Molecular solid glasses: new insights into frustrated systems

To cite this article: S Pilla et al 2001 New J. Phys. 3 17

View the article online for updates and enhancements.

You may also like

- Power dissipation in HTS coated conductor coils under the simultaneous action of AC and DC currents and fields
  Boyang Shen, Chao Li, Jianzhao Geng et al.

- Resonant transport through a carbon nanotube junction exposed to an ac field
  S E Shafranjuk

- Effective response of nonlinear cylindrical coated composites under external AC and DC electric field
  Shen Yu-Yan, Chen Xiao-Gang, Cui Wei et al.
Molecular solid glasses: new insights into frustrated systems

S Pilla†, J A Hamida, K A Muttalib and N S Sullivan
Department of Physics, University of Florida, Gainesville, Florida 32611, USA
E-mail: manyam@physics.ucsd.edu (S Pilla)

New Journal of Physics 3 (2001) 17.1–17.8 (http://www.njp.org/)
Received 2 August 2001
Published 19 September 2001

Abstract. High sensitivity dielectric constant and heat capacity measurements are reported for solid N₂–Ar mixtures as well as pure N₂ in the presence of a small external ac electric field in the audio frequency range. Unexpected field-induced aging and memory effects are observed for thermal cycles of field cooled samples, above a well-defined temperature $T_h$. The magnitude and temperature dependences of the effects exclude any simple interpretation in terms of lattice defects. The results show that the free energy surface includes a complexity that allows for metastable states and that tunnelling can occur between the states.

1. Introduction

The development of an understanding of the underlying physics of the glass state is one of the most outstanding problems of contemporary physics [1, 2]. The broad family of glasses includes a wide range of materials from polymer melts to metallic glasses, magnetic spin–glasses and common structural glasses [3]–[7]. A deeper understanding of the microscopic origin of the universal features of glasses is of great significance not only for the fundamental science but also for future materials development. Since geometric frustration, symmetry breaking and disorder are all considered to be important ingredients in glass transition, experimental studies of particularly simple systems where these properties are well characterized are of great interest. The simplest molecular solids (H₂, N₂, CO, O₂) for which well known electrostatic interactions determine the low temperature orientational properties of the molecules serve as particularly clean examples of frustrated systems [8, 9] where the effects of disorder can be controlled very precisely. In this paper we show for the first time, from high sensitivity dielectric susceptibility and thermodynamic heat capacity measurements, that these systems also show characteristic...
aging effects and hysteresis with thermal cycling in an applied electric field, in analogy to the geometrically frustrated magnetic systems and consistent with previous NMR and neutron scattering measurements [9, 10]. For high levels of frustration, these glassy features occur not only in the presence of disorder, but surprisingly in certain pure systems as well. Moreover, the results show that the systems may be prepared in a variety of metastable states leading to a free energy landscape with experimentally ‘tunable’ barriers, and that tunnelling may occur between these states on laboratory timescales. It is this access by applied external fields to observable time scales (milliseconds to tens of seconds) that makes these systems especially valuable for gaining further insights into the fundamental nature of glass formation. The molecular solids mentioned above are truly simple electric analogues of the geometrically frustrated magnetic pyrochlores and garnets, or magnetic analogues of ice [11]. The principal interactions that determine the molecular alignments (with respect to a fixed lattice for the centres of mass) are combinations of short range electrostatic quadrupole–quadrupole interactions that favour long range orientational order and the steric hindrance from near overlap of the electronic charge densities that tend to oppose it. These interactions are highly frustrated because the minimum energy states for pairs or small clusters (determined by the symmetry properties of the orientational interactions) are incompatible with the close-packed lattice imposed by the much stronger isotropic interactions. Disorder is introduced by replacing at random sites a given fraction of the quadrupolar diatomic molecules by non-interacting spherical atoms like argon, producing a well characterized solid mixture. It has been established from neutron scattering and NMR studies [10, 12] of such N$_2$–Ar mixtures that in the presence of sufficient disorder (more than 25% Ar in N$_2$) long range orientational order is prevented at low temperatures and that the low temperature state is an ensemble of randomly oriented molecular axes. What has been suspected but not previously observed is that these states also show the characteristic features of glass formation for the rotational degrees of freedom. The temperature for the onset of hysteresis is consistent with the changes in local molecular alignments and spin–glass-like ordering reported in earlier NMR studies [12].

