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This paper is dedicated to the late Svyatoslav Gabuda

MOLECULAR GLASSES: NMR AND DIELECTRIC SUSCEPTIBILITY MEASUREMENTS

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We review the properties of simple diatomic molecular glasses as explored by nuclear magnetic resonance techniques and measurements of the dielectric susceptibility. We focus on the behavior of classical molecular rotors formed by solid N_2—Ar mixtures and discuss the time dependent behavior in terms of replica symmetry breaking theories.

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INTRODUCTION

Understanding the underlying physics of glass systems remains a major challenge for contemporary condensed matter physics. Of all the different types of glasses: fragile glasses [1], spin glasses [2], orientational glasses [3—6], and quadrupolar glasses [7, 8], the simple molecular glasses [9] provide a particularly straightforward case where the characteristic glass features of frustration and disorder can be formulated clearly and realized experimentally without ambiguity. These systems provide a valuable test for generalized theories of glass formation and dynamics. In this review we will discuss the properties of molecular glasses formed by solid mixtures of diatomic molecules and isoelectronic diluents, and in particular solid *ortho-para* H_2 and solid N_2—Ar alloys and analyze the characteristic hysteresis in terms of a generalized fluctuation-dissipation theorem introduced by Cugliandolo and Kurchan [10].

Long-range orientational ordering of the molecular axes of pure diatomic molecular solids occur in several cases — *ortho*-H_2, N_2, O_2 … at low temperatures. Note that for hydrogen the orbital angular momentum J is a good quantum number with $J = 1$ for *ortho*-H_2 molecules at low temperatures and $J = 0$ for spherical *para*-H_2 molecules. *Ortho*-H_2 and N_2 molecules possess an electric quadrupole moment as well as an interatomic axis both of which are free to fluctuate with respect to the molecule′s fixed center of mass in the lattice structure at high temperatures. At low temperatures, however, the anisotropic electrostatic interactions (mainly quadrupole-quadrupole) between the molecules become significant and the axes of the molecules orient parallel to specific crystalline axes to lower the total free energy. In the case of solid H_2 and solid N_2 the gain in energy is sufficient to generate a lattice change from h.c.p. to f.c.c. The final long-range ordered structure is a Pa3 structure consisting of four interpenetrating simple cubic sub-lattices with the molecular alignments parallel to a given body diagonal of one of the sub-lattices. This structure is shown in Fig. 1.

The frustration for the interacting quadrupoles in the f.c.c. structure is geometrical in nature and arises because of the anisotropy of the quadrupole-quadrupole interactions. The minimum energy for two axial quadrupoles is a mutually perpendicular arrangement that cannot be realized for any close packed lattice. This is analogous to the frustration of the magnetic interactions between vectorial spins

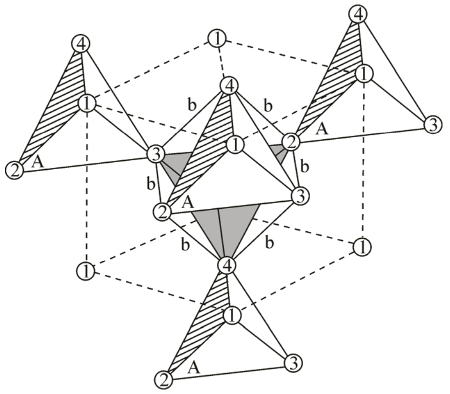

Fig. 1. Schematic representation of the Pa3 structure with four interpenetrating sub-lattices one of which is shown by the dotted lines. The nearest neighbor interactions form highly frustrated corner-connected tetrahedra. Each number designates molecules with the same alignment axis parallel to one of the four body diagonals of the f.c.c. lattice (After Fig. 2 of ref. [8])

