Random bonds and random fields in two-dimensional orientational glasses

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Abstract. Two-dimensional orientational glasses are studied using Monte Carlo simulation. The glasses are modelled using rigid rotors, with fixed positional distribution, chosen using either a random parking algorithm, or by randomly diluting a triangular lattice. The glass-like behaviour has its origin in the coupling, inherent in all anisotropic intermolecular pair potentials, between the rotational degrees of freedom and the quenched random positions. We show how this coupling can be broken down into random bond terms that lead to spin glass-like behaviour and random field terms that favour single-particle freezing. We study in detail the quadrupolar interaction and illustrate this behaviour by an *ad hoc* variation of the relative strength of the two types of term. For small random field a rich ground-state structure is observed, with the existence of many non-symmetry related equivalent orientational states. At finite temperature we observe two temperature regimes for the spin glass order parameter. There is a field dependent regime giving some spin glass-like order out to high temperatures, while at low temperatures a cross-over to a field independent regime is observed, which we interpret as cooperative freezing to a low-temperature dis-ordered phase. Comparison is made between our results and experiment, as well as with theoretical models for spin and orientational glasses. Finally we investigate the time dependence of the cooperative freezing, and find behaviour consistent with dynamical freezing, and loss of ergodicity on a finite observation time.

1. Introduction

Quadrupolar or orientational glasses, such as mixed crystals of ortho- and para-hydrogen (Sullivan *et al* 1978), mixed crystals of argon and nitrogen molecules, $(N_2)_xAr_{1-x}$, (Esteve *et al* 1982, Press *et al* 1982, Klee *et al* 1988), or the rather more complicated system of $K(CN)_xKBr_{1-x}$ (Michel and Rowe 1980, Wochner and Petry 1990) freeze, at low temperature, into an orientational glass phase, analogous to that of a spin glass. (For a recent review see Höchli *et al* 1990.)

There has been a long debate in the literature concerning the nature of this freezing (Harris and Mayer 1984, Carmesin and Binder 1987a,b, Hammes *et al* 1989, Bostoen and

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Michel 1988, 1991). The first class of questions one might ask concerns the equilibrium thermodynamics of quadrupolar, or orientational glasses: does the freezing of the orientational degrees of freedom involve a phase transition? It is clear that the randomness of the distribution of quadrupolar molecules is vitally important for the resulting frozen-in orientational disorder (Lewis and Klein 1986). However, the important question is how the disorder manifests itself in the orientational interactions. To exhibit spin glass-like cooperative behaviour the interaction must include random bond frustration (Toulouse 1977). On the other hand, if the system is dominated by site disorder, or random fields, then no cooperative freezing occurs and the system freezes gradually into a disordered, non-degenerate ground state configuration. If both forms of interaction are present, it is not clear what effect the random fields will have on the cooperative behaviour of the system.

In experimental spin glass systems, the relaxation time-scales increase extremely rapidly over a very small range of temperature. As a result, ergodicity is lost on the time-scale of experimental observation at a well defined temperature, and a dynamical freezing is observed (for example: Bontemps *et al* 1983, Dekker *et al* 1988, 1989). It is usually not clear if this dynamical freezing is a precursor to a static equilibrium phase transition, or if it is a purely dynamical effect, with the time-scale diverging only at zero temperature (for a discussion see Binder and Young 1986). Hence one must also investigate the question: is it possible to observe the equilibrium properties of quadrupolar glasses or is the observed behaviour purely dynamical?

The experimental evidence is rather contradictory, with varying reports for the abruptness of the onset of freezing in both the H_2 and the $(N_2)_x Ar_{1-x}$ systems (Harris and Mayer 1984 and references therein, Esteve *et al* 1982, Klee *et al* 1988). Sullivan and Esteve (1981) measured the change in nuclear relaxation rate, τ, with temperature, for an ortho-para hydrogen mixture. They observed that τ increases smoothly, yet extremely rapidly over a small temperature range, at about 500 mK. For the mixed crystal $K(CN)_x KBr_{1-x}$, inelastic neutron scattering data is strongly suggestive of a glass-like transition, and an abrupt loss of ergodicity (Michel and Rowe 1980, Wochner and Petry 1990).

Theoretical studies have, for the most part, taken one of two approaches. Either calculations and simulations have been performed, which attempt to make a realistic reconstruction of an orientational glass (Bostoen and Michel 1988, 1991, Lewis and Klein 1989), or Edwards–Anderson (1975) models have been studied, in which the random dilution of the crystal has been replaced by a lattice of rotors of appropriate symmetry with random coupling constants (Hammes *et al* 1989 and references therein).

In the former case, studies concentrated on the KBr–KCN system (Boesten and Michel 1988, 1991) where a mode–mode coupling theory has been constructed describing the behaviour of the molecules under the influence of random fields, resulting from the dilution of the CN^- sublattice with spherical Br^- ions. The fields are self-consistent and the theory predicts distinct regimes where an ergodicity breaking occurs, and where gradual freezing occurs. The theory includes, as an important element, the relaxation of the particle positions due to coupling between the translational and rotational degrees of freedom. Lewis and Klein (1986, 1989) have attempted a full molecular dynamics simulation of the experimental system, with particles interacting via a model pair potential, with fitted atomic charge distributions. They developed an accurate description of the molecular freezing and showed the importance of having a quenched random distribution of the two types of anion. However, the use of such a detailed microscopic model makes it difficult to extract quantitative information about the transition.

