Orientational Glasses

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Abstract

In this paper we present a brief conceptual introduction to orientational glasses. Orientational glasses are used to study randomly diluted molecular crystals, where crystals composed of molecules with electric multipolar moments are diluted with molecules with no orientational degrees of freedom. The disorder introduced by dilution induces a glassy state at low temperatures where the orientational degrees of freedom are in random frozen-in configurations. After a general introduction to the field, some experimental observations of the glassy state are introduced followed by a discussion of some mean field-type models applied to the quadrupolar glass. Finally, results from computer simulations are presented and discussed.

1 Introduction

In this paper, we present *Orientational glasses* (OG) as a model system to study randomly diluted molecular crystals at low temperature. By randomly diluted molecular crystals we mean a mixture of molecular species which posses different types of electric multipole moments (dipolar, quadrupolar, octopolar, etc) arranged in a well defined crystal structure. Even though systems with many types of multipole moments fall under this category, we will concentrate on systems composed of molecules whose primary interaction is quadrupolar, diluted with molecules that have no multipole moments.

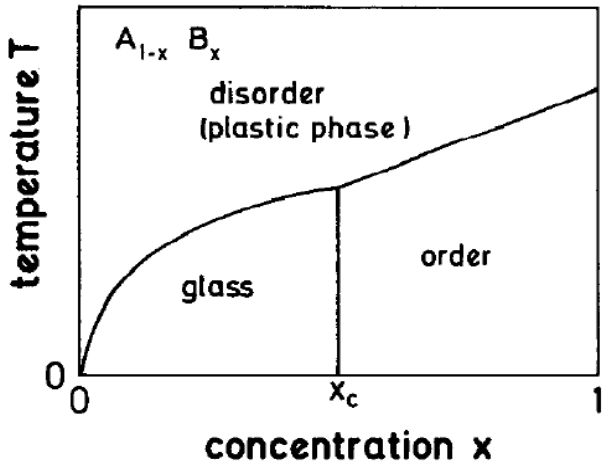

Figure 1: Schematic diagram of $A_{1-x}B_x$ mixed crystals in the (x,T) plane. A represents the molecule with no orientational degrees of freedom.

In the low dilution regime (high concentration of the quadrupolar molecules) the orientational degrees of freedom undergo an order-disorder transition from an isotropic state at high temperature, where the angular distribution of the quadrupole moments is isotropic resembling a freely rotating molecule, to a highly anisotropic state at low temperatures characterized by the emergence of long-range order. The addition of site disorder, by adding molecules with no quadrupole moment, significantly reduces the long-range orientational order at low temperatures until a critical concentration is reached where the order disappears. In this new phase, the orientational glass or quadrupolar spin glass phase as is also known, the orientational degrees of freedom are in a frozen-in disordered state with no long-range structure [1]. Locally the moments become fixed around some random value, but globally there is no structure. The glassy state is a consequence of the site disorder introduce upon dilution. Figure 1 shows a schematic diagram in the (x,T)

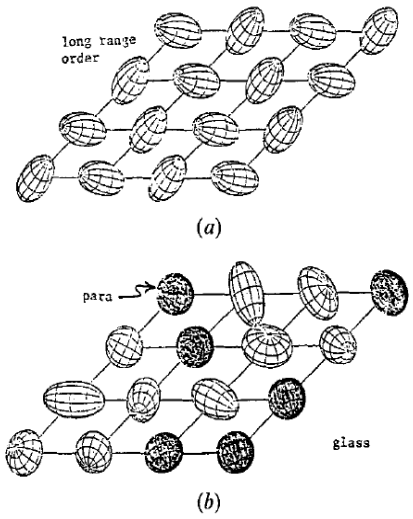

Figure 2: Schematic diagram of the molecular orientations in the phase with (a) long-range order and (b) with frozen-in disorder.

plane showing the main features of the OG transition, while figure 2 presents a schematic diagram of the difference between the phase with long-range order and the phase with frozen-in polarization. It is important to note that the disordered state appears not as a consequence of the slowing down of thermally activated processes at low temperature, but as a consequence of the collective freezing of the orientational degrees of freedom [2]. Orientational glasses posses features common to other disordered systems like spin glasses (magnetic analogues), canonical glasses and amorphous systems. On the one hand, the relaxation phenomena of the orientational degrees of freedom is very similar to the analogous phenomena in spin glasses [5], but on the other hand their thermodynamic, elastic and dielectric properties have been shown to be characteristic of amorphous states [2].