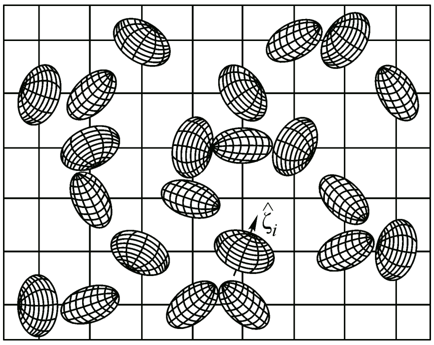

Fig. 2. Illustration of a quadrupolar glass by ellipsoids of different shapes and sizes with respect to the alignment axes ς_i. The shape of the ellipsoid represents the probability distribution for the intermolecular axes (After Fig. 4, *c* of ref. [7])

in a triangular or h.c.p. lattice. As quadrupole bearing molecules are replaced by spherical molecules the quadrupoles try to reorient and eventually, below a critical concentration, long range ordering is lost. For solid-*ortho-para* hydrogen mixtures the critical concentration is 55 % and for solid N_2—Ar mixtures it is 77 %. Fig. 2 shows the phase diagram for the orientational ordering in solid *ortho-para* H_2 mixtures. Below the critical concentration one does not observe long range order but only local ordering in the random electrical fields produced by the surrounding molecules. On cooling samples in this low concentration region NMR studies observed a fairly rapid freezing of both the molecular orientations and also the quadrupole moments with respect to those axes, and this lead to the suggestion that these systems formed quadrupolar glasses [7]. If $(\Theta_i(\mathrm{eq}), \Phi_i(\mathrm{eq}))$ are the polar angles for the equilibrium orientation of the molecular axes for molecule *i* with respect to the crystalline axes, and (θ_i,φ_i) designate the instantaneous orientations of the axes with respect to the equilibrium axes, then the classical quadrupolar order parameters are given by the expectation values of the spherical harmonics; $\langle Y_{20}(\theta_i,\varphi_i)\rangle$ and Re $\langle Y_{22}(\theta_i,\varphi_i)\rangle$. For *ortho*-$H_2$ molecules with $J = 1$, these are simply $\sigma = \langle 3J_z^2 - 2\rangle$ and $\eta = \langle J_x^2 - J_y^2\rangle$. There are five order parameters, the axes $\zeta_i = (X_i, Y_i, Z_i)$ for the equilibrium alignment and the quadrupolarization about ζ_i given by (σ_i, η_i). The NMR studies assumed axial symmetry for simplicity and analyzed the NMR spectra for $\eta = 0$ at each site.

The NMR spectra of samples aged below *ortho* concentrations for 50 % showed very broad line shapes that could only be interpreted in terms of a broad distribution of local order parameters σ_i and alignment axes ζ_i. This quadrupolar glass state is illustrated in Fig. 2. The ellipsoidal shapes refer to the degree of quadrupoalrization or value of σ_i at each site. In addition to the line shapes the characteristic molecular re-orientation times τ_Q were also measured by NMR [11] and found to change very rapidly over a small temperature range. Fig. 3 shows the observed variation as a function of temperature resembling the familiar Fulcher—Vogel behavior seen in most glass forming systems. If there was only a distribution of axes

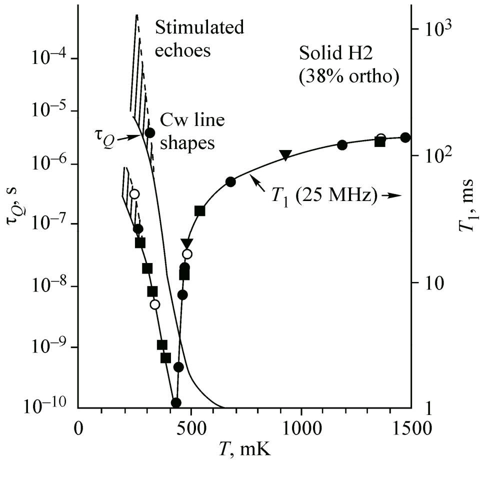

Fig. 3. Temperature dependence of the characteristic rotational times deduced from NMR measurements of the nuclear spinlattice relaxation times T_1 in solid *ortho-para* H_2 mixtures (After Fig. 1 of ref. [11])

