-range spin glasses and the domination of the long-term relaxation by low-energy large-scale-cluster excitations.

The orientational glasses[1] [solid ortho-para H_2 mixtures,[2] N_2-Ar mixtures,[3] and the $KBr_{1-x}K(CN)_x$ (Ref. 4) mixed crystals] from a subgroup of the general family of spin glasses which continues to generate intense interest because of the apparently universal low-temperature properties observed for a very diverse range of examples (dilute magnetic alloys, mixed crystals [$Eu_xSr_{1-x}S$ (Ref. 5), $Rb_{1-x}(NH_4)_xH_2PO_4$ (Ref. 6), $KBr_{1-x}K(CN)_x$ (Ref. 4)], dilute mixtures of rotors [ortho-para H_2 (Ref. 2), N_2-Ar,[3] partially doped semiconductors,[7] Josephson junctions arrays,[8] and others). The most striking universal features[1,9] are an apparent freezing of the local degrees of freedom on long-time scales without any average periodic long-range order, characteristic slow relaxations, and history dependence following external field (magnetic, electric, elastic-strain, etc.) perturbations, and a very large number of stable low-energy states (increasing monotonically with the number of active atomic or molecular centers). The existence of a true thermodynamic phase transition has been questioned, but many workers believe that the magnetic moments in the canonical spin glasses such as *Cu*Mn are thermodynamically frozen and that the transition is not purely kinetic.

There has been considerable progress in achieving an understanding of ∞-range Ising spin glasses (in the context of the Sherrington-Kirkpatrick model[10,11] and interest is now turning to develop models for the short-range systems such as $Eu_xSr_{1-x}S$. A new intuitively appealing picture of the short-range spin glasses has been recently offered by Fisher and Huse[12] based on an ansatz for the scaling of low-energy large-scale droplet excitations. They were able to show that spatial correlations decay as a power law of distance, that the ac susceptibility diverges as a power of $\ln\omega$, and that the temporal autocorrelation functions have a characteristic $\log t$ dependence at low temperatures. The purpose of this Rapid Communication is to compare the low-temperature relaxation reported previously[13] for the orientational glass phases of solid ortho-para H_2 mixtures with that predicted by the model of Fisher and Huse. We will also provide a unified quantitative explanation of the low-temperature behavior of the heat capacities and the explicit time dependence of the slow relaxation in terms of the low-energy density of states.

The dilute molecular systems (ortho-para H_2,[2] N_2-Ar mixtures[3]) consist of random arrays of interacting electric quadrupoles and have an interesting analogy with the spin glasses. The ortho-H_2 molecules with orbital angular momentum $J=1$ interact via their electric quadrupole moments while the para species with $J=0$ (a spherically symmetric state) serve as almost ideal diluents. At low temperatures the $J=1$ molecules align along local axes to minimize their highly anisotropic interaction energies achieving a periodic antiferro-orientational ordering in a $Pa3$ structure for high quadrupole concentrations. In dilute mixtures ($X<55\%$), only short-range order with a random variation of molecular alignments from site to site is observed. Both the local molecular axes ξ_i *and* the local molecular alignments $\sigma_i=\langle 3J_\xi^2-J^2\rangle_i$ vary at random, and in this sense the low-temperature dilute phase has been referred to as a "quadrupolar glass" phase in distinction from an "orientational glass" in which only the axes are randomly oriented. The N_2/A mixtures are examples of classical rotors with the N_2 molecules bearing the active (quadrupole) moments, and in this case also, one observes[3] only a purely local ordering at low temperatures in dilute mixtures. In both cases a smooth growth of local order is observed on cooling and there is no evidence in recent studies for any well-defined phase transition.[14,15] This absence of a clear transition is due to the fact these quenched solid-molecular mixtures do not display broken symmetry.[14] Solid H_2 remains hcp down to the lowest temperatures studied for $X<55\%$, and the random occupation of lattice sites leads to the existence of local electric field gradients, the field conjugate to the local order parameter, which plays the same role as the magnetic field for the dipolar spin glasses. This random local field therefore makes the problem of local orientational ordering in random mixtures equivalent to the local dipolar ordering in spin glasses in the presence of random magnetic fields, and thus smears out any phase transition. It should be emphasized, however, that the gradual transition to the glass state in these systems involves strong cooperativity as evidenced by Monte Carlo calculations[16] and studies of the temperature dependence of the relaxation rates.