The anisotropic component of the dielectric susceptibility is directly related to the local molecular orientations through $\alpha_{\text{aniso}} = \Delta \alpha \langle \left(3 \cos^2 \theta_E - 1 \right) \rangle_{\tau}$, where $\Delta \alpha$ is the difference between the anisotropic molecular polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$ for electric fields applied parallel and perpendicular to the molecular axis and $\theta_E$ is the polar angle defining the orientation of the molecular axis to the applied electric field. The double brackets refer to a configurational average over the phase space accessed in a time $\tau$ by the applied field. In the thermally disordered state the configurational average vanishes, but for a finite local ordering there is a finite contribution to $\alpha_{\text{aniso}}$ and hence to the dielectric constant ($\varepsilon$) which is related to $\alpha$ through the Clausius–Mossotti equation. The temperature dependence of the dielectric susceptibility observed for several N$_2$–Ar solid mixtures, each with a different N$_2$ concentration, is shown in figure 1.

2. Results

Each sample in figure 1 is prepared first by mixing the gases at room temperature for more than 24 h and then condensing to the liquid phase at least two times. After each condensation the sample was brought back to room temperature before re-condensing to ensure proper mixing of the gases, and then finally annealed near the solid–liquid transition temperature for 6–8 h to obtain polycrystalline powdered samples. All the dielectric measurements were carried out using a very high sensitivity ac capacitance bridge with a two parts per billion sensitivity for the
Figure 1. $\varepsilon(T)$ of N$_2$–Ar mixtures below 20 K for 1 kHz and 5 kV m$^{-1}$ applied electric field where $\varepsilon'$ is the value at 4.2 K on the lower curve. The hysteresis loop increases with decreasing N$_2$ concentration. The onset of the glass regime (indicated by $T_g$) is characterized by the change of slope of $\varepsilon(T)$. W and C designate warming and cooling cycles respectively.

The real part of the dielectric constant in the audio frequency range [13]. The dielectric data obtained from multiple solid samples (for the same gas mixture) clearly showed that phase separation of N$_2$ and Ar did not occur for any of the mixtures studied. The samples were then cooled to 4.2 K in the absence of the applied field and held at 4.2 K for an extended period of time (typically 10 hours); an ac electric field in the audio frequency range (0.2 to 20 kHz) was then
applied and the dielectric constant measured through a warming and cooling cycle. For high concentrations of N$_2$ for which an fcc structure occurs at low temperatures, only a small hysteresis loop is observed. The region of the loop corresponds to the region where NMR results imply a random or glass-like freezing of the molecular axes. For low concentrations where only the hcp lattice structure occurs, the hysteresis loop is open ended at low temperatures and a sharp onset of reversible behaviour is seen on warming through a well-defined temperature, $T_g$, for a given field strength and ac frequency. However, while obtaining this set of low temperature data, the sample temperature was never raised above $\sim 40$ K. These values of $T_g$ are in good qualitative agreement with the glass phase diagram implied by the NMR, x-ray diffraction and simulation results [12, 14]. The observed hysteresis implies that the part of configuration space averaged over has changed during the time scale of the thermal cycle ($\sim 8$ hours in figure 1). This view is consistent with a slow evolution of the system in a complex free energy landscape.