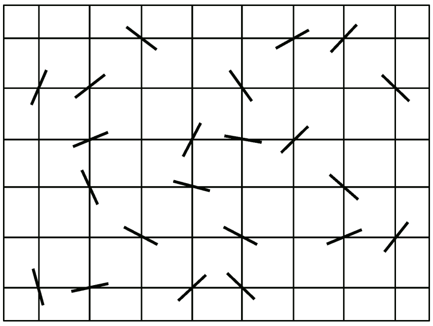

Fig. 4. Illustration of the orientational glass state by rods representing the molecular alignment axes ς_i that vary in direction from one site to another (After Fig. 4, *b* of ref. [7])

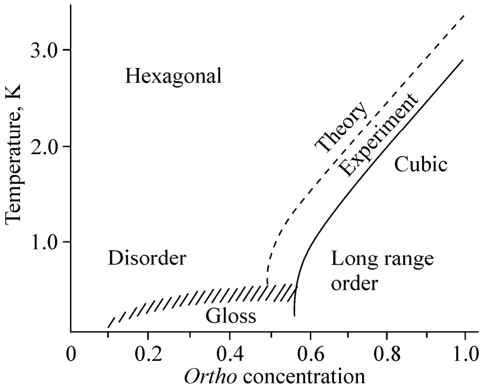

Fig. 5. Schematic phase diagram for solid *ortho-para* hydrogen mixtures. There is no sharp phase transition between the disordered phase and the glass state but a continuous growth of local quadrupolarization over a small temperature interval (After Fig. 1 of ref. [12])

ζ_ι, the line shapes would have been simple Pake doublets and the system would have been described as an orientational glass as pictured in Fig. 4.

The phase diagram for solid *ortho-para* H_2 mixtures is shown in Fig. 5. Long range order in the form of a Pa3 structure is only observed above a critical concentration with *ortho* concentration $x = 55$ %. Below this critical concentration one observes a quadrupolar glass state but there is no sharp transition on cooling into the glass state. In the glass state the characteristic rotational time constants change rapidly with temperature.

The lack of a sharp transition is not unexpected because below the critical concentration the lattice structure is hexagonal close packed and the effect of dilution is to create a local electric field gradient so that for H_2 the transition to the quadrupolar glass state is similar to the cooling of a magnetic spin glass in the presence of a magnetic field. The result is a smeared phase transition but does not change the dramatic temperature dependence of the dynamics.

SIMPLE MODEL OF QUADRUPOLAR GLASS FORMATION

We express the quadrupole-quadrupole interaction between H_2 molecules in terms of the irreducible operator equivalents of the spherical harmonics in the manifold $J = 1$, that is we use

$$\langle JM \,|\, Y_{2m}(i) \,|\, JM\rangle = -(2/5)\langle JM \,|\, O_{2m}(i) \,|\, JM\rangle,$$

where for a molecule at site i

$$O_{20}(i) = \frac{1}{\sqrt{6}}(3J_z^2(i) - J^2), \qquad O_{2(\pm1)} = \mp(J_z J_\pm + J_\pm J_z)(i), \qquad O_{2(\pm2)} = \frac{1}{2}(J_\pm^2).$$

If axial symmetry is preserved in the states we only consider $\langle O_{20}(i)\rangle = \sqrt{6}\sigma_i$.

The interaction Hamiltonian can then be simply written as

$$H = \sum_{ij}\sum\nolimits_{m,n} \Gamma_{ij} O_{2m}(i) O(j)_{2n}^{\dagger},$$

where the Γ_{ij} are the interaction constants. We assume that there is a Gaussian distribution for the Γ_{ij} with probability distribution

$$P(\Gamma_{ij}) = \left(\frac{1}{2\pi\Gamma_1^2}\right)^{1/2} \left[\exp\left\{-\frac{(\Gamma_{ij} - \Gamma_0)^2}{\Gamma_1^2}\right\}\right],$$

where Γ_0 is the mean value and Γ_1^2 is the variance. Using the model of Edwards and Anderson to average over different replicas of an ensemble one can calculate the mean free energy F in terms of the average local alignment $S = \sqrt{6}\,\overline{\langle O_{20}(i)\rangle}$ and average quadrupolarization (the quadrupolar glass order parameter) $Q = \overline{6\langle (O_{20})_{\mu} (O_{20})_{\nu} \rangle}$, where μ and ν refer to different replicas. One finds [12]

$$S = \left(\frac{1}{2\pi}\right)^{1/2} \int e^{1/2y^2} F(\eta)dy,$$

where $\eta = [\Gamma_1 (zQ)^{1/2} y + \Gamma_0 (zS)] / k_B T$ and $F(x) = \left(\frac{1}{2}\right)\left[-1 + \tanh\left(\frac{3}{2}x + \frac{1}{2}\ln 2\right)\right]$.

