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‘Fragile’ glass-forming behaviour of a three-dimensional Ising ferromagnet with uniform frustration

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Abstract

By using Monte Carlo simulation, we study the dynamics around equilibrium of a uniform frustrated three-dimensional Ising model with nearest-neighbour ferromagnetic interactions and small, but long-range (coulombic) antiferromagnetic interactions. This model exhibits a strong slowing down of the relaxations for temperatures below the critical temperature of the unfrustrated model. The characteristics of this slowing down—super-Arrhenius activated temperature dependence of the relaxation time and non-exponential decay of the correlation function—are similar to those observed in fragile glass-forming liquids.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The physical origin of the dramatic increase of viscosity and relaxation times observed in supercooled liquids when lowering the temperature, an increase that leads to the ‘glass transition’, remains an open question. Part of the puzzle is the fact that no marked changes in any of the structural quantities accompany the spectacular evolution of the dynamical quantities. The slowing down, with the concomitant development of non-exponential character of the relaxation functions, is seen in a wide variety of systems, most noticeably in weakly bonded liquids such as organic molecular liquids, molten salts, or polymeric systems. In the latter, known as ‘fragile’ glass formers, the viscosity and the primary (α -) relaxation time increase by up to 15 orders of magnitude when temperature is decreased by a mere factor of two [1–3]. This behaviour is typical of a thermally activated process, but, instead of showing the usual Arrhenius dependence, the effective activation barrier increases as the temperature decreases (at least below a crossover temperature T^*), which seems to indicate that the relaxation is also collective and cooperative. There have been a number of suggestions regarding possible sources for generating such activated, cooperative relaxation, among which is the introduction

of spin–glass-like quenched randomness or specific kinetic constraints. We take here another route in which the constraint is global and is derived from a feature that is claimed to be genuine for all liquids: structural frustration.

One notion underlying the concept of structural (or geometric) frustration is that of a *locally preferred structure* (LPS). This latter describes the local order of a system and corresponds to configurations that locally minimize the energy and maximize the packing. For instance, the LPS is well established in the case of hard spherical objects in two and three dimensions [4–6]: in two dimensions, the local motif which optimizes packing is a disc surrounded by six neighbours forming a perfect hexagon; in three dimensions, the densest local packing is provided by spheres arranged at the vertices of regular tetrahedra, and 20 such tetrahedra form a 13-atom icosahedron. A more realistic example is given by liquid water [7]. In the low-pressure liquid, water molecules are thought to arrange themselves in a local structure formed by two adjacent pentamers bonded via two hydrogen bonds: this structure is a low-entropy, high-specific-volume, but low-energy state. On the other hand, the high-pressure liquid has a different LPS in which two adjacent pentamers are more closely packed, but non-bonded, thereby forming a high-energy, but high-entropy and low-specific-volume state. *Structural frustration* denotes the fact that a LPS cannot be simply replicated to tile the whole space periodically. The canonical example is again provided by systems of spherical particles: whereas the local hexagonal pattern of discs can be extended in space to form a triangular lattice, icosahedra, because of their fivefold rotational symmetry, cannot form a pure crystal in three-dimensional (Euclidean) space. The two-dimensional case has no frustration; it also has no supercooled fluid and no glass transition, but the three-dimensional system does. More on geometric or structural frustration can be found in [5, 6].

Assuming the existence of a LPS and of structural frustration in liquids, Kivelson, Tarjus, and co-workers [8] have proposed the following picture for supercooled liquids and the glass transition: molecules in a liquid tend to arrange themselves in a LPS that minimizes some local free energy. The tendency to extend this LPS in space is opposed by a (strain) free-energy cost generated by the structural frustration. This strain free energy tends to grow super-extensively with system size (or distance), thereby preventing any long-range extension of the LPS. As a result of the competition between the local tendency to order and the frustration-induced strain, the liquid, below some crossover temperature T^* , breaks up into domains whose size and further growth upon decreasing the temperature are limited by the frustration. Note that these domains are equilibrium entities. Their presence can explain activated, cooperative dynamics and non-exponential relaxation [8, 9], but it should be stressed that the dynamics considered is still at equilibrium and does not involve domain coarsening. A simple implementation of the above picture can be obtained by introducing a coarse-grained Hamiltonian model in which the tendency to order is described by a short-range, attractive effective interaction and the frustration-induced *super-extensive* strain is mimicked by a weak, but *long-range* competing interaction:

$$H = - \sum_{\mathbf{r}, \mathbf{r}'} J(\mathbf{r} - \mathbf{r}') \mathbf{O}(\mathbf{r}) \cdot \mathbf{O}(\mathbf{r}') + \frac{Qa_0}{2} \sum_{\mathbf{r}, \mathbf{r}'} \frac{\mathbf{O}(\mathbf{r}) \cdot \mathbf{O}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (1)$$

where $J(\mathbf{r})$ is a short-range interaction with a typical energy scale J , a_0 is the characteristic length associated with the local structure, i.e., is of the order of the mean intermolecular distance in a liquid, $\mathbf{O}(\mathbf{r})$ is a local order variable associated with the LPS, and $0 < Q \ll J$. Without the frustration term, the reference Hamiltonian is chosen to have a continuous transition for a temperature $T_c^0 \sim J$.

2. The Coulomb frustrated Ising ferromagnet

2.1. The model and its phase diagram

In this paper, we specify the model as follows: the system is defined on a three-dimensional cubic lattice whose spacing a_0 is taken equal to 1, and $O(\mathbf{r})$ is a (two-state) Ising variable. The Hamiltonian is then

$$H = -J \sum_{\langle ij \rangle} S_i S_j + \frac{Q}{2} \sum_{i \neq j} \frac{S_i S_j}{|\mathbf{r}_{ij}|} \quad (2)$$

where J and Q are both positive and denote the strength of the ferromagnetic and the antiferromagnetic interaction, respectively; $S_i = \pm 1$ is the Ising spin variable. For the ferromagnetic interaction, the bracket $\langle ij \rangle$ corresponds to a summation over all distinct pairs of nearest neighbours, whereas for the antiferromagnetic one, the summation is over all pairs of spins.

To ensure the existence of the thermodynamic limit, the Coulomb potential imposes that the total magnetization of the system be zero. Therefore, long-range ferromagnetic order is prohibited at all temperatures for any non-zero value of the frustration parameter Q/J ; this describes the effect of the global constraint imposed by structural frustration, which forbids any long-range order based on the periodic repetition of the LPS. At zero temperature, the phase diagram can be calculated exactly [10]. For small values of the frustration parameter Q/J , the ground state consists of lamellar phases in which lamellae of width m made up by parallel planes of ferromagnetically aligned spins form a periodic structure of length $2m$ along the perpendicular direction; this phase is conventionally denoted as $\langle m \rangle$ [11]. The period of the lamellar phases increases when Q/J decreases. When the latter goes to zero, the width of the lamellae diverges as $(Q/J)^{-1/3}$ and the range of stability of the successive lamellar phases shrinks to zero as $(Q/J)^{4/3}$. For larger frustration parameter ($Q/J > 1$), the ground state is formed by tubular or cubic phases. (For studying the dynamics, we shall restrict ourselves to the small-frustration ($Q/J < 1$) region for which the ground states are lamellar phases.) The mean-field theory [10] predicts a complex temperature–frustration phase diagram in which the low-temperature region displays an infinite sequence of ‘flowers’, formed by an infinite number of modulated phases with more and more complex modulation patterns as the temperature increases, and is separated from the high-temperature paramagnetic region by a line of second-order phase transitions. Recently, extensive Monte Carlo simulations [12] have shown that whereas the low-temperature phase diagram has a complex structure similar to that predicted by the mean-field approximation, the transition line between the modulated and the paramagnetic phases is of first order. Following Brazovskii [13], this latter result can be interpreted on the basis of the self-consistent Hartree approximation which predicts the occurrence of a fluctuation-induced first-order transition (a transition with no nearby low-temperature spinodal). Figure 1 displays a simplified picture of the phase diagram.