In the second approach the dynamical coupling between translational and rotational degrees of freedom is neglected and one considers a random distribution of point quadrupoles, with Hamiltonian (Kanter and Sompolinsky 1986)

$$H = \sum_{ij} \sum_{\mu\nu\mu'\nu'} J_{ij}^{\mu\nu\mu'\nu'} f_i^{\mu\nu} f_j^{\mu'\nu'} \qquad (1.1)$$

$$f_i^{\mu\nu} = n_i^\mu n_i^\nu - \delta_{\mu\nu}/m. \qquad (1.2)$$

n_i are the 1., μ ... m components of the unit vector of the ith point quadrupole. The coupling constants $J_{ij}^{\mu\nu\mu'\nu}$ depend on the magnitude and direction of the intermolecular vector r_{ij} (see section 2) and the randomness is due to the random positional distribution of the quadrupoles. As in the Edwards–Anderson spin glass model, the real coupling constants above are replaced by independent random variables (Kanter and Sompolinsky 1986). The simplest model involves a scalar interaction

$$J_{ij}^{\mu\nu'\mu'\nu} = J_{ij}(\delta_{\mu\mu'} + \delta_{\nu\nu'}). \qquad (1.3)$$

However, the true coupling constants, $J_{ij}^{\mu\nu'\mu'\nu}$, break the continuous rotational symmetry. This has been modelled by introducing cubic anisotropy (Carmesin 1989) and by studying a three-state Potts spin glass (Carmesin and Binder 1988, Banavar and Cieplak 1989, Scheucher *et al* 1990). In both cases the preliminary evidence was for a low, but finite transition temperature. More recent detailed simulations suggest that the lower critical dimensionality d_c is exactly three in the case of the three-state Potts spin glass (Scheucher *et al* 1990).

A considerable amount of information has been extracted from these Edwards–Anderson models, using mean field calculation and by performing proper scaling analysis of computer simulation results. Their relevance to real molecular glasses and to the mode–mode coupling theory is, however, not clear, and there is a need to fill the gap between the two approaches described above.

In this paper we have studied systems of point quadrupoles in different quenched random configurations. We neglect the dynamic coupling between the translational and rotational degrees of freedom, but retain a model physical interaction between the anisotropic molecules. The randomness and orientational frustration is due to the random positional configuration. We have restricted our study to two-dimensional systems, with anisotropic particles constrained to lie in the plane. In this case it is straightforward to decompose the pair potentials into terms that provide random bond frustration, and into random site terms. Our approach is similar to that used by Devoret and Esteve (1983) who performed a simulation of rigid three-dimensional rotors on a randomly diluted FCC lattice, interacting via the quadrupole potential. They observed cooperative freezing into a system of many disordered low temperature states.

Our results are relevant to experiment, as a two-dimensional orientational glass could possibly be realized by adsorbing a random mixture of nitrogen and argon onto a graphite substrate. LEED experiments have been performed on such a system (You and Fain 1986): for N_2 concentrations less than 75% the orientational order becomes rather tenuous and You and Fain suggest the existence of an orientational glass phase. The substrate provides an external potential fixing the molecular positions. In this case it is a reasonable first approximation to neglect the dynamic coupling between the translational and rotational degrees of freedom, and to model the system with a single quenched positional distribution.

We expect our system to be below d_c and that the freezing will be dynamical in nature. However, the work on the Edwards–Anderson models reviewed above illustrates that

the same may well be true for three-dimensional orientational glasses, and even if d_c is less than three for some systems, dynamical freezing will be observed at temperatures above the static freezing temperature. In this case an understanding of our system is useful and relevant for three-dimensional orientational glasses.

The rest of the paper is organized as follows: in the next section we define our two-dimensional orientational glass models and introduce the quadrupole potential, from which we isolate random bond and random field-like terms. In section three we show quenched ground state structures found from zero temperature Monte Carlo simulations. In section four we show finite temperature Monte Carlo results.

2. Anisotropic pair potentials and orientational glass models

Anisotropic molecular pair potentials are non-separable in molecular and intermolecular orientations. That is, the pairwise interaction depends, not only on the orientation of the axes of anisotropy, n_i and n_j, of molecules i and j and the distance between the molecules $|r_{ij}|$, but also on the direction of the intermolecular vector r_{ij}:

$$V^{NS} = V^{NS}(r_{ij}, n_i, n_j). \tag{2.1}$$

The non-separability leads to a coupling between the translational and rotational degrees of freedom and makes the local structure vitally important in determining the orientational behaviour of the system. Examples of non-separable potentials are the dipole, induced dipole–dipole, or anisotropic van der Waals interaction, and quadrupole interactions:

$$V_d = \varepsilon_d(\sigma/r_{ij})^3[n_i \cdot n_j - 3(n_i \cdot e_{ij})(n_j \cdot e_{ij})] \tag{2.2a}$$

$$V_{vdw} = -\varepsilon_v(\sigma/r_{ij})^6[n_i \cdot n_j - 3(n_i \cdot e_{ij})(n_j \cdot e_{ij})]^2 \tag{2.2b}$$

$$V_q = \varepsilon_q(\sigma/r_{ij})^5[1 - 5(n_i \cdot e_{ij})^2 - 5(n_j \cdot e_{ij})^2 + 2(n_i \cdot n_j)^2] + \varepsilon_q(\sigma/r_{ij})^5$$
$$\times [35(n_i \cdot e_{ij})^2(n_j \cdot e_{ij})^2 - 20(n_i \cdot e_{ij})(n_j \cdot e_{ij})(n_i \cdot n_j)]. \tag{2.2c}$$

Here r_{ij} is the modulus $|r_{ij}|$ of the intermolecular vector and e_{ij} is the unit vector in the direction r_{ij}. ε_d, ε_v, ε_q, and σ set the energy and length scales in (2.2a–c).

We have recently shown the importance of the rotational–translational coupling in a two-dimensional liquid crystal (Gingras *et al* 1989, 1990, 1991), where the molecular ordering in the nematic phase produced order in a nearest neighbour bond orientational field, as in tilted hextic liquid crystals (Nelson and Halperin 1980). If the molecules are fixed on a lattice, the non-separability leads to a crystal field that breaks the continuous orientational symmetry. In an amorphous solid, where the translational degrees of freedom are frozen in a random configuration, the system cannot relax and the oreintational degrees of freedom suffer random frustration (Holdsworth *et al* 1989, 1991a).