The quasistatic local orientational order parameters are the alignments $\sigma_i=\langle 1-3/2J_z^2\rangle_i$ (assuming axial symmetry, otherwise one must introduce an additional order parameter) and the corresponding autocorrelation functions $C_i(t)=\sigma_i(0)\sigma_i(t)$ can be studied directly by NMR. The nuclear intramolecular dipole-dipole interaction is directly proportional to σ_i for each molecule, and the NMR line shape can be understood in terms of a broad distribution of local order parameters. The NMR relaxation rates are determined by the Fourier components of the $C_i(t)$ at ω_0 and $2\omega_0$, where ω_0 is the Larmor frequency. Conventional NMR relaxation studies (measurements of the longitudinal and transverse relaxation times) probe the molecular dynamics for relatively short time scales, typically μsec–msec, and special techniques are needed to explore the slow relaxation regime.

Nuclear-spin-stimulated echoes have proved to be very effective for the study of ultraslow molecular motions both in the molecular orientational glasses[13] and in ordinary ("window-pane") glasses.[17] The stimulated echoes are formed by a three-pulse sequence. Two initial rf pulses separated by a short time τ prepare the system with a "fingerprint" of the local order parameters σ_i; the *local* nuclear-spin temperatures for a 90_x-τ-90_x sequence depend on σ and vary as $\cos(D_i\sigma_i\tau)$, where $D_i = DP_2(\cos\delta_i)$. $D = 5.438\times10^5$ rad/sec specifies the strength of the intramolecular nuclear dipole-dipole interaction, and δ_i is the angle between the mean symmetry axis of the molecule at site i and the applied magnetic field. After a waiting period t_w (short compared to the nuclear-spin-lattice relaxation time T_1, but long compared to the transverse relaxation time T_2), a third rf pulse is applied (generally a 90° pulse) and a stimulated echo is formed a time τ after this "reading" pulse with amplitude[13]

$$A(t_w) = C\langle\langle\cos[D_i\tau\sigma_i(0)]\cos[D_i\tau\sigma_i(t_w)]\rangle\rangle\,. \qquad (1)$$

The double angular brackets refer to a configurational average, and C is a constant ($\propto T^{-1}$). The important point is that if the local order parameters σ_i remain fixed during the "waiting period," there is no damping of the stimulated echo, while if σ_i changes during t_w due to local reorientations, then the contribution to the echo can be severely attenuated. The product $D\tau$ can, in practice, be made very large, and this method can then be used to study ultraslow motions in solids.

The most striking result observed for the decay of stimulated echos has been a characteristic logarithmic decay seen at long times[13] (Fig. 1) for low temperatures. This behavior has been seen for both solid ortho-para H_2 mixtures and for solid N_2-A mixtures. Yu, Washburn, Calkins, and Meyer[18] reported only the initial slopes for the decay of their stimulated echos, but their long-time behavior is in qualitative agreement with the slow relaxation studies[13] (Fig. 1). This logarithmic decay can be understood quantitatively within the context of the scaling model of Fisher and Huse.[12] The low-energy excitations which dominate the long-distance and long-time correlations are given by *clusters* (or droplets) of coherently reoriented spins. The basic assumption that the density of states (near $E = 0$) for a cluster of size L scales as $L^{-\theta}$ with $0 < \theta \leqq (d-1)/2$ allow one to regard the thermally excited droplets as dilute and "therefore treated as noninteracting two-level systems." Fisher and Huse further assumed that the free-energy barriers E_B (for cluster formation) scale as $E_B \sim \Delta L^{\psi}$ with $\theta \leqq \psi \leqq d-1$. The tunneling rate for a characteristic barrier E_B at temperature T is $\Gamma(E_B) = \Gamma_0\exp(-E_B/kT)$ where Γ_0 is the characteristic attempt frequency for clusters of this size. In the long-time limit Γ_0 is reasonably well defined because it is associated with a characteristic cluster size. In the hierarchical process of relaxation, the low-energy barriers (small clusters) must be overcome before the larger ones, because the dynamics with the faster degrees of freedom constrain the slower ones. In a time t the only barriers crossed will be those satisfying $0 < E_B < E_{\max}(t)$ where $E_{\max}(t) = k_BT\ln\Gamma_0 t$. Any barriers crossed lead to significant changes in the local order parameters, and the stimulated echoes contributed by these groups of molecules will be negligible, while those groups for which the barriers are not overcome will still contribute to the echo. The amplitude of the total stimulated echo signal is then simply