The rest of the paper is organized as follows. In section II some experimental results involving the OG phase and the OG phase transition will be presented. This will be followed by a brief discussion of basic theoretical concepts needed to study disordered systems in section III. In section IV, a brief discussion of the replica theory of the uniaxial quadrupolar glass is presented. Finally, in section V, results from computational studies of related models using primarily Monte Carlo techniques will be discussed. This paper is only meant to provide a brief conceptual introduction to the field, the interested reader should consult some of the excellent review articles and

books listed in the references; orientational glasses [1, 2, 3, 4], spin glasses [5, 6, 7].

2 Experimental Results

In this section we will concentrate our discussion on one of the most important systems in the field of OG, $(KBr)_{1-x}(KCN)_x$. This system exhibits many of the characteristic features universal to all orientational glasses. It belongs to a bigger class of cyanide compounds all exhibiting low temperature disordered states of the orientational degrees of freedom $[(NaCN)_{1-x}(KCN)_x$, $(KCl)_{1-x}(KCN)_x$, $(NaCl)_{1-x}(NaCN)_x$,...]. This system is particularly important because, as a consequence of the strong coupling of its rotational and translational degrees of freedom, the collective freezing of the local orientations break the long-range translational order of the crystal. At low temperatures, the scattering intensity at reciprocal lattice points $\vec{\mathbf{q}}$ changes from a δ-function like peak to a diffuse cusp of the form I($\vec{\mathbf{q}}$) $\propto$ exp(-c$\|\vec{\mathbf{q}}\|$). An important consequence of this is that the ordering of the local moments is reflected in the elastic properties of the system, and because the rotation-translation coupling is bilinear, the elastic constants probe the quadrupolar susceptibility directly [1].

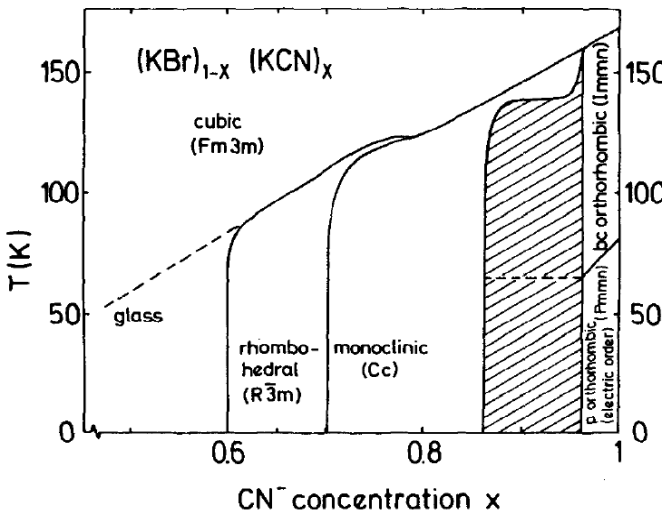

Figure 3: Phase diagram of $(KBr)_{1-x}(KCN)_x$ in the (x,T) plane. The dashed line represents the transition to the glassy state.

Figure 3 shows the phase diagram in the (x-T) plane of this system. At zero dilution and high temperatures, KCN exhibits a cubic structure (NaCl-

type). At 168K there is a first order phase transition (elastic transition) to an orientationally ordered state in an orthorhombic structure, where the CN^- ions are aligned along the former $< 110 >$ cubic axes. At 83K the static dipoles of the CN^- molecules acquire an antiferromagnetic order. By addition of spherical Br^- atoms, the elastic transition temperature decreases until it reaches 0K at about x=0.6. Further dilution takes the system into the disordered state. For $x < 0.6$, the system stays in a pseudo-cubic structure as the temperature is lowered.

