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# Evidence for "fragile" glass-forming behavior in the relaxation of Coulomb frustrated three-dimensional systems

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We show by means of a Monte Carlo simulation study that three-dimensional models with long-range frustration display the generic phenomena seen in fragile glass-forming liquids. Due to their properties (absence of quenched disorder, physical motivation in terms of structural frustration, and tunable fragility), these systems appear as promising minimal theoretical models for describing the glass transition of supercooled liquids.

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The viscous slowing down of supercooled liquids, which leads to glass formation when the temperature is sufficiently lowered, remains a challenging problem of liquid-state and condensed-matter physics. The phenomenon seems dramatic enough [a change by 15 orders of magnitude of the viscosity $\eta$ and the primary ($\alpha$) relaxation time $\tau_\alpha$ for a mere decrease of the temperature $T$ by a factor of 2] and general enough to call for a universal explanation. Yet, the search for an underlying universality is thwarted by the absence of observed criticality, e.g., by the absence of a diverging, or rapidly growing, static susceptibility or correlation length [1].

If one accepts the premise that the distinctive features of most glass-forming liquids, namely, the rapid super-Arrhenius increase of $\eta$ and $\tau_\alpha$ with decreasing $T$ and the nonexponential character of the relaxation functions, result from collective or cooperative behavior, progress could be made by identifying the key physical ingredients and formulating a *minimal theoretical model* based on these ingredients, in much the same way as spin glasses have been described in terms of quenched disorder and frustration and modeled by the Edwards-Anderson Hamiltonian. One such attempt has been recently made [2], based on the concept of structural frustration [3]. Such frustration arises because a locally preferred structure, i.e., an arrangement of neighboring molecules that minimizes some local free energy, cannot tile the whole space because of the global constraint [3]. The canonical example is a three-dimensional system of spherical particles whose locally preferred structure, an icosahedral cluster of 13 particles, cannot form a pure crystal because of the fivefold rotational symmetry of the icosahedron [3]. In the frustration-limited domain theory (FLDT) of supercooled liquids [2], structural frustration is implemented as the competition between effective interactions acting on very different length scales: a short-range ordering term that favors the extension of the locally preferred structure and a weak, but long-range ($1/r$) frustrating term that generates a strain-free energy growing super-extensively with the linear size of the ordered region. These ingredients are most simply incorporated in three-dimensional Coulomb ($1/r$) frustrated lattice models with the following Hamiltonian,

$$H = -J\sum_{\langle ij\rangle} \mathbf{S}_i\cdot\mathbf{S}_j + \frac{Q}{2}\sum_{i\neq j}\frac{\mathbf{S}_i\cdot\mathbf{S}_j}{|\mathbf{r}_{ij}|}, \tag{1}$$

where $J$ and $Q$ are both positive and denote the strength of the ordering and frustrating interactions, respectively; $\langle ij\rangle$ is a sum over distinct pairs of nearest neighbors and $|\mathbf{r}_{ij}|$ is the distance between sites $i$ and $j$ (the lattice spacing is taken as unit length); and the tunable ratio $Q/J$ characterizes the frustration strength. In such models, glassiness has to be self-induced and does not result from quenched randomness or from specific kinetic constraints.

In this paper, we present an extensive Monte Carlo simulation study of Coulomb frustrated models on a cubic lattice. We focus on the relaxation to equilibrium and we do not consider at this stage out-of-equilibrium dynamics and aging phenomena in a nonequilibrated, glassy state. We show that: (i) the relaxation displays the main features characteristic of the slowing down of ''fragile'' glass-forming liquids (nonexponential decay of the relaxation function, super-Arrhenius activated $T$ dependence of $\tau_\alpha$); (ii) the fragility of the system, e.g., its degree of departure from Arrhenius behavior, increases as the frustration decreases, thereby providing a description that spans the whole range from strong to very fragile glass-former via tuning of the relative amplitude of the frustrating interaction; (iii) the slowing down occurs without the rapid growth of a correlation length and does not follow the standard critical slowing down pattern; (iv) the results, including the existence of a crossover temperature in the vicinity of the critical point of the unfrustrated system, confirm the scenario proposed by the FLDT.

In using Eq. (1), we have chosen spin variables $\mathbf{S}_i$ that can take several orientations; most of the results have been obtained for the five-state clock model ($\mathbf{S}_i = [\cos(2\pi\theta_i/q),\sin(2\pi\theta_i/q)]$, with $\theta_i$ the orientation of the planar spin and $q=5$) and the Ising model ($q=2$), but we have also studied the $q=11$ state clock model.

In the absence of frustration ($Q=0$), the models have a critical point at a temperature $T_c^0$, below which they are ferromagnetic. The long-range, Coulombic interaction requires that the total magnetization of the system be zero in order to ensure a proper thermodynamic limit. Therefore, long-range ferromagnetic order is prohibited at all $T$'s for any nonzero value of the frustration parameter $Q/J$; in the FLDT, this

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mimics the effect of structural frustration that forbids any long-range order based on the periodic repetition of the locally preferred structure. The models with discrete orientations studied here can still form ordered phases characterized by modulated patterns (e.g., lamellar phases) [4], but as shown recently by Monte Carlo simulation of the Ising model [5], the transition between paramagnetic and modulated phases is first order. Following Brazovskii [6], this result can be interpreted on the basis of the self-consistent Hartree approximation that predicts the occurrence of a fluctuation-induced first-order transition, a transition with no nearby low-$T$ spinodal. All the simulations discussed below are made in the disordered (paramagnetic) phase. Since the transition to the modulated phases at $T_{DO}(Q)$ is first order, one could in principle supercool the paramagnetic phase to lower temperatures; however, we have found that the lattice sizes achievable in practice are too small to allow for a proper supercooling below $T_{DO}$.

To study the relaxation of the frustrated systems, we have considered the dynamics associated with the Monte Carlo algorithm (simple or slightly modified Metropolis rule [7]), time being the number of sweeps per spin. In all cases, the total magnetization is constrained to be zero, as it should be in the thermodynamic limit. The dynamical quantity that we have monitored is the spin-spin self-correlation function $C(t)=(1/N)\Sigma_i\langle \mathbf{S}_i(t')\mathbf{S}_i(t'+t)\rangle$, where the brackets denote the thermal average and $N$ is the total number of lattice sites. We stress that $C(t)$ is an equilibrium correlation function that is computed once the system has reached equilibrium. In practice, the thermal average has been performed as an average over 20 different initial times $t'$, all chosen longer than the relaxation time. Most simulations have been done on cubic lattices of size $16^3$ to $22^3$ with periodic boundary conditions, and the Coulomb interaction has been handled via the Ewald sums. In one special case (see below), we have performed a finite-size study with lattices of linear size $L=5,10,15$, and 20. We have covered two orders of magnitude in the frustration parameter $Q/J$, always in the weak-frustration regime ($Q/J \ll 1$). In what follows, we take $J=1$.

The evolution of $C(t)$ with $T$ is illustrated in Fig. 1 for the five-state clock ($Q=0.1$ and $Q=0.006\,25$), the 11-state clock ($Q=0.05$), and the Ising ($Q=0.001$) models. At the highest frustration, illustrated by Fig. 1(a), the decay of $C(t)$ appears to proceed in a single step at all $T$'s. For lower frustrations, a two-step decay develops as $T$ is lowered [see Figs. 1(b) and 1(d)]. At high $T$'s, typically above the critical point of the corresponding unfrustrated model ($T_c^0 \simeq 2.1$ and $T_c^0 \simeq 4.51$ for the five-state clock model and the Ising model, respectively), the whole time dependence of $C(t)$ is well fitted by a simple exponential, $\exp[-t/\tau_0(T)]$; this is shown in Fig. 2, but is true for all models and all frustrations. At low $T$'s, below $T_c^0$, it is impossible to describe the entire decay of $C(t)$ by a single exponential; as illustrated in Fig. 2, the emerging second step of the relaxation can be described by a stretched exponential, $\exp[-(t/\tau_{KWW}(T)]^{\beta(T)}$, while the first step can still be fitted by a simple exponential, $\exp[-t/\tau_0(T)]$. This nonexponential behavior and emergence of a two-step decay, both of which become more marked as $T$ is decreased, are typical of many actual glass-forming systems, especially the fragile supercooled liquids [1]. One may, however, notice that the time-scale separation between the two relaxation steps that can be achieved in the simulations is not sufficient to observe the development of a true plateau at intermediate times.

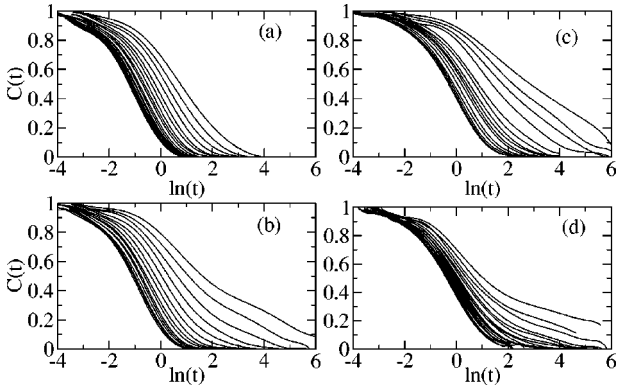


FIG. 1. Spin-spin correlation function $C(t)$ versus $\ln(t)$ for several temperatures: five-state clock model for $Q=0.1$ (a) and $Q=0.006\,25$ (b), 11-state clock model for $Q=0.05$ (c), and Ising model for $Q=0.001$ (d). In all cases, curves from left to right are for decreasing $T$'s.

To study in more detail the characteristics of the slowing down of the relaxations as one lowers $T$, a phenomenon already visible in Fig. 1, we have monitored as a function of $T$ the relaxation times characteristic of the short- and long-time behaviors, $\tau_0(T)$ and $\tau_\alpha(T)$, respectively. The former is obtained from the fit to a simple exponential (see above), but an equivalent behavior is obtained from the condition $C(\tau_0)=0.9$. The latter is defined, as often for spin systems, by the condition $C(\tau_\alpha)=0.1$; in this case indeed, there was too much uncertainty in using the three-parameter stretched-exponential fit that also requires the introduction of a lower cutoff time. The results are illustrated in Fig. 3 for the five-state clock model. We have plotted the logarithm of $\tau_0$ and $\tau_\alpha$ versus $1/T$. One can see that over the range of $T$ studied,

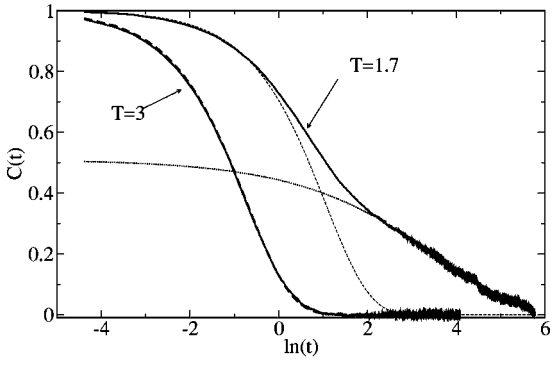


FIG. 2. $C(t)$ versus $\ln(t)$ for the five-state clock model with $Q=0.006\,25$. Left curve: $T=3>T_c^0$; the dashed line, virtually indistinguishable from the data, is an exponential. Right curve: $T=1.7<T_c^0$; the dashed curve is an exponential and the dotted curve is a stretched exponential with $\beta=0.4$.

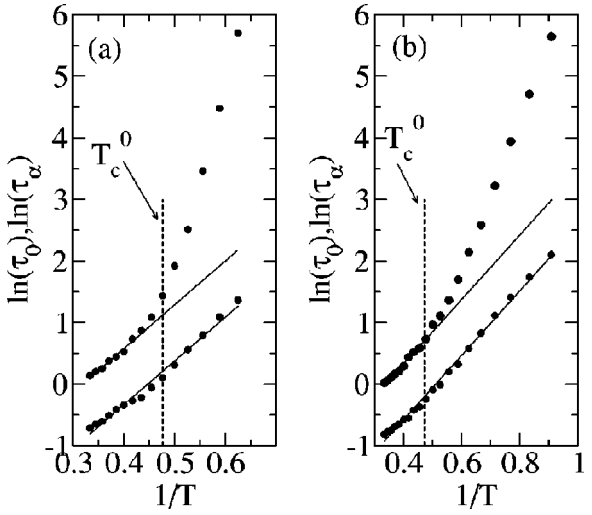


FIG. 3. Arrhenius plots of $\tau_0$ (lower curve) and $\tau_\alpha$ (upper curve) for the five-state clock model with $Q=0.006\,25$ (a) and $Q=0.05$ (b).

the dependence of $\tau_0(T)$ is essentially Arrhenius-like, i.e., linear on the diagram, $\tau_0(T)\simeq\tau_{0,\infty}\exp(E_\infty/T)$, whereas the dependence of $\tau_\alpha(T)$ shows a marked deviation from Arrhenius behavior below some crossover temperature in the vicinity of $T_c^0$. Note that at high $T$'s (above $T_c^0$), $C(t)$ is essentially exponential and the two times $\tau_0(T)$ and $\tau_\alpha(T)$ differ by a trivial constant, so that in this $T$ range the Arrhenius dependences of $\tau_0$ and $\tau_\alpha$ are the same. At lower $T$'s, $\tau_0$ is characteristic of a "secondary" or "precursor" relaxation; one expects it to be associated with a local, weakly or noncooperative, mechanism of relaxation. On the other hand, the super-Arrhenius rise of $\tau_\alpha$ versus $1/T$ is indicative of cooperative behavior.

The crossover from Arrhenius to super-Arrhenius behavior of $\tau_\alpha$ is shown in Fig. 4 for the five-state clock model for five different frustrations from $Q=0.1$ down to $Q=0.006\,25$. A similar trend is observed for all other models studied (for the Ising model, see Refs. [7,8]). Several points

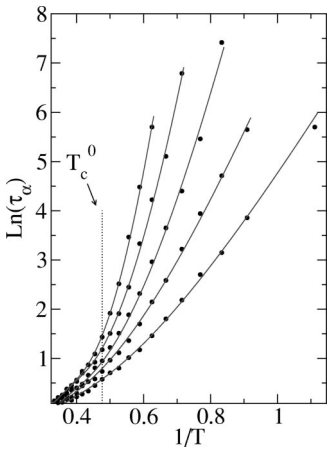


FIG. 4. Arrhenius plot of $\tau_\alpha(T)$ for the five-state clock model; from left to right: $Q=0.006\,25$, $Q=0.0125$, $Q=0.25$, $Q=0.05$, and $Q=0.1$. The full lines are the best fits to Eqs. (2,3).