2.2. Dynamical properties

Contrary to the case for systems composed of atoms, whose time evolution follows from the Newton equations and can be studied by means of molecular dynamics, there is no intrinsic equation of motion for classical spin models. Since only the long-time behaviour is relevant for our purpose, most local dynamical rules for evolving the spins are equally justified, and we have chosen the Metropolis algorithm (with the constraint of zero total magnetization) as the basic dynamics. The elapsed time t is then the number of Monte Carlo sweeps per spin. Let

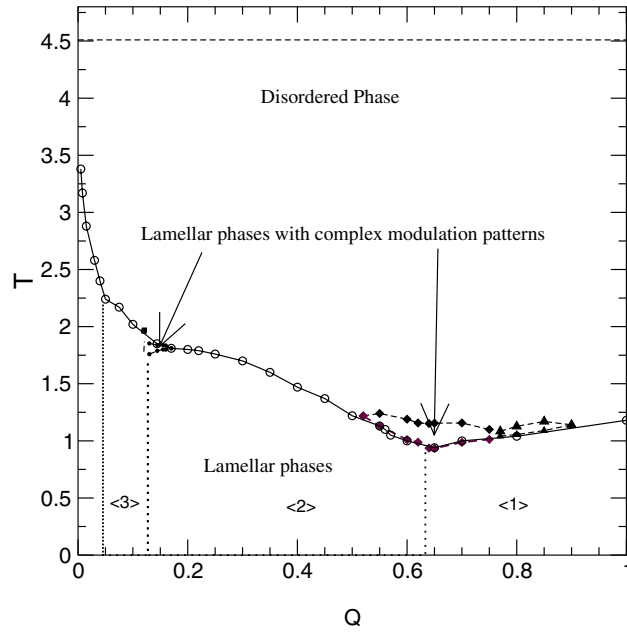


Figure 1. The simplified phase diagram obtained by Monte Carlo simulation [12]. The melting line of the simple lamellar phases (full, dark curve and open symbols) displays cusps around $Q \simeq 0.04$, $Q \simeq 0.13$, and $Q \simeq 0.65$. In these regions, intermediate modulated phases appear that correspond to mixed lamellar phases (dashed lines and filled symbols). The units are chosen such that $k_B = J = 1$. The horizontal dashed line corresponds to the transition temperature of the Ising model in the absence of frustration.

us recall that for the frustrated Ising model, the total magnetization is not the order parameter, as opposed to the case for the simple Ising model.

The quantity that we have computed for studying the relaxational properties is the spin-spin self-correlation function defined as

$$C(t) = \frac{1}{N} \sum_i \langle S_i(t') S_i(t' + t) \rangle \quad (3)$$

where the bracket denotes the thermal average and N is the total number of lattice sites. We stress that $C(t)$ is an equilibrium correlation function, which is monitored once the system has reached equilibrium. In practice, the thermal average is performed as an average over twenty different initial times t' , all chosen larger than the relaxation time. All simulations were done for a 16^3 cubic lattice with periodic boundary conditions, and the Coulomb interaction was handled via Ewald sums. In what follows, we take $J = 1$.

3. Results and analysis

Figure 2 shows the correlation function $C(t)$ for three values of the frustration parameter Q ((a) $Q = 0.11$, (b) $Q = 0.006$, (c) $Q = 0.001$) and for temperatures decreasing from $T = 6$ to a temperature slightly above the first-order transition to modulated phases (from left to right). Indeed, although possible in principle, we have not been able to study the disordered phase at lower temperatures, the lattice sizes achievable in practice being too small to allow a proper supercooling of the phase below the first-order transition.