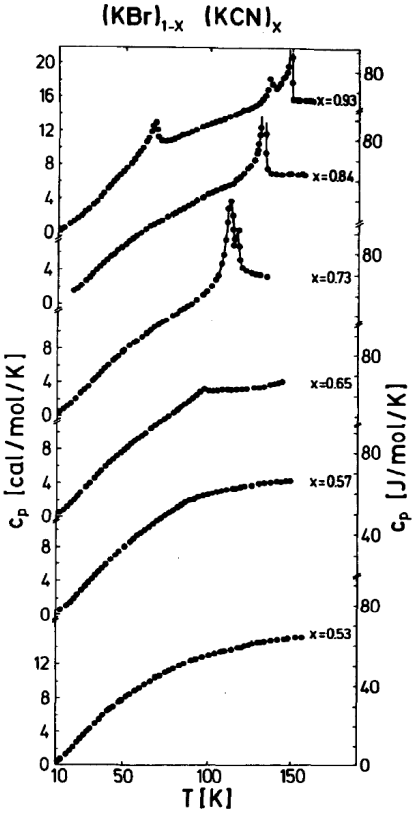

Figure 4: Adiabatic specific heat for $(KBr)_{1-x}(KCN)_x$ as a function of temperature for different concentrations, x.

Specific heat measurements across the entire dilution range have been performed on this system. Figure 4 shows the adiabatic specific heat as a function of temperature for various concentrations. As can be seen, the anomalies at $x > 0.6$ indicate the phase transition into the different phases with long-range order. For $x < 0.6$ no anomalies in the specific heat can be seen, which is typical behavior in orientational glasses. This results seems to

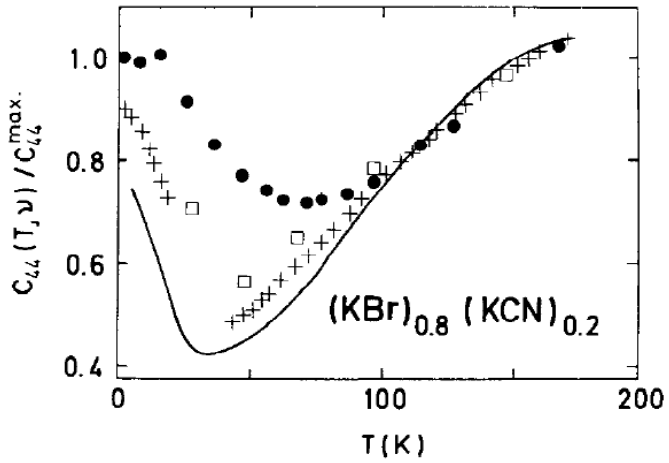

Figure 5: Elastic constant $c_{44}(T, f)$ of $(KBr)_{0.8}(KCN)_{0.2}$ as a function of temperature for various frequencies.

suggest that the freezing process is not sudden but gradual across a temperature range, producing no discontinuities at a transition temperature. The low temperature specific heat shows a linear variation with temperature, and an excess contribution over the normal Debye behavior in traditional solids, which is an universal feature amorphous systems [2].

Information on the freezing of the orientations can be obtained by studying both the frequency dependent elastic constants and the central peak (ω = 0) of the scattering function S($\vec{\mathbf{q}}$,ω), which can be shown to be related to the glass order parameter [1]. Similar to spin glasses, the transition in orientational glasses is indicated by a cusp in the appropriate multipolar susceptibility. As mentioned before, the quadrupolar susceptibility can be measured indirectly through the dependence of the elastic constants in frequency and temperature. Figure 5 shows the temperature dependence of the elastic constants for various frequencies for a concentration of x = 0.2, the minima in the elastic constant at low temperature is related to the freezing process of the local orientations. Figure 6 shows the neutron scattering line shapes at various temperatures. The intensity of the central peak can be viewed as a direct measure of the glass state, as it is directly related to the order parameter of the phase, as mentioned before.