In addition to the above results, dramatic aging effects were observed as a function of the applied ac electric fields and the thermal history of the sample. Figure 2 shows the change in the observed dielectric constant $\varepsilon$ after cooling a 70% N$_2$ sample in a field of 5 kV m$^{-1}$ at 1 kHz. The observed hysteresis and the associated spontaneous change in electric polarization are primarily due to the thermal cycling when the sample is cooled from a temperature $T_{\text{max}} > T_h$ in the presence of the external ac electric field, which we refer as ‘field cooling’ in this paper. In contrast, the data in figure 1 show the hysteresis due to the well known orientational glass phase, which is observed only in samples without a prior history of field cooling. Once the sample is field cooled, the resulting hysteresis, which is much stronger, completely suppresses the effects of fragile orientational glass formation. The field induced change of almost 1% in $\varepsilon$ for $T < 10$ K, and pronounced hysteresis behaviour shows that the applied electric field significantly modifies the free energy landscape of complex potential energy minima. In addition, a few sharp drops in the value of $\varepsilon$ are observed on cooling (but not on warming). These appear to be sharp transitions between neighbouring configurational minima. The lack of such events on warming implies an effective erasure of memory effects on warming following aging at low temperatures analogous to the phenomena observed in spin–glass systems and consistent with recent views of glass formation in terms of replica symmetry breaking [15]. These dramatic field cooling effects were observed up to 49% dilution of N$_2$ sample with Ar, however with decreasing intensity. For all samples studied, $T_h$ is similar within experimental errors. The aging and memory effects reported here for molecular glasses are very similar to those observed for magnetic spin–glasses by Jonason et al [16]. Measurements of the magnetic susceptibility of two different spin glasses at low ac frequencies showed that below a characteristic glass temperature $T_g$, the susceptibility evolved slowly and depended on the time spent below $T_g$. The susceptibility was fully reinitialized on reheating above $T_g$ and on recycling perfectly retraced the previous aging history.

What is most striking is that although global measurements of the heat capacity [17] and NMR spectra [12] show no measurable hysteresis or memory effects, this is not true for high sensitivity dielectric studies. Figure 3 shows clear evidence for hysteresis effects in pure N$_2$. The differences between the curves in figure 3 are due only to the final turn-around temperatures $T_{\text{max}} > T_h$ from which the samples are field cooled. These memory effects observed for pure samples are similar to the effects observed in mixtures for which the frustrated free energy landscape is thought to be the origin of the glass formation. In order to test this picture of a complex landscape for both the glass state and the pure system, we measured the thermal heat capacity of the field cooled samples, using a very high sensitivity dual-slope calorimeter [18].

New Journal of Physics 3 (2001) 17.1–17.8 (http://www.njp.org/)
Figure 2. $\varepsilon(T)$ of 70% N$_2$–Ar mixture for 1 kHz and 5 kV m$^{-1}$ electric field relative to the value at 4.2 K on curve (1) ($\varepsilon'$). $\varepsilon'=1.4119$. Curve 1 is obtained after cooling a carefully annealed (near melting temperature) powdered sample in the absence of applied field to 4.2 K. A kink near $T_h$ (along curve 1) is observed only during the first warming cycle. $\downarrow$ mark the spontaneous change in $\varepsilon$ at random temperatures indicating the non-equilibrium dynamics in the sample. $\rightarrow$ along each curve indicates the direction of the change in $T$. W and C designate warming and cooling cycles respectively. The inset shows the high temperature data where a sharp change in $\varepsilon(T)$ is observed at $T_\lambda$.

The results in figure 4 clearly show remarkable field-induced effects in the entire temperature range studied. Our observations indicate that below $T_h$, for zero field cooled samples of N$_2$–Ar mixtures as well as pure N$_2$, $\varepsilon(T)$ attains equilibrium value very quickly (typically in a few seconds) when $T$ is changed, but for field cooled samples the time required to attain equilibrium value varies from a few minutes to a few hours depending on the temperature. In particular, for
Figure 3. $\varepsilon(T)$ of solid N$_2$ at 5 kV m$^{-1}$ and 1 kHz excitation field relative to the value at 4.2 K on curve (1) $(\varepsilon'_1)$. $\varepsilon'_1 = 1.4255$. Curves (1–4) show the gradual increase in hysteresis with the highest temperature ($T_h < T_{\text{max}} < 51$ K) reached along each curve. Curves (5–9) are obtained after annealing at $50 < T < 53$ K for 10–12 h. The indices b and e indicate the beginning and end, respectively, of each curve. The reversible behaviour in $\varepsilon$ with thermal recycling below $T_h$ is indicated by ↔. The inset shows the high temperature data where a sharp change in $\varepsilon(T)$ is observed at $T_\lambda$.

$41.5 < T < 43$ K, $\varepsilon(T)$ changes slowly in 6–8 h resulting in a kink at $T_h$ and for $50 < T < 53$ K it changes in 10–12 h resulting in a peak at 52 K. For $T < 41$ K as well as for $53 < T < 56$ K, $\varepsilon(T)$ attains equilibrium value in a few minutes but for $T > 56$ K the response is similar to the zero field cooled samples (i.e., a few seconds). Due to the constraints of the experimental method for measuring heat capacity we are unable to make similar observations while measuring heat capacity, but the data in figure 4 clearly show the ageing behaviour of field cooled samples.
Figure 4. Heat capacity ($C_P$) of $\sim 0.36$ mole solid $N_2$. Different curves near 56.5 K (in curves (2) and (3)) obtained with 3 h intervals indicate the slow thermal evolution of $C_P$ with time near $T_\lambda$. Due to the experimental constraints of the method employed, the data along curve (3) show $C_P$ of the sample with thermal history of curve (2) field cooled to 4.2 K and then its $C_P$ measured upon warming.

For all the samples studied, if the applied field is turned off and the samples are annealed for extended period of time (more than 12 h), we once again obtained the results for zero field cooled samples. These results can only be understood in terms of the short range steric hindrance due to charge overlap of neighbouring $N_2$ molecules that we expect to be influenced by applied electric fields. The results are surprising in that the interaction energy with the external fields is very
17.8

weak $\sim 10^{-8}$ of the anisotropic intermolecular interactions. However this scale is also seen in structural (silicate) glasses where small magnetic fields induce anomalies seen only at very low temperatures [19] for systems with interaction energies of $\sim 103$ K.

3. Conclusion

Considerable theoretical work is needed to obtain a quantitative understanding of these remarkable new features observed in the dielectric response of molecular glass systems. The qualitative results are very clear. The dielectric response shows strong field-induced memory effects in the temperature range where NMR studies showed a freezing of the molecular axes in random orientations. While the NMR results were too insensitive to detect hysteresis effects, these new high sensitivity techniques show that not only the dielectric susceptibility but also the thermodynamic heat capacity show features that are common to other glass formers. The special interest in these results is that these simple molecular systems provide a new window for probing glass formation in one of the most straightforward prototypes for frustration, for which the disorder can be controlled precisely and for which the experimenter has access to the relevant time scales for the glass state: milliseconds to hours for the molecular systems, as opposed to centuries for the common window pane glasses.

Acknowledgments

This work supported is supported by a grant from the National Science Foundation No DMR-962356.

References

[1] Anderson P W 1995 *Science* **267** 1615
[2] Jäckle J 1986 *Rep. Prog. Phys.* **49** 171
[3] Franz S, Mezard M, Parisi G and Peliti L 1998 *Phys. Rev. Lett.* **81** 1758
[4] Ramirez A P 1994 *Ann. Rev. Mater. Sci.* **24** 453
[5] Angell C A 1995 *Science* **267** 1924
[6] Meissner M et al 1985 *Phys. Rev. B* **32** 6091
[7] Alberici F, Doussineau P and Levelut A 1997 *Europhys. Lett.* **39** 329
[8] Binder K and Reger J D 1992 *Adv. Phys.* **41** 547
[9] Hamida J A, Sullivan N S and Evans M D 1994 *Phys. Rev. Lett.* **73** 2720
[10] Press W, Janik B and Grimm H 1982 Z. *Phys. B* **49** 9
[11] Harris M J, Bramwell S T, McMorrow D F, Zeiske T and Godfrey K W 1997 *Phys. Rev. Lett.* **79** 2554
[12] Hamida J A, Genio E B and Sullivan N S 1996 *J. Low Temp. Phys.* **103** 49
[13] Pilla S, Hamida J A and Sullivan N S 1999 *Rev. Sci. Instrum.* **70** 4055
[14] Klee H, Carmesin H O and Knorr K 1988 *Phys. Rev. Lett.* **61** 1855
[15] Kurchan J, Parisi G and Virasoro M A 1993 *J. Physique I* **3** 1819
[16] Jonason K, Vincent E, Hammann J, Bouchaud J P and Nordblad P 1998 *Phys. Rev. Lett.* **81** 3243
[17] Manzheli V G and Freiman Y A 1997 *Physics of Cryo Crystals* (Woodbury, NY: AIP Press)
[18] Pilla S, Hamida J A and Sullivan N S 2000 *Rev. Sci. Instrum.* **71** 3841
[19] Strehlow P, Enss C and Hunklinger S 1998 *Phys. Rev. Lett.* **80** 5361

*New Journal of Physics* **3** (2001) 17.1–17.8 (http://www.njp.org/)