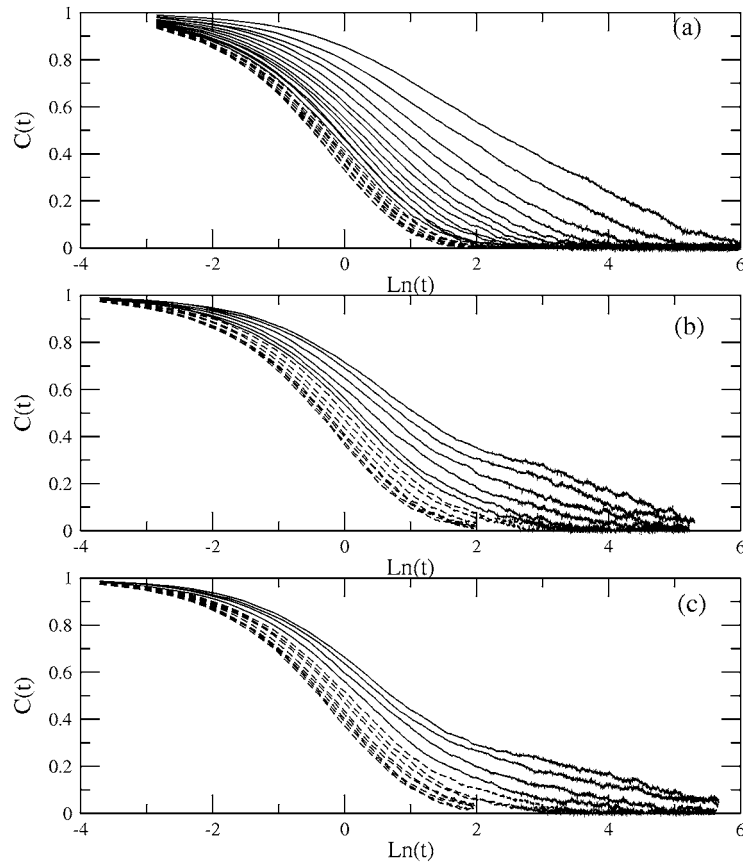


Figure 2. Spin-spin correlation function $C(t)$ versus $\ln(t)$: (a) $Q = 0.11$, (b) $Q = 0.006$, (c) $Q = 0.001$. The curves from left to right correspond to temperatures decreasing from $T = 6$ to a temperature slightly above the first-order transition. The dashed curves indicate temperatures higher than $T_c^0 \simeq 4.51$, the critical temperature of the unfrustrated Ising model.

One observes in figure 2 a change of behaviour as frustration decreases. Whereas the decay of $C(t)$ at the highest frustration ($Q = 0.11$) seems to occur in a single step at all temperatures, a two-step decay develops as temperature is lowered in the two other cases. At high temperatures, typically above $T_c^0 \simeq 4.51$, the critical temperature of the unfrustrated Ising model (dashed curve in figure 2), the whole time dependence of the correlation function is well fitted by a simple exponential, $\exp(-t/\tau_0(T))$. This is true for all values of the frustration. At lower temperatures, it is impossible to describe the entire decay by a single exponential. The emerging second step of the relaxation, clearly visible for $Q = 0.006$ and 0.001 , is well described by a stretched exponential, $\exp(-(t/\tau_{\text{KWW}}(T))^\beta)$, with the stretching exponent β decreasing as T decreases. On the other hand, the first step (short-time regime) can still be fitted by a simple exponential $\exp(-t/\tau_0(T))$. A two-step decay is typical of many glass-forming systems, especially the fragile supercooled liquids [1–3]. One notices, however, that the timescale separation seen in figure 2 between the two steps is not large enough for one to observe the development of a plateau at intermediate times.

We have monitored as a function of temperature both the short- and the long-time relaxation times, $\tau_0(T)$ and $\tau_\alpha(T)$ respectively. In order to avoid the uncertainty associated with the use

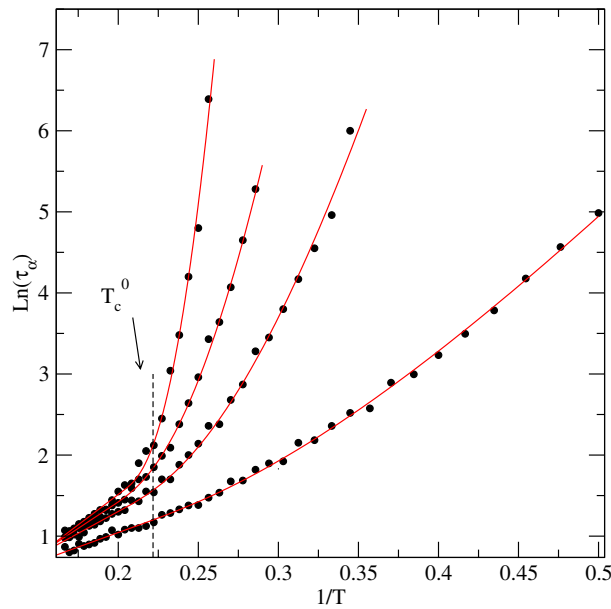


Figure 3. An Arrhenius plot of the relaxation time τ_α for different values of the frustration parameter Q (from left to right, $Q = 0.001, 0.006, 0.02, 0.11$). The full curves correspond to the FLDT predictions (see the text).

of the three-parameter stretched-exponential fit, we have defined $\tau_\alpha(T)$, as is often done in spin systems [14], by the condition $C(\tau_\alpha) = 0.1$.