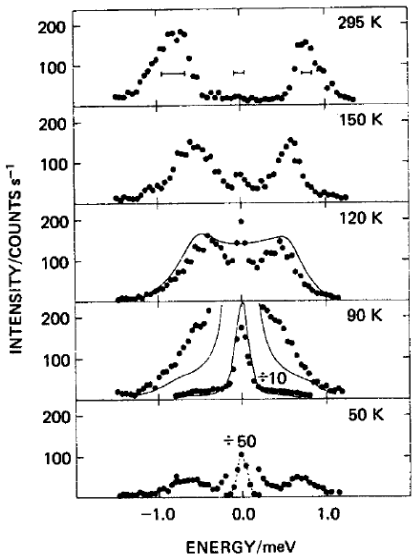

Figure 6: Neutron scattering line shape S(q,w) for $(KBr)_{0.5}(KCN)_{0.5}$ at various temperatures.

3 Basics of Disordered Systems

One of the key difficulties in treating disordered systems comes from the fact that the disordered is *quenched*. This means that the impurities have almost zero mobilities, so that their relaxation times become much greater than the duration of any experimental observation. On the other hand, if the impurities can diffuse without too much difficulty through the crystal they will quickly reach thermal equilibrium states; this case is known as annealed disorder. For systems in their solid phases, diffusion processes become almost non-existent so that we need to treat the disorder as quenched. This has important consequences in the properties of the system, as any observable must be averaged over all the configurations of the impurities consistent with concentration. In systems with annealed disorder, thermal averages and configurational averages can be interchanged because the impurities are assumed to be in thermal equilibrium at all times. On the other hand, when quenched disorder is present, the configurational average must be made after the thermal averages. For a given configuration of the impurities, $\{\vec{\mathbf{J}}\}$, the free energy becomes:

$$\beta F\left[\{\vec{\mathbf{J}}\}\right] = -lnZ\left[\beta, \{\vec{\mathbf{J}}\}\right] \tag{1}$$

$$Z\left[\beta, \{\vec{\mathbf{J}}\}\right] = Tr_X exp\left(-\beta H(\{\vec{\mathbf{J}}\}, \{\vec{\mathbf{X}}\})\right) \quad , \tag{2}$$

where the trace is only over the internal variables $\{\vec{\mathbf{X}}\}$(spins, quadrupoles, etc). Then the free energy must be averaged over all consistent configurations $\{\vec{\mathbf{J}}\}$:

$$[F]_{quenched} = \int F\left[\{\vec{\mathbf{J}}\}\right] P\left[\{\vec{\mathbf{J}}\}\right] d\left[\{\vec{\mathbf{J}}\}\right] \tag{3}$$

where the impurities are assumed to be distributed according to $P(\{\vec{\mathbf{J}}\})$. In practice, averaging the partition function with respect to disorder is much easier than averaging the free energy, so the *replica trick* is usually used:

$$\left[lnZ\left(\{\vec{\mathbf{J}}\}\right)\right]_{quenched} = \lim_{n\to 0} \frac{\left[Z^n\left(\{\vec{\mathbf{J}}\}\right)\right] - 1}{n} \tag{4}$$

where $[Z^n(\{\vec{\mathbf{J}}\})]$ refers to an average in a space of n replicas of the system.

4 Mean Field Theory - Sherrington-Kirkpatrick Model

Besides computer simulations, almost all of the theoretical results for this system come from adaptations of mean field theory models developed for spin glass systems. In this section we'll briefly discuss the main results of one of those methods; the mean-field theory of a set of uniaxial quadrupoles interacting through randomly quenched and frustrated exchange [8], solved using the replica method. This model is analogous to the Sherrington-Kirkpatrick model for spin glasses. In this model, the quadrupoles are assumed to have an axis of symmetry and their interactions are distributed according to:

$$P(J_{ij}) = \left(\frac{N}{2\pi J^2}\right)^{1/2} exp\left(-\frac{(J_{ij} - J_o/N)^2}{2J^2/N}\right). \tag{5}$$

The Hamiltonian for the model can be written as (up to constant terms):

$$H = -\sum_{ij} \vec{\mathbf{J}}_{ij}\left(\vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j\right)^2 \tag{6}$$

where $\vec{\mathbf{S}}_i$ is a vector along the axis of symmetry of the quadrupole at site i.