Here z is the number of nearest neighbors. Similarly,

$$Q = 2 - S - \left(\frac{1}{2\pi}\right)^{1/2} \int e^{1/2y^2} F'(\eta)dy \quad \text{with} \quad F'(x) = \partial F(x)/\partial x.$$

In the case of a fixed interaction with $\Gamma_1 = 0$ we have $Q = 2 - S$ and $3z\Gamma_0 S = \ln\left[\frac{2+2S}{2-2S}\right] \Big/ k_B T$, which is the familiar mean field result for pure *ortho*-H_2 and the solution has a first order phase transition at $T_c = 3z\Gamma_0/(2\ln 2)k_B$. Z is the number of nearest neighbors. For a very broad distribution of interaction constants, the quadrupolar glass parameter becomes $Q = \frac{5}{2} - \frac{27}{2} e^{B^2} erfc(B)$, where $erfc(x)$ is the complementary error function and $B = 3\Gamma_1 (zQ/2)^{1/2}/k_B T$. One finds a non-trivial Q for $T > T_G = \frac{5}{27}\sqrt{\frac{2\pi z}{3}}\Gamma_1 / k_B$. For solid hydrogen T_G has been estimated [12] to be of the order of $0.4x^{1/2}K$ where x is the fractional *ortho* concentration. This result is in reasonable qualitative agreement with the data shown in Fig. 5.

N_2—Ar CLASSICAL ORIENTATIONAL GLASS

In contrast to solid *ortho-para* H_2 mixtures, one case where the symmetry of the lattice is cubic and is a candidate for a sharp transition to a quadrupolar glass state is the classical molecular glass formed by solid nitrogen-argon alloys. N_2 has an electric quadrupole moment and in the pure state undergoes a sharp first order phase transition to a Pa3 structure. Unlike H_2 where the order parameters are the expectation values of spin-1 tensorial operators, the order parameters for N_2 are the expectation values of the spherical harmonics Y_{2m} (θ_i, φ_i), and the local axes of symmetry ς_i. It was known for many years that solid N_2—Ar mixtures formed f.c.c. lattices at both high and low N_2 concentrations with an h.c.p. structure for nitrogen concentrations $57 < x < 77$ % (Fig. 6) [13]. NMR studies of the ^{15}N line shapes showed that for mixtures in the h.c.p. part of the phase diagram the broad spectra observed could only be explained in terms of a quadrupolar glass state with a distribution of both local symmetry axes and local quadrupolarizations [14]. In this range of N_2 concentrations the transition to the glass state occurred over a broad temperature interval similar to the behavior seen for solid hydrogen mixtures.

What is different for the samples with low N_2 concentrations ($x < 57$ %) and low temperatures ($T < 10$ K) is the formation of a clear orientational glass state that has approximately constant values of the quadrupolarizations at each site [8, 15]. This state was determined from the unique NMR line shapes observed in the concentration range $40 < x < 56$ %. At concentrations below 40 % one observes the line shapes characteristic of a quadrupolar glass state similar to those observed in the h.c.p. structure for $57 < x < 77$ %.

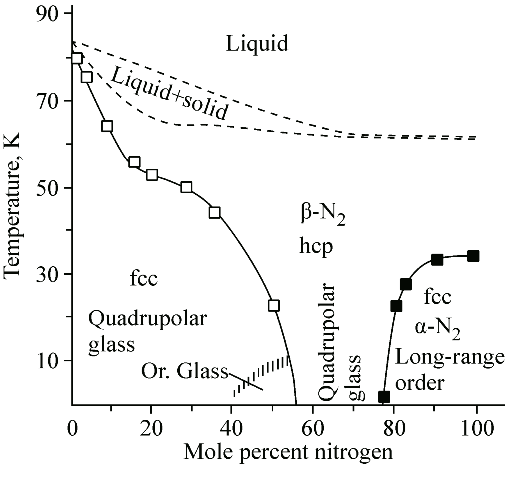

Fig. 6. Phase diagram for solid N_2—Ar mixtures, showing the cubic and hexagonal lattice structures and the ranges for quadrupolar and orientational glass formation (After Fig. 4 of ref. [8])

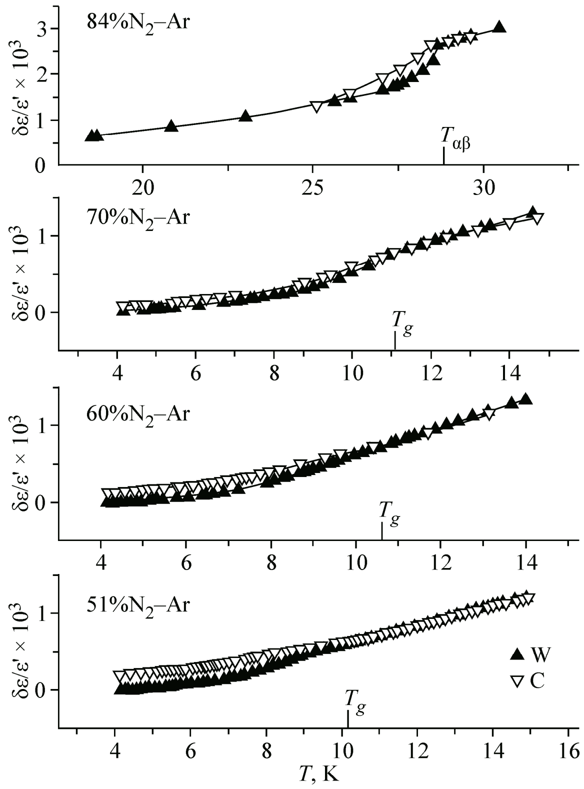

Fig. 7. Observed hystereses in the temperature dependence of the ac dielectric susceptibility for solid N_2—Ar mixtures. Closed hystereses were observed for N_2 concentrations of 84 % and 80 %. The sharp onset of the hystereses is the first observation of a sharp tran sition to an orientational glass state in solid N_2—Ar mixtures (After Fig. 1 of ref. [9])

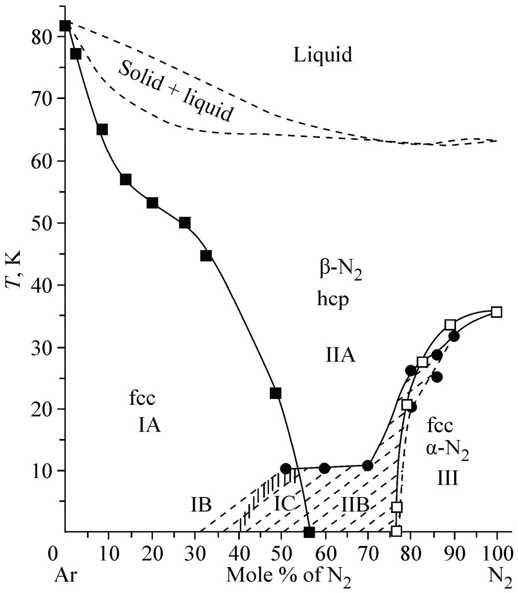

Fig. 8. Modified phase diagram for orientational ordering in solid N_2—Ar mixtures. The squares refer to lattice structural changes seen in X-ray studies by Barrett and Meyer [13] and the closed circles refer to the sharp onset of hysteretic behavior observed in dielectric susceptibility measurements [9]. The dashed region represents quadrupolar glass states (IB and IIB) except for the the $39 < x < 50$ % region IC which is an orientational glass (After Fig. 1 of ref. [22])

In order to study the dynamics of the classical orientational glass states of N_2—Ar mixtures the dielectric susceptibilities were measured at audio frequencies [9, 16], as a function of temperature using a high sensitivity capacitance bridge [17]. The anisotropic component of the dielectric susceptibility α_{aniso} depends on the local orientational order parameters (σ_i, η_i) according to $\alpha_{\text{anizo}} = -\frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp})\{\sigma_i P_2[\cos\Theta_E(i)] + \frac{3}{2}\eta_i \sin^2\Theta_E(i)\cos[2\Phi_E(i)]\}$ where $(\alpha_{\parallel}, \alpha_{\perp})$ are the polarizabilities parallel and perpendicular to the molecule's inter-nuclear axes, respectively. $(\Theta_E(i), \Phi_E(i))$ designate the polar angles for the orientation of the applied electric field relative to the local symmetry axes for each molecule *i.* The susceptibilities were measured by slowly sweeping the temperature of the samples from above the transition temperatures down to 4 K and then reversing the temperature sweep. The remarkable result shown in Fig. 7 is the observation of very distinctive hystereses in the values of the susceptibilities with well-defined onset temperatures. For the long range ordered cubic *Pa*3 structure the hysteresis is closed and is interpreted as evidence of a narrow region of a glass state in a small temperature interval between the disordered β-phase and ordered α-phase (*Pa*3 structure) as shown in Fig. 8. The open hysteresis loops imply that the glass states persist down to 4 K. This is consistent with the NMR studies [15].

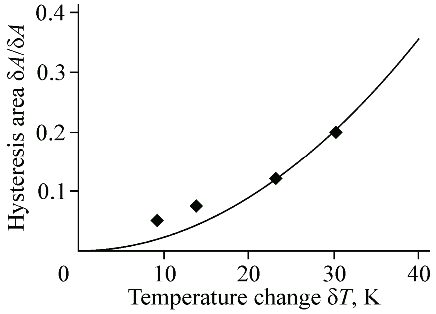

Fig. 9. Comparison of hysteresis loops for thermal sweeps shown in Fig. 6 with expectations (solid line) for simple replica symmetry breaking (After Fig. 4 of ref. [9])

GENERALIZED FLUCTUATION DISSIPATION THEOREM

A very effective test of the interpretation of the NMR and dielectric susceptibility measurements for N_2—Ar mixtures in terms of frustrated glass phases is to compare the observed thermal histories with those predicted [18—20] by replica symmetry breaking models for regular spin glasses. Cugliandolo and Kurchan [10, 21] have developed a generalized fluctuation-dissipation relation for simple replica symmetry breaking in terms of a spin-glass correlation function $C(t, t_\mathrm{w}) = \langle q_i(t_\mathrm{w})q_i(t + t_\mathrm{w})\rangle$, where t_w is a waiting time at low temperatures. Below a characteristic dynamical freezing temperature T_G the change in the response function depends on the wait time t_w because of the changes in the free energy landscape during that time. They showed that the integrated response function satisfies a general off-equilibrium fluctuation-dissipation theorem given by

$$R_I(t,t_\mathrm{w}) = \frac{1}{k_\mathrm{B}T}\int_{C(t,t_\mathrm{w})}^{C(t,t_\mathrm{w})}\chi(C)dC,$$

where $\chi(C)$ is the relevant susceptibility. For large waiting times the derivative $\partial R_I/\partial C$ becomes a universal function. In this model Pilla et al. [22, 23] showed that the area of the hysteresis loops for the dielectric susceptibility defined by

$$A = \sum k_\mathrm{B}T(\Delta R_I)$$

scales as $(\Delta T/T_G)^2$. Fig. 9 shows the variation of the area of the hysteresis with temperature. The solid blue line is the result predicted for the generalized fluctuation dissipation theorem. The agreement is qualitatively very good.

CONCLUSIONS

Classical molecular glasses in the form of solid N_2—Ar mixtures show clear signatures of orientational glass states at low temperatures. Careful NMR studies show that the low temperature states consist of a broad distribution of glass parameters, namely the local symmetry axes and the degree of quadrupolarization with respect to those axes provided the concentration of the N_2 molecules is below a critical value. In addition sharp onsets of thermal hysteretic behavior are observed and the integrated response functions over the hysteresis loops show the expected behavior of Cugliandolo and Kurchan′s generalized fluctuation dissipation theorem. We conclude that the N_2—Ar mixtures form orientational glass states obeying replica symmetry breaking and represent a fertile ground for studying the fundamental physics of this class of spin glass states.

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