The temperature dependence of the relaxation time $\tau_\alpha(T)$ is shown in figure 3 for four different values of the frustration parameter Q on an Arrhenius plot. At high temperature, the T -dependence is essentially Arrhenius-like, i.e., a straight line on the plot in figure 3. At lower temperature, $\ln(\tau_\alpha(T))$ increases more and more rapidly as the temperature decreases, thereby departing from Arrhenius behaviour to become ‘super-Arrhenius’. Two features are worth stressing. First, as predicted by the frustration-limited domain theory (FLDT) [8] (see above), the departure from Arrhenius dependence becomes noticeable below a crossover temperature that lies in the vicinity of T_c^0 . Secondly, this departure becomes more marked as frustration decreases.

The super-Arrhenius behaviour is typical of the viscous slowing down of fragile glass-forming liquids: the more fragile a liquid, the more pronounced the super-Arrhenius character [1–3]. The Coulomb frustrated Ising model thus displays some major aspects of the phenomenology of glass-forming liquids: non-exponential relaxation and super-Arrhenius, activated behaviour. In addition, ‘fragility’, i.e., the degree of departure from Arrhenius T -dependence, can be continuously varied by tuning one parameter, the frustration strength Q/J . To our knowledge, there is no other microscopic model showing this property. We finally point out that the relaxation time $\tau_0(T)$, characteristic of the first step of the relaxation (at high temperature above T_c^0 where $C(t)$ is essentially decaying as a simple exponential; the two times $\tau_0(T)$ and $\tau_\alpha(T)$ are of course simply related via a constant factor), has an Arrhenius-like T -dependence, $\tau_0(T) = \tau_{0,\infty} \exp(E_\infty/T)$, except at the very lowest temperatures at which some deviations can be detected [15]¹. This seems to indicate that proper cooperative

¹ Note that the dynamics of the unfrustrated case ($Q = 0$) shows standard critical slowing down as T_c^0 is approached, and that, as expected, the relaxation time is well described by a power law.

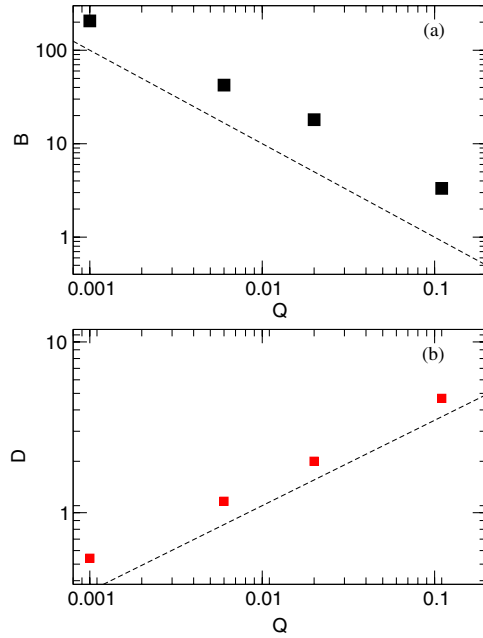


Figure 4. (a) FLDT parameter B versus frustration Q . The dashed line is the Q^{-1} FLDT prediction [2]. (b) VTF parameter D versus frustration Q . The dashed line corresponds to the $Q^{1/2}$ -power law predicted by Westfahl *et al* [18].

behaviour in the dynamics of the model distinctly sets in below T_c^0 and is responsible for the second step of the relaxation.

We have performed a number of quantitative analyses of the simulation data, all motivated by existing theoretical approaches. We focus here on the dependence on T (and Q) of the relaxation time $\tau_\alpha(T)$. One has to remember that the range of relaxation times spanned by our data is limited (as in most simulations of glass-forming systems), quite far from the 15 decades observed experimentally in supercooled liquids. With this cautionary note in mind, we find that the data are compatible with the activated-type expressions, $\tau_\alpha(T) \propto \exp(E_\alpha(T)/T)$, predicted by the FLDT [8,9] and the entropic droplet approach [16–18], but are poorly described by a power-law temperature behaviour, $\tau_\alpha(T) \propto |T - T_c|^{-\nu}$ [15].

The FLDT [8] predicts an effective activation energy $E_\alpha(T)$ that behaves as

$$E_\alpha(T) = E_\infty \quad T > T^* \quad (4)$$

$$= E_\infty + BT^* \left(1 - \frac{T}{T^*}\right)^{8/3} \quad T < T^* \quad (5)$$

where $E_\alpha(T) = T \ln(\tau_\alpha(T)/\tau_\infty)$, with τ_∞ a characteristic high- T time. *A priori*, four adjustable parameters (τ_∞ , E_∞ , B , T^*) are needed for each frustration. This number can be reduced by using the parameters obtained from the analysis of the first-step decay time $\tau_0(T)$, which provides τ_∞ and E_∞ . Only two parameters, B and T^* , are then left adjustable for each Q . The resulting curves are displayed in figure 3, and the agreement with the simulation data is very good. As predicted by the theory, the crossover temperature T^* is found close to T_c^0 ($T^*/T_c^0 \simeq 1.04$ – 1.12) and the super-Arrhenius parameter B , shown in figure 4(a), varies roughly as Q^{-1} ; again, small frustration implies a large degree of super-Arrhenius character and large fragility. Note that the value $8/3 \simeq 2.67$ of the exponent in equation (5) should

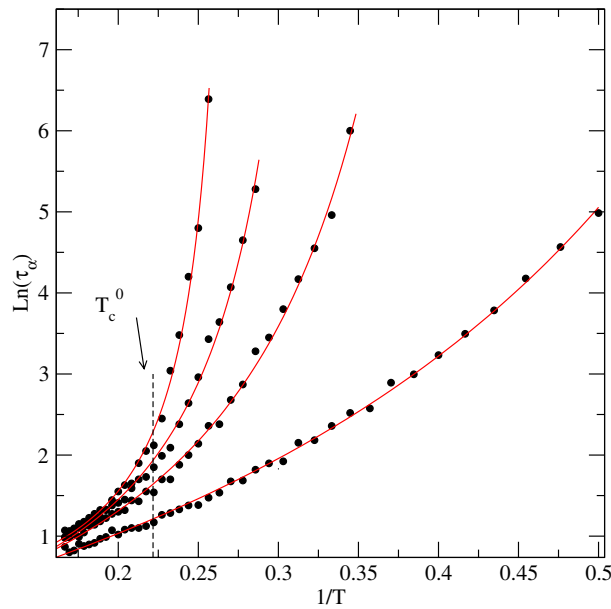


Figure 5. An Arrhenius plot of the relaxation time τ_α for different values of the frustration parameter Q (from left to right, $Q = 0.001, 0.006, 0.02, 0.11$). The full curves correspond to the VTF predictions (see the text).

not be overinterpreted [8]: indeed, a similar agreement between theory and simulation data is obtained for values between 2.5 and 2.9, an interval that includes $4\nu_{\text{Ising}} \simeq 2.52$.

The approach developed by Schmalian, Wolynes, and co-workers [16–18] combines an analysis of the free-energy landscape within the replica formalism with a dynamical scaling argument based on entropic droplets. (This approach was first used in the context of generalized spin glasses [19].) It leads to the well-known Vogel–Tammann–Fulcher (VTF) formula, widely used to describe the viscous slowing down of glass-forming liquids [1–3]:

$$\tau_\alpha = \tau_0 \exp \left[\frac{DT_0}{T - T_0} \right]. \quad (6)$$

Three parameters, τ_0 , D , and T_0 , must be adjusted for each frustration, and we have found no way to reduce this number as in the previous analysis. Figure 5 shows a comparison between the simulation data and the best fits to the VTF expression. The agreement is again good, with some slight discrepancies at high temperature and small frustration. As predicted by Schmalian and Wolynes [16, 17], the ‘ideal glass transition’ temperature T_0 increases when Q decreases (T_0 , the temperature at which the configurational entropy is predicted to vanish, is always rather below the temperature of the first-order transition to the modulated phases, i.e., is in the supercooled paramagnetic phase); as also predicted, the parameter D , inversely related to the fragility, increases with Q , roughly as $Q^{1/2}$ (see figure 4(b)).

4. How ‘fragile’?

As we have already mentioned, the notion of ‘fragility’ for glass-forming systems roughly characterizes how strongly the T -dependence of the primary relaxation time or of the viscosity deviates from an Arrhenius behaviour: the more fragile, the more super-Arrhenius. To quantify

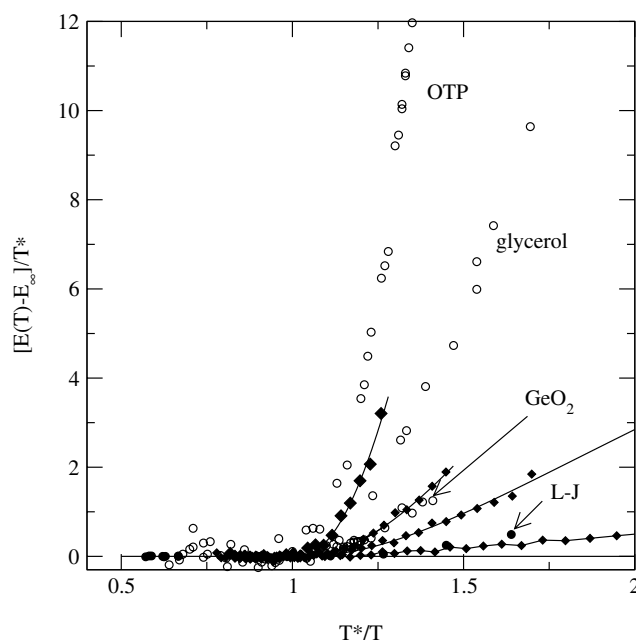


Figure 6. The super-Arrhenius contribution to the activation energy of the α -relaxation (in units of T^*) versus the inverse temperature T^*/T . Open circles: three representative glass-forming liquids (ortho-terphenyl, glycerol, GeO_2) [20]; filled circles: binary Lennard-Jones systems [21]; filled diamonds and lines: Coulomb frustrated Ising model for $Q/J = 0.11, 0.02, 0.006, 0.001$. (Note that the OTP data go up to about 20, but have been truncated for clarity.)

this notion and compare systems that are very different at a microscopic level, one must at least rescale the temperature. The ‘glass transition’ temperature T_g was originally proposed by Angell as the scaling temperature [22]. However, T_g is defined operationally, e.g., as the temperature at which τ_α is of the order of 10^2 – 10^3 s, and simulation data for various models always stop (for practical reasons) many orders of magnitude below macroscopic times typical of the experimental glass transition temperatures. For this reason, a scaling of the temperatures with respect to the crossover temperature T^* at which one observes the passage from Arrhenius to super-Arrhenius behaviour has been suggested [23]. The determination of T^* is of course subject to uncertainty, but a good description of many glass-forming liquids [20], of a binary Lennard-Jones fluid model [21], and, as seen above, of the Coulomb frustrated Ising model can be achieved in this way.

We thus plot in figure 6 the super-Arrhenius contribution to the effective activation energy for relaxation, $E_\alpha(T) - E_\infty$, in units of T^* versus T^*/T for three representative glass-forming liquids [20], a very fragile (ortho-terphenyl), an intermediate (glycerol), and a non-fragile or strong one (GeO_2), together with simulation data on a binary Lennard-Jones model [21] and our present results on the Coulomb frustrated Ising model for four different frustrations. Figure 6 illustrates the difference between the range of reduced activation energies spanned by the fragile glass-forming liquids and that obtained for computer-simulated models. It also shows that by varying the frustration strength by two orders of magnitude (from $Q = 0.11$ down to 0.001), one covers with the Coulomb frustrated model a broad spectrum of fragilities, quite comparable to that observed in glass-forming liquids.

5. Conclusions

The global constraint associated with the structural frustration may generate a competition of effects operating on very different length scales. We have shown that this competition, in the absence of any externally imposed quenched disorder, leads to the emergence of slow dynamics, whose characteristics (activated super-Arrhenius temperature dependence of the relaxation time and non-exponential, two-step decay of the correlation function) are similar to those observed in glass-forming liquids. An appealing feature of Coulomb frustrated systems is that the fragility of the system, characterized here by its degree of departure from Arrhenius behaviour, can be continuously varied by changing the frustration strength. Interestingly, the ‘fragile glass-forming’ behaviour of such uniformly frustrated systems is supported by both the phenomenological scaling analysis of the FLDT [8] and the entropic droplet argument based on the ideal glass transition scenario [16, 19].

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