Figure 7 and 8 show the phase diagrams predicted by this model in the case of 2 and 3 dimensions respectively. As can be seen, the glass phase replaces the paramagnetic phase at low temperatures and small J_o/J (small mean disorder or large variance). Notice that, in both cases, the ferromagnetic phase is stable for large values of J_o/J and, in 3 dimensions, the ferromagnetic phase is inevitable at low temperatures.

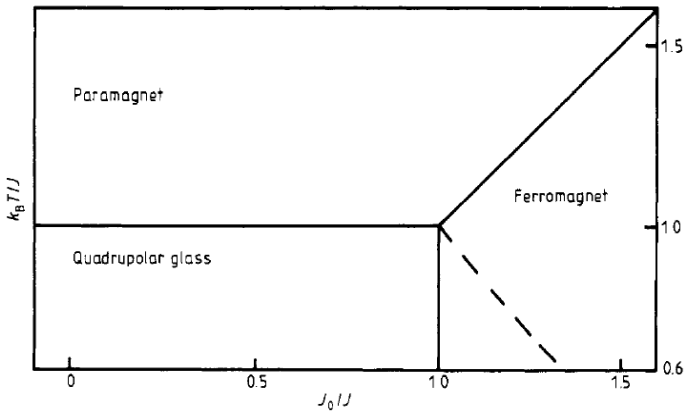

Figure 7: Phase diagram for the uniaxial quadrupole glass with m=2.

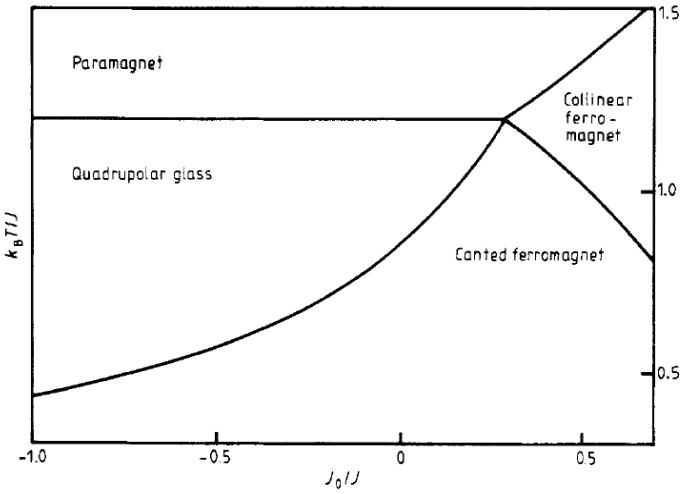

Figure 8: Phase diagram for the uniaxial quadrupole glass with m=3.

5 Computational Studies

Analytical methods become increasingly difficult when short-ranged interactions are considered, so computer simulations become the primary tool to study these models. There is still no general consensus about the best theoretical model of quadrupolar glasses. Many different systems have been investigated using various computational techniques. Among the different models studied are: Potts models with random fields, Edwards-Anderson type of models generalized to quadrupolar glasses, models with full atomistic details, and many others [4, 1]. Even though Monte Carlo is usually the preferred technique, some other techniques have been used like: Molecular Dynamics, Transfer Matrix calculations for system in 2 dimensions, etc. Below we show some results from a simulation of an isotropic orientational glass using Monte Carlo techniques.