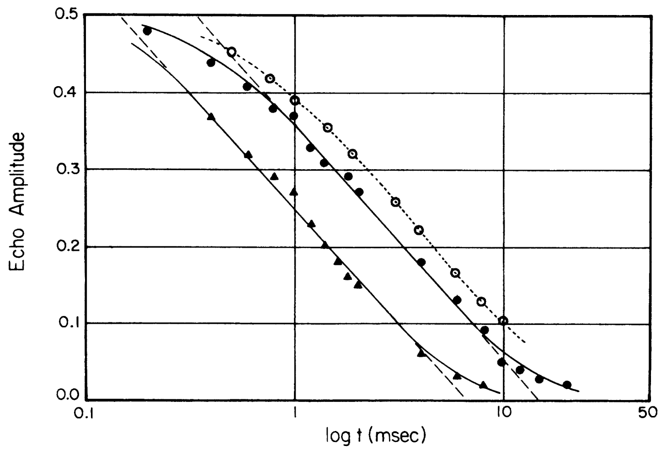

FIG. 1. Comparison of observed decay of nuclear-spin-stimulated echos in solid ortho-para H_2 mixtures with decay calculated from the heat-capacity data (dashed line). Solid circles, $D\tau = 1.7$; triangles, $D\tau = 3.5$ (Ref. 13, $T = 0.22$ K, $X = 0.54$); open circles, $D\tau = 7.77$ (Ref. 17, $T = 0.153$ K, $X = 0.43$).

$$A(t) = \frac{C}{2}\left[1 - \int_0^{E_{\max}(t)} P(E_B)\,dE_B\right]. \qquad (2)$$

At low temperatures, we need only consider the density of states near $E \simeq 0$,

$$A(t) = \frac{C}{2}[1 - k_BP(0)T\ln(t/t_0)]\,.$$

If σ changes by the order of unity in a time Γ_0^{-1}, then the characteristic decay time for $A(t_w)$ is $t_0 \simeq \pi/(D\tau)\Gamma_0$. The prefactor $P(0)$ can be determined from the low-temperature behavior of the heat capacity.

We can associate a simple two-level system with the ortho-H_2 molecules which have angular momentum $J = 1$, the states $J_{\xi_i} = \pm1$ being separated from the state $J_{\xi_i} = 0$ by a gap $3\Delta_i$. (The states $J_\xi = \pm1$ are degenerate if there are no interactions which break time-reversal symmetry.) At low energies we can, following the above arguments, identify the low-energy excitations (which determine C_v at low T) with a broad distribution $P(\Delta)$ of energy gaps for $0 < \Delta < \Delta_0$. Candela, Buchman, Vetterling, and Pound[19] interpreted the NMR line shapes in terms of $P(\Delta)$. Identifying $P(\Delta)$ with the density of low-energy barriers, $P(E)$, we have

$$\frac{C_v}{NXR} = \tfrac{2}{3} t\Delta_0 \int_0^{3/t} \frac{u^2 du}{4e^{-u}+4+e^{u}} P(E) \,, \tag{3}$$

where the reduced temperature $t = k_B T/\Delta_0$, $u = 3E/k_B T$, and X is the ortho concentration. C_v has a linear temperature dependence at low T in close resemblance to the temperature behavior observed by Haase, Perrell, and Saleh.[20] A flat barrier-height distribution (dashed lines, Fig. 2) does not describe the high-temperature data[21–23] very well, and we adjusted the density of states $P(E)$ to provide the best overall fit (solid lines, Fig. 2) to the low-temperature data for $X = 0.45$,[20] and the high-temperature data for $X = 0.43$ reported by Meyer and Washburn.[22] The density of states at low energies (inset of Fig. 2) is $P(0) = 0.55 \pm 0.05$. For this value of $P(0)$ the stimulated echo decay is calculated to be

$$A^{\mathrm{calc}}(t) = \mathrm{const} - 0.28 \log_{10}(t/t_0) \,, \tag{4}$$

which is to be compared with the observed decay (triangles in Fig. 1)

$$A^{\mathrm{obs}}(t) = 0.55 - 0.30 \log_{10}(t/t_0) \tag{5}$$

at 0.22 K for $X = 54\%$. The agreement is remarkably good.

Furthermore, the shift of the two experimental plots in Fig. 1 (for $\tau = 12.5$ μsec and $\tau = 25$ μsec) is also quantitatively understood in the context of this model. The only parameter dependent on τ is t_0, which scales linearly with $1/D\tau$. For the same "reading-time" t, the relative shift of the decays (in the log$t$ regime) is

$$\left[\frac{A(t)}{A_{\max}}\right]_{\tau = 12.5\,\mu\mathrm{sec}} - \left[\frac{A(t)}{A_{\max}}\right]_{\tau = 25\,\mu\mathrm{sec}} = k_B P(0) T \ln 2 \,, \tag{6}$$

and is independent of the microscopic rate Γ_0. The experimental shift gives $k_B P(0) = 0.6 \pm 0.1$ K^{-1} in good agreement with the value deduced from the slope of the log$t$ decay.

The *only* unknown parameter in the above analysis is the "attempt" frequency Γ_0 which determines t_0. The experimental values of t_0 can be understood using the mean-field arguments of Sethna and co-workers[24] who estimate $\Gamma_0 \simeq \Gamma_{(\mu)} e^{-E_F/kT_g}$, $\Gamma_{(\mu)}$ being the microscopic rate ($\sim h/ma^2$), E_F the mean-field free energy, and T_g the characteristic temperature for the establishment of a nontrivial order parameter distribution (e.g., $\langle\sigma\rangle_{\mathrm{rms}} = 0.5$). For H_2, $\Gamma_{(\mu)} \simeq 10^{12}$ sec^{-1}, $E_F \simeq 6$ K, $T_g \simeq 0.35$ K, and we find $\Gamma_0^{-1} = 2.8 \times 10^{-5}$ sec and $t_0 \simeq 10^{-4}$ sec (using $D\tau = 3.5$). This value of t_0 provides a measure of the time scale over which the molecular orientations can be considered to be frozen. The essential point is that the *time scale* of the slow relaxations in the glass phase is simply related to the low-temperature behavior of the heat capacity.

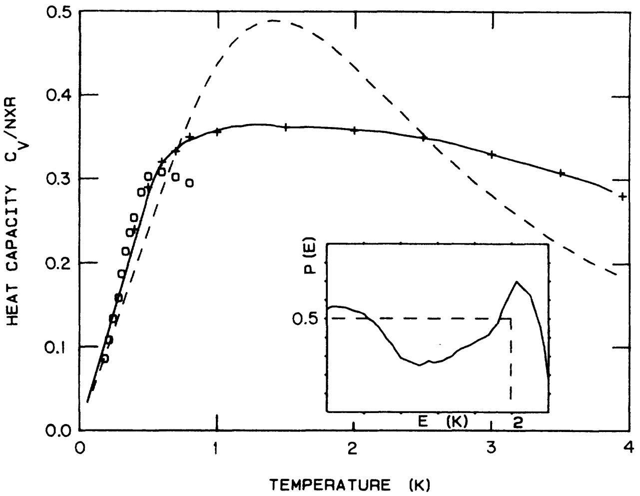

FIG. 2. Calculated low-temperature heat capacity for solid ortho-para H_2 mixtures: Dashed line is for a continuous distribution of two-level systems, the solid line refers to a distribution adjusted to fit the high-temperature data (+) (Ref. 17). The open circles refer to the data of Haase *et al.* (Ref. 20). The two distributions for $P(E)$ are shown in the inset, the solid line being the $P(E)$ needed to fit the heat-capacity data.

The specific-heat measurements of the solid-hydrogen mixtures are expected to show a characteristic time dependence analogous to that seen for amorphous Si (Ref. 25) and $KBr_{1-x}(KCN)_x$ mixtures.[4] We expect that low-temperature C_v measurements carried out for short time scales of 0.1–10 msec would be smaller by an order of magnitude than those for time scales greater than 100 msec for $T < 50$ mK (i.e., well below the onset of the glass state). Measurements of this nature would provide a valuable test of the model presented here.[26] The characteristic times t_0 are much shorter than the spectral-diffusion time scale (~ 1 sec) seen by the recovery of holes burnt in the NMR line shape.[27]

In conclusion, we have offered a unified explanation of the slow-relaxation behavior observed by NMR studies and the low-temperature heat capacity of the orientational glass phase of solid hydrogen in terms of the density of low-energy excitations in the system. The density of states can also be used to determine the temperature dependence of the spin-lattice relaxation. The analysis presented used Fisher's and Huse's new picture of the short-range Ising-spin-glass phases based on the scaling of low-energy large-scale-cluster excitations, which is also expected to be valid for vector spin glasses.

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