In what follows, we restrict ourselves to two-dimensional systems with the three-dimensional molecules constrained to lie in the plane. In this case the origin of the frustration can be seen more clearly if we express the unit vectors n_i, n_j and e_{ij} in terms of the angles within the plane φ_i, φ_j and θ_{ij}. Then the potential (2.2a) can be re-written

$$V_d = -\tfrac{1}{2}\varepsilon_d(\sigma/r_{ij})^3[\cos(\varphi_i - \varphi_j) + 3\cos(\varphi_i + \varphi_j - 2\theta_{ij})]. \tag{2.3a}$$

The van der Waals and quadrupolar potentials can be written as

$$V_{vdw} = -(\varepsilon_v/8)(\sigma/r_{ij})^6[10 + \cos(2\varphi_i - 2\varphi_j)$$
$$+ 6F(\varphi_i, \theta_{ij}) + 6F(\varphi_j, \theta_{ij}) + 9G(\varphi_i, \varphi_j, \theta_{ij})] \tag{2.3b}$$

$$V_q = (\varepsilon_q/8)(\sigma/r_{ij})^5[3 + 3\cos(2\varphi_i - 2\varphi_j)$$
$$+ 10F(\varphi_i, \theta_{ij}) + 10F(\varphi_j, \theta_{ij}) + 35G(\varphi_i, \varphi_j, \theta_{ij})] \qquad (2.3c)$$

with

$$F(\varphi_i, \theta_{ij}) = \cos[2(\varphi_i - \theta_{ij})] \qquad (2.4a)$$

and

$$G(\varphi_i, \varphi_j, \theta_{ij}) = \cos(2\varphi_i + 2\varphi_j - 4\theta_{ij}). \qquad (2.4b)$$

The origin of the disorder is the quenched random angles θ_{ij}, which enter into the potentials in two ways. The terms F are field-like and depend on a single molecular orientation, φ_i, and the random phase angle, θ_{ij}. Hence they play the role of random fields in the interaction. Terms of the form G, on the other hand, depend on both orientations φ_i and φ_j and on the random phase angle θ_{ij} and provide random bond frustration. As we show in sections 3 and 4, G leads to spin glass-like behaviour, and we refer to it as the random bond, or spin glass term. In addition, there is the term $\cos(2\varphi_i - 2\varphi_j)$ that favours parallel alignment of rotors in the van der Waals interaction and perpendicular alignment in the quadrupolar case. As the coefficient of this term is small compared to that for the random bond or random field terms, and does not play an important role in the quadrupole interaction (Harris *et al* 1984), we neglect its effect in the following simulations. In both the quadrupole and the van der Waals potentials the random bond term has a discrete four-fold symmetry, hence if all the molecules are rotated by $\pi/2$ the initial and final configurations are completely equivalent. In the case of the dipolar interaction there is a random bond and ferromagnetic term only and no random field terms are present.

We model quenched random positional configurations of orientational glasses in two ways; in the first case we use a random parking algorithm (Hinrichsen 1986). Discs are randomly and sequentially placed on a plane by choosing a position and testing for overlap with discs already parked. If no overlap occurs, then the disc is placed, otherwise random positions are continuously selected until a non-overlapping position is found. The time to find a vacant position diverges at the jamming limit, which is at 54.7% coverage for discs on a plane. We typically used samples containing 512 particles of unit diameter on a square of side 28.5, giving a coverage of 49.5%. In the second case we randomly dilute a triangular lattice and place particles on the remaining sites. For very small dilution the low temperature state will still have the long-range orientational order of the undiluted triangular lattice (Harris *et al* 1984). The LEED experimental results of You and Fain (1986) show that long-range order is lost at about 25% dilution of nitrogen molecules with argon atoms, while we studied samples with between 30% and 50% dilution. In each case, once the positions are chosen they remain fixed. Our orientational glass models consist of placing rotors, interacting via a chosen pair potential, at the centre of each disc, or at each occupied position. In this paper we show results for quadrupolar glasses only, while preliminary results have already been presented for an induced dipole–dipole orientational glass (Holdsworth *et al* 1989, 1991a).

In real quadrupolar glasses the random mixing of different molecules of different sizes leads to a relaxation of each species away from the Bravais lattice positions of the pure samples and to random frozen-in strains and elastic distortions (Knorr and Loidl 1985, Lewis and Klein 1986, 1989). One of the things we wished to examine was the nature of the randomness that is important in orientational glasses, and our two orientational glass models represent two extremes of relaxation.
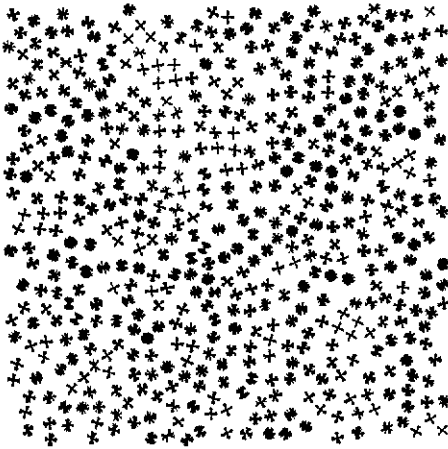
Figure 1. Superposition of 20 orientational ground states, for particles in a random parked positional configuration and interacting via potential {i}.
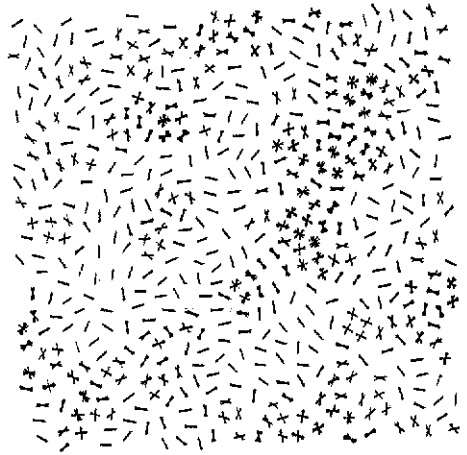

Figure 2. Superposition of 20 orientational ground states, for particles in a random parked positional configuration and interacting via potential {iv}.

3. Ground-state structures

In this section we look at the ground-state structure of the quadrupolar glass with random parked configuration. In order to first illustrate the effect of competing random bond and random field interactions we found the ground states, using zero temperature Monte Carlo simulation, of modified quadrupolar glasses interacting via one of the following four potentials.

{i} The random bond, or spin glass part of the quadrupole interaction only (see (2.3c))

$$V_{\{i\}} = \tfrac{1}{8}\varepsilon_q (\sigma/r_{ij})^5 G(\varphi_i, \varphi_j, \theta_{ij}). \tag{3.1}$$

This was compared with the full quadrupole interaction with modified field strength

$$V_q = (\varepsilon_q/8)(\sigma/r_{ij})^5 [3 + 3\cos(2\varphi_i - 2\varphi_j)$$
$$+ 10\eta\{F(\varphi_i, \theta_{ij}) + F(\varphi_j, \theta_{ij})\} + 35G(\varphi_i, \varphi_j, \theta_{ij})]. \tag{3.2}$$

Potentials {ii}, {iii} and {iv} had $\eta = 1, 4$ and 8 respectively (the unmodified quadrupole potential, (2.3c) corresponds to $\eta = 1$).

The system was started in a random orientational configuration and quenched directly to $T = 0$. A stable low energy state was attained after about 2000 Monte Carlo steps per particle (MCS). The potentials were cut off at a distance $d = 2.5\sigma$, giving an interaction at cut off of less than 1% of that at contact.

In figure 1 we show 20 superimposed ground states, for the same random park of positions, to illustrate the existence of many disordered, non-symmetry related low lying energy states. The discrete four-fold symmetry is visible as many particles have only four preferred orientations and their superimposed ground state orientations make a well-defined cross. However, there are regions where particles find ground state configurations with an essentially continuous orientational distribution. We found an extremely small spread in ground state energy E_{gs}. The relative dispersion $(\Delta E_{gs})/|E_{gs}|$

was in the range 0.1–0.3% for all random field strengths, with the statistics taken over the 20 ground states.

The above results are suggestive of the ground state structure of the Sherrington–Kirkpatrick spin glass model (Kirkpatrick and Sherrington 1975, Parisi 1980a), where the spin glass transition is to a set of broken symmetry states, with non-trivial overlap. However, the analogy is, at this level, only qualitative as we have made no attempt to distinguish between low lying metastable states and true ground states. Furthermore, our system was quenched and the probability of selection of a single state was far from equilibrium. We wish only to show that, in the case where the potential is dominated by the random bond terms there exists a system of many equivalent low energy states.

We expect the inclusion of competing random field terms to modify the ground state structures. Particles whose interaction is dominated by the field term will have a uniquely defined orientation at zero temperature, and the system of metastable states will reduce to a single well-defined ground state at large field. This behaviour has already been seen for the induced dipole–dipole glass (Holdsworth *et al* 1991a). The configurations found for potentials {ii} and {iii} are similar to those for {i} and are not shown here. There are some changes at the individual particle level, indicating that the fields modify the microscopic structure of the many equivalent states, and for potential {iii} some particles have a noticeably reduced space of orientations available to them. However, to see a dramatic change in behaviour it is necessary to look at the ground states for potential {iv}, as shown in figure 2. For this potential, with strong random fields, large areas have a uniquely defined low temperature state, with only small isolated areas where a spin glass-like many-state structure is observed.

The same kind of analysis was made for the quadrupolar glass model with particles on a triangular lattice with 50% dilution. The details were similar and are not shown, the only difference was that there was some local orientational structure due to the underlying Bravais lattice. In the undiluted triangular lattice the ground state is the six-fold degenerate herringbone structure (Harris *et al* 1984), and in the generated ground states for the diluted system one can see small, randomly orientated herringbone domains.

4. Finite temperature results

We have performed finite temperature Monte Carlo simulation on both our random park and our dilute lattice orientational glass models, interacting with quadrupole, and modified quadrupole potentials, as described below. We had three objectives in performing the simulations. Firstly, we wished to investigate the relative importance of random bond and random field disorder in these two-dimensional orientational glass models. Secondly, we investigated the type of randomness necessary to produce orientational glass behaviour and to establish if relaxation away from Bravais lattice positions is qualitatively important for the behaviour of real orientational glasses. Finally we studied the dynamics and the behaviour of the systems on different Monte Carlo time-scales. This is particularly important for our two-dimensional systems, as we expect them to be below the lower critical dimensionality for an equilibrium spin glass transition. Hence we expect any spin glass behaviour to be due to rapidly increasing, but not diverging, time scales.

We studied both a time dependent and a static spin glass order parameter (Edwards and Anderson 1975, Carmesin and Binder 1987a,b). The time dependent order parameter $q(t)$ is defined as

$$q(t) = \frac{1}{N} \sum_i \left[\frac{1}{t_{\text{obs}}} \int_{t_{\text{obs}}}^{t} \cos[2\{\varphi_i(\tau + +t_0) - \varphi_i(t_0)\}] \, d\tau \right]_{\text{av}} \tag{4.1}$$

$\varphi_i(t)$ is the orientation of particle i at time t, and t_0 is the Monte Carlo time taken for equilibrium. The data is averaged over an observation time t_{obs} and $[\ldots]_{\text{av}}$ is the average over bond configurations.

For the static spin glass order parameter, q^s, we calculated, for each particle i, the traceless matrix

$$A_i^{\alpha\beta} = \langle f_i^{\alpha\beta} \rangle \tag{4.2}$$

where $f_i^{\alpha\beta}$ is as defined in (1.2), and $\langle \ldots \rangle$ means the thermal average over the full production run time t_1.

q^s is then

$$q^s = \left[\frac{1}{N} \sum_i \lambda_i \right]_{\text{av}} \tag{4.3}$$

where λ_i is the positive eigenvalue of matrix $\underline{A}_i$.

In the case of potential {i} one can define the spin glass susceptibility in a standard way for a system with two-fold orientational symmetry (Carmesin and Binder 1987a, b)

$$\chi_{\text{sg}} = \left[\frac{4}{N-1} \sum_{i,j} \langle \cos\{2(\varphi_i - \varphi_j)\}\rangle^2 \right]_{\text{av}}. \tag{4.4}$$

The summation i, j is over all pairs of particles, and the normalization factor ensures that $\chi_{\text{sg}} = N$ at zero temperature. For potentials {ii}–{iv} the resultant random field on each site breaks the local orientational symmetry, giving an order N contribution to χ_{sg} at all temperatures.

An identical analysis was made for the random park model and for the diluted lattice model, with 610 particles on a 1024 site lattice, giving a coverage of approximately 60%. For data analysis at fixed time, the equilibration time, t_0, and production run time, t_1, were 10 000 Monte Carlo steps per particle (MCS), while the observation time, t_{obs}, for $q(t)$ was set at 3000 MCS. In each case, 3–6 different bond configurations (random park configurations, or dilute lattice configurations) were used. An initial random orientational configuration was chosen and for each run the system was cooled in steps of size $\Delta T = 0.1\varepsilon_q/k_B$. To speed up the simulation, data was collected every 5 MCS.

Experience in the field of spin glasses has shown that several hundred realizations of the disorder, as well as computing times of up to 10^6 MCS are required to obtain reliable quantitative results in randomly frustrated (glassy) systems (see for example Hammes *et al* 1989, Binder and Young 1986, and references therein). Due to computing power limitations we restricted ourselves to much smaller running times, and numbers of realizations. As a result, the present study is not expected to yield very precise quantitative information. However, despite these caveats, our results show distinctly the different physical effects at play in our orientational glass systems.

In figures 3(*a*), (*b*) and (*c*) we show $q(t_1)$, the specific heat C_v, and χ_{sg} for the random park model, with particles interacting via $V\{i\}$. The averaging is over six random park configurations. Below $T = 1.5 \, \varepsilon_q/k_B$ fluctuations of $q(t_1)$ about zero become visible,
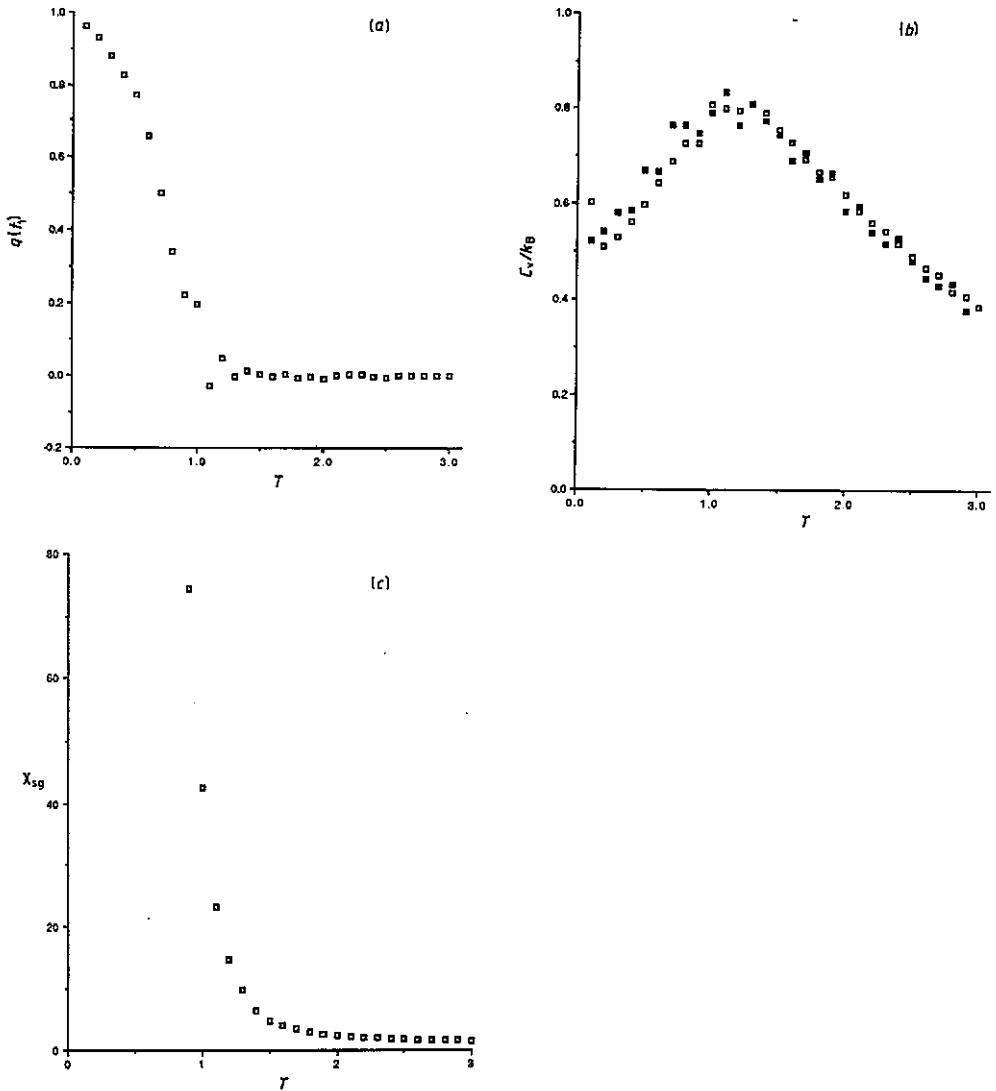
Figure 3. (a) $q(t_1)$, (b) C_v and (c) χ_{sg} for particles with a random parked positional configuration and interacting via potential {i}. In 3(b) □ represents C_v calculated from the energy fluctuations and ■ from the differentiation of the energy curve.

indicating that the time scales increase, in this region, to the same order as the simulation and at $T_f \sim 1.0 \; \varepsilon_q/k_B$ a dramatic freezing is observed. The specific heat, calculated from both fluctuations, and from differentiating the energy curve, shows an accompanying peak. The peak is quite broad, in keeping with typical spin glass behaviour where a rounded finite peak is observed. C_v/k_B approaches 0.5 as T approaches zero, as one expects for this classical system. χ_{sg} shows the rapid development of correlations in the region of T_f. From our limited results it is impossible to comment on the divergence of χ_{sg} at finite temperature, however the change in behaviour of our system from single particle to collective behaviour is well defined and extremely abrupt.
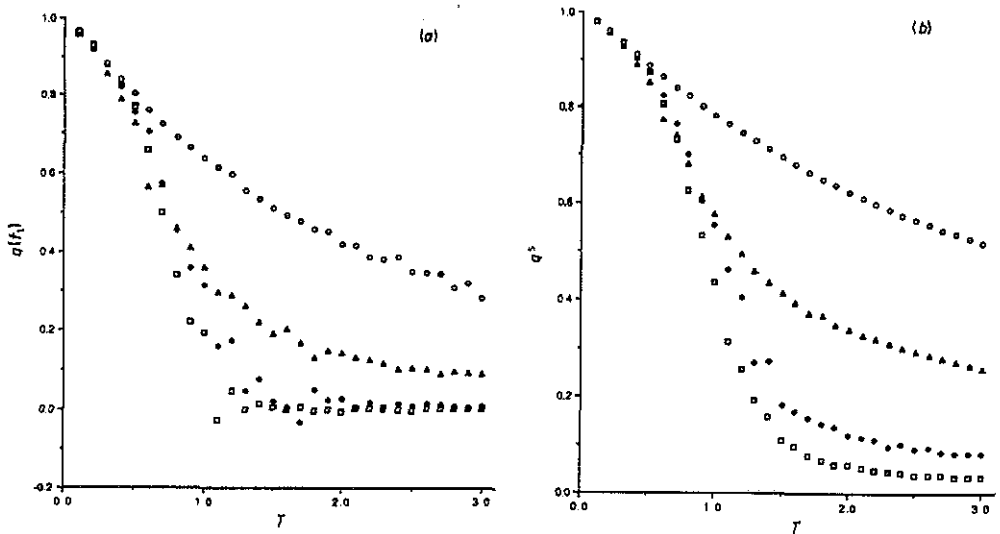
Figure 4. (a) $q(t_1)$ and (b) q^s for particles with a random parked positional configuration and interacting via potential {i} (□), {ii} (◇), {iii} (△), {iv} (○).

In figures 4(a) and (b) we show $q(t_1)$ and q^s for the random parked system with particles interacting via all four potentials. The data for potentials {ii}–{iv} is taken from three random park configurations. For finite random field strength the order parameters remain non-zero out to infinite temperature. As seen in section 3, the random fields define, for some particles, a unique ground state and the symmetry of these particles is always broken in the direction of this ground state orientation. What results is a regime of single particle freezing, with a gradual increase, with decreasing temperature, of the order parameters. For interactions {ii} and {iii} there is a cross-over, at low temperature, to a second regime where the order parameter is approximately independent of random field strength. We interpret this second regime as a remnant of the dynamical freezing, but cannot tell from our results if the cross-over is continuous, or discontinuous. For potential {iv} with eight times the field strength of the quadrupolar interaction, it is questionable if a cross-over exists, and the freezing appears continuous over the whole temperature range. This is consistent with the fact that an almost unique ground state exists in this case.

We note, with caution, the similarity between the above observation and the predictions for the Sherrington–Kirkpatrick spin glass model, in the presence of a constant magnetic field (Parisi 1980b). Here, the low temperature phase, with replica symmetry breaking, is valid below a finite critical field strength, (de Almeida and Thouless 1978) and the observable order parameter is predicted to have a very weak dependence on field strength (Parisi 1980b). Above the critical field the correct solution is replica symmetric, and the order parameter is field dependent with a non-zero value out to infinite temperature. Hence, the theory predicts two-order parameter regimes, separated by a real spin glass transition, and a corresponding singularity in the slope of the order parameter curve versus temperature. The Almeida–Thouless line of critical field strengths exists also, in the case of the Sherrington–Kirkpatrick spin glass model with random fields (Koshenev and Litvin 1987, Pirc *et al* 1987) and the full Parisi solution of the Sherrington–Kirkpatrick model should predict similar behaviour in this case.
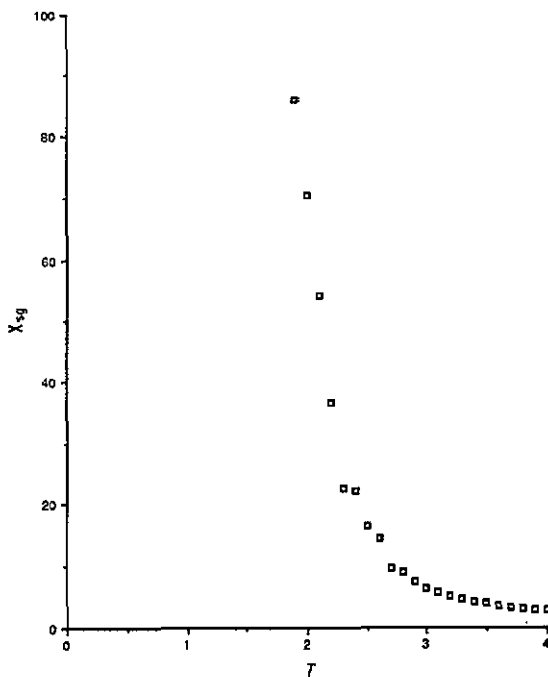
Figure 5. χ_{sg} for particles on a diluted triangular lattice, with 610 particles on a 1024 site lattice. The particles interact via potential {i}.

However, we stress again, that our system is below the lower critical dimensionality for an equilibrium spin glass phase transition, and that the freezing we observe is purely dynamical. Hence there is no *a priori* reason why the agreement between the above theory and our simulation results should be anything more than qualitative, or even coincidence.

Similar behaviour, with two order parameter regimes, has been observed in recent experiments on the $K(CN)_xKBr_{1-x}$ system (Wochner and Petry 1990), and is predicted by the mode–mode coupling theory of Bostoen and Michel (1988, 1991). The high temperature regime is interpreted as being due to internal random fields, and the relative importance of the two regimes is changed by changing the concentration x. The mode–mode coupling theory predicts a discontinuous change of slope in the order parameter versus temperature curve, as does the Sherrington–Kirkpatrick spin glass model discussed above.

In figure 5 we show χ_{sg} for the diluted lattice model, with particles interacting via potential {i}. A rapid change in correlations is once again observed at a well-defined transition temperature T_f, indicating spin glass-like behaviour, at least on the time scale used. In figure 6 we show q^s for particles interacting via potentials {i}, {ii} and {iii}. The two temperature regimes, with q^s field dependent and field independent are clearly defined, and the behaviour is essentially the same as that of the random park model. In each case the results are averaged over three independent particle configurations.

The quadrupolar ground state configuration for an undiluted triangular lattice is the six-fold degenerate herringbone structure. To be sure that the orientational freezing in our system is to a disordered state, and not to the ordered state of the pure system, we
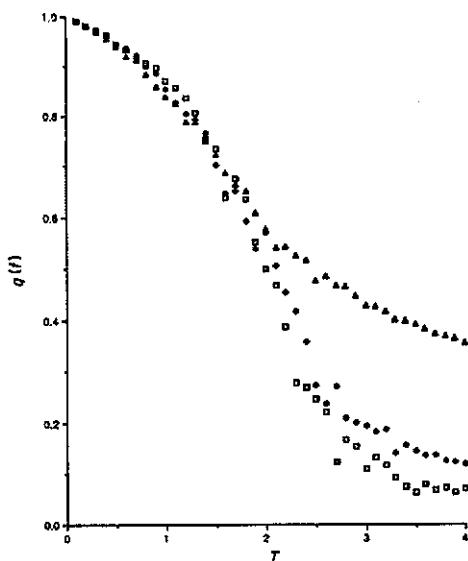
Figure 6. $4q^s$ for particles on a diluted triangular lattice, with 610 particles on a 1024 site lattice. The particles interact via potential {i} (□), {ii} (◇), {iii} (△).

monitored the presence of long range herringbone order by performing a finite size scaling analysis, at $T = 0$, of the relevant order parameters Y_1, Y_2 and Y_3 (Harris *et al* 1984)

$$Y_i = \frac{1}{N}\sum_j \langle \sin(2\varphi_j - 2\gamma_i) \exp(iQ_i \cdot r_j)\rangle \tag{4.5}$$

$$Q_1 = (0, 2\pi/\sqrt{3}), \gamma_1 = 0$$
$$Q_2 = (-1/\pi, -\pi/\sqrt{3}), \gamma_2 = 2\pi/3 \tag{4.6}$$
$$Q_3 = (1/\pi, -\pi/\sqrt{3}), \gamma_3 = 4\pi/3.$$

For a system of 128 particles, the largest order parameter was around 0.5, while for the above system, with 610 particles this figure had reduced to about 0.1. We interpret this result as a finite size effect and conclude from it that no long-range order exists in our system.

From our simulation results it appears that relaxation of the anisotropic particles away from the Bravais lattice sites of the underlying lattice structure is not necessary for the formation of an orientational glass phase. However, the freezing temperature T_f is around $2.2\ \varepsilon_q/k_B$, for the diluted lattice system, compared with $1.0\ \varepsilon_q/k_B$ for the random parked model. The difference is large in comparison with the densities: $\rho = 0.54$ for the dilute lattice and $\rho = 0.49$ for the random park (both in reduced units) and could be due to the different random distributions. For a completely filled triangular lattice of interacting quadrupoles, the random field terms sum to zero on each site (Harris *et al* 1984), while they make a non-zero contribution for finite dilution, hence the importance of the random fields should increase with dilution. This is consistent with the predictions of mode–mode coupling theory, that the internal random fields become increasingly important as the CN$^-$ ion concentration is decreased, in the K(CN)$_x$KBr$_{1-x}$ system.
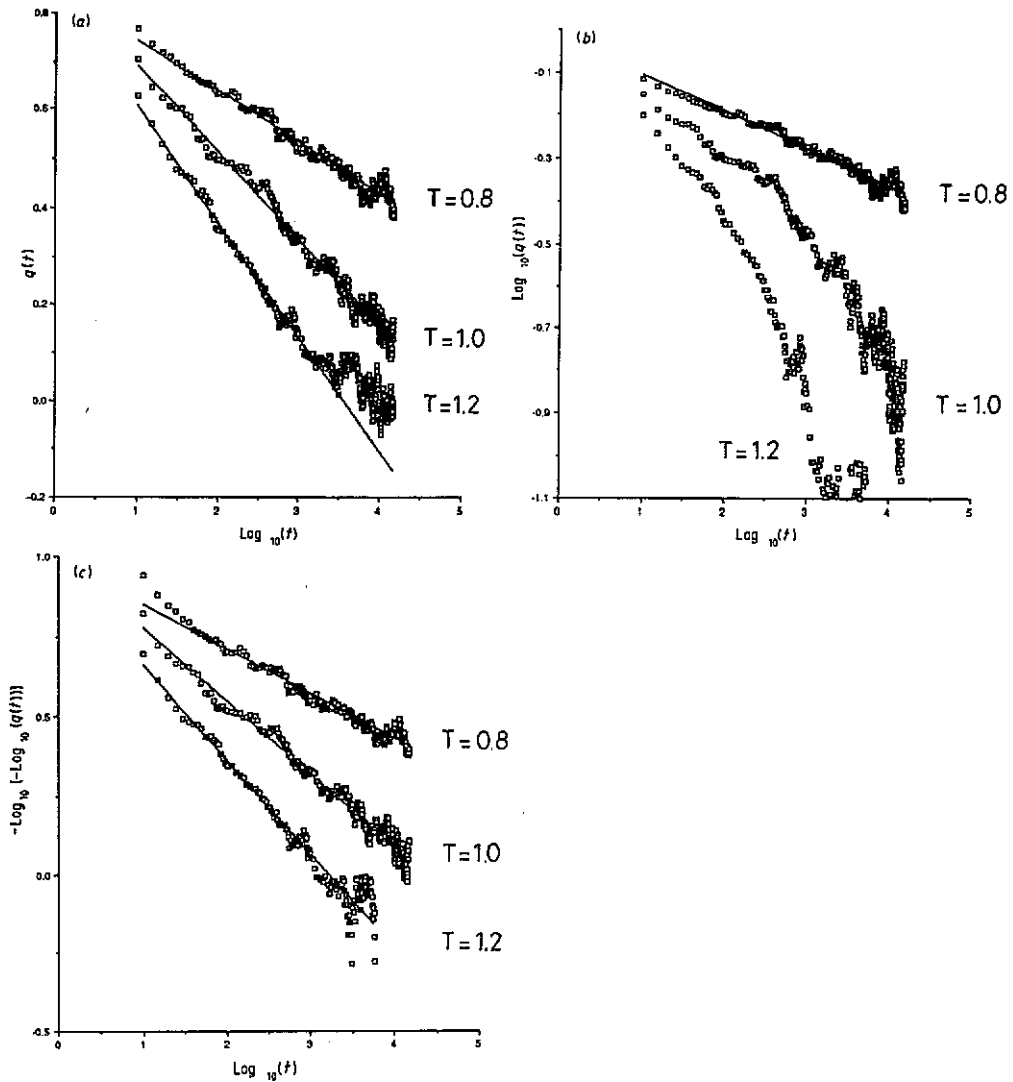
Figure 7. Time dependence of the order parameter $q(t)$, for particles with a random parked distribution and interacting via potential {i}. The figures are for (a) $q(t)$ versus $\log_{10}(t)$; (b) $\log_{10}(q(t))$ versus $\log_{10}(t)$; and (c) $-\log_{10}(-\log_{10}(q(t)))$ versus $\log_{10}(t)$. The temperatures shown are in reduced units of ε_q/k_B. In each case the line is a fit to the Monte Carlo data, as described in the text.

The last part of our study involves the investigation of the time dependence of the order parameter $q(t)$, for the random park system, with particles interacting via potential {i}. In figures 7(a), (b) and (c) we show $q(t)$ versus t, which is tested against the following laws (Hammes *et al* 1989)

$$q(t) = \text{const} - \log_{10}(t) \tag{4.7a}$$

$$q(t) = t^{-\alpha} \tag{4.7b}$$

$$q(t) = \exp[-(t/\tau)^{\beta}]. \tag{4.7c}$$

The results are averaged over nine runs in total, made up from three runs each for three different configurations. In each case the last configuration at the end of the runs shown in figure 3 was taken as the starting configuration (i.e. t_0), the observation time t_{obs} (4.1) was taken as 100 MCS. We show temperatures below, equal to, and above the freezing temperature T_f ($T = 0.8\varepsilon_q/k_B$, $T = 1.0\varepsilon_q/k_B$, $T = 1.2\varepsilon_q/k_B$ respectively) and where possible we have fitted a straight line to the data. In the case of $T = 1.2$, $q(t)$ decays to zero on a time-scale less than that of the full simulation, and we have fitted the straight line to the points between $t = 0$ and that time at which $q(t) = 0$ for the first time.

We have not had at our disposal the computing resources necessary to make a detailed analysis (Hammes *et al* 1989), however from figure 7 some points are already clear. The results, at least on the time scales we have used, are consistent with a dynamical transition and we observe the slow decay of $q(t)$ towards zero below T_f, and not to a non-zero value, as would be the case if our system exhibited a static equilibrium phase transition. It is clear from figure 7(*b*) that one cannot describe the decay of $q(t)$ by a power law. However, it is not possible to distinguish between the simple logarithmic decay (4.7*a*) and the stretched exponential decay (4.8*c*) Kohlrausch–Williams–Watts law). For other models, both continuous (Hammes *et al* 1989), and discrete (Carmesin and Binder 1988), the stretched exponential law best describes the decay. Our results slightly favour the simple logarithmic decay, in that the chi-squared of the straight line fits are consistently slightly smaller for (4.7*a*) than for (4.7*c*).

5. Discussion

In this paper we have investigated the form of the microscopic interactions that lead to orientational glass behaviour in two-dimensional systems and addressed the debate in the literature concerning the nature of the freezing in orientational glasses. We have shown that the non-separability of anisotropic pair potentials in the molecular orientation, and intermolecular orientations, leads to a coupling between the translational and rotational degrees of freedom. In an orientational glass system, with randomly quenched positional degrees of freedom, this coupling can lead to orientational disorder down to zero temperature. We have isolated terms in the anisotropic potentials that are either random bond-like or random field-like, and which are directly responsible for cooperative and single particle freezing respectively. For finite random field strength we observe two temperature regimes for our orientationally disordered systems: at high temperatures there is continuous single particle freezing, due to the random field interactions. The spin glass order parameter is field dependent and has a non-zero value out to high temperature. At low temperatures we observe a field independent regime, which we interpret as a remnant of the cooperative freezing observed for zero random field strength.

For the two-dimensional quadrupole interaction the ratio of the strength of the random field term to that of the random bond term is small, and we find predominantly random bond, or spin glass-like behaviour for our models of two-dimensional quadrupolar glasses. Positional disorder was modelled by both a random parking algorithm and by a randomly diluted triangular Bravais lattice. The models show the same qualitative behaviour, from which we conclude that relaxation away from Bravais lattice sites is not an essential ingredient for the formation of an orientational glass phase. From

these results we suggest that a positionally quenched, random mixture of argon atoms and nitrogen molecules adsorbed onto a graphite surface, could exhibit strong cooperative freezing to a low temperature orientational glass state. (Neutron diffraction studies of this system are in progress and the results will be presented elsewhere (Holdsworth 1991b).)

Current understanding from the field of spin glasses is that two-dimensional systems with short range interactions do not exhibit a static equilibrium transition, and that any orientational freezing should be dynamical in nature and correspond to a loss of ergodicity on the time scale of observation only. We have studied the time dependence of the order parameter below the freezing temperature and found behaviour consistent with this statement.

The question as to whether or not a static transition exists in three dimensions is still an open one. However, dynamic effects will be important in three-dimensional systems, irrespective of the answer to the above question, and understanding the behaviour of orientational glasses involves understanding the dynamical freezing. It is thus useful and instructive to study the much simpler two-dimensional systems.

Acknowledgments

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