The Hamiltonian in this case is the same as in the Sherrington-Kirkpatrick model of the uniaxial quadrupolar glass presented before, eqn. 6. The ferromagnetic and glass correlation functions are [1]:

$$g_{ferro}(\vec{\mathbf{r}}) = \Big[< (\vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j)^2 - 1/m >_T\Big]_{quenched} \propto exp[-r/\xi_{ferro}(T)] \tag{7}$$

$$g_{glass}(\vec{\mathbf{r}}) = \Big[< (\vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j)^2 - 1/m >_T^2\Big]_{quenched} \propto exp[-r/\xi_{glass}(T)] \tag{8}$$

where m is the dimension of the quadrupoles and $\xi_{g/f}(T)$ is the correlation lengths of the phase. Figure 9 shows a log-log plot of both correlation lengths as a function of temperature. As can be seen both seem to diverge as $T \to 0$, which is consistent with the fact that the model has a glass phase transition at T=0. Figure 10 shows a log-log plot of the temperature dependence of the susceptibility of the glass phase, defined as [1]:

$$\chi_{glass} = 1 + \sum_{\vec{r}\neq 0} g_{glass}(\vec{r}). \tag{9}$$

The susceptibility exhibits a power-law divergence as $T \to 0$ consistent with $\chi_{glass} \propto T^{-\gamma_o}$. The exponents for the correlation length and the susceptibility obtained from these simulations are: $\nu(d=2) \approx 0.63, \nu(d=3) \approx 1.03, \gamma(d=2) \approx 1.35, \gamma(d=3) \approx 2.7$.

6 Conclusion

In this paper we presented a brief conceptual introduction to the field of orientational glasses. Orientational glasses play an important role in the field

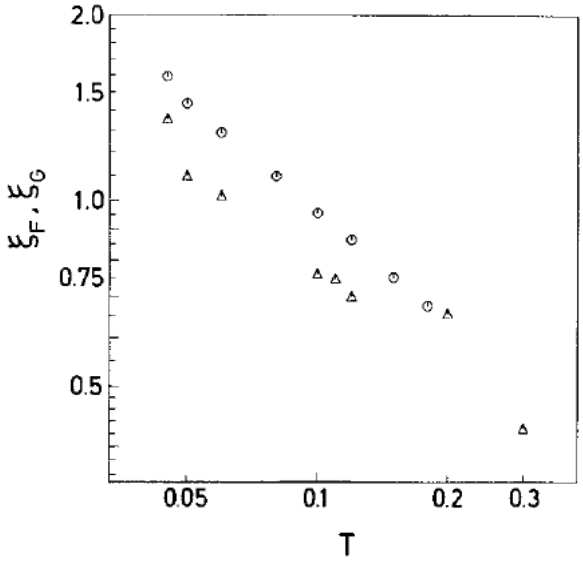

Figure 9: Log-log plot of ferromagnetic (triangles) and glass (circles) correlation lengths as a function of temperature for m=3 ,d=2.

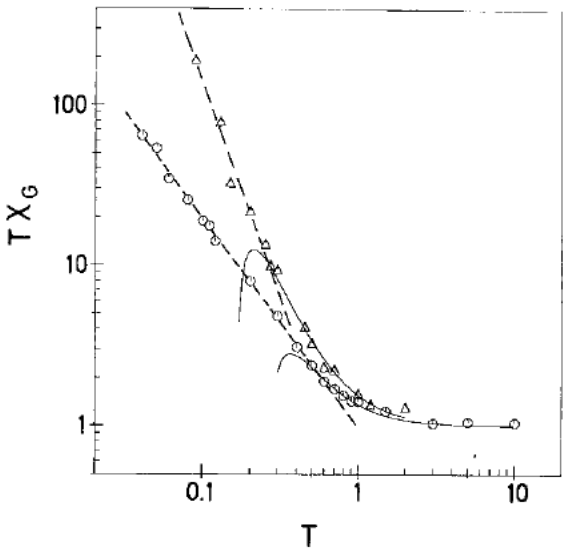

Figure 10: Log-log plot of the glass susceptibility of the isotropic quadrupolar glass with m=3. Circles are for the case d=2, while triangles are for d=3. Dashed lines represent the power law expansions, while full lines represent the high temperature series expansion of the appropriate model.

of disordered systems and can become a model system to study amorphous solid. Although this system has received much attention during the last decades, there are still many open questions and unresolved problems. From a theoretical point of view, computational studies present the most promising route to obtain a better understanding of the properties of the system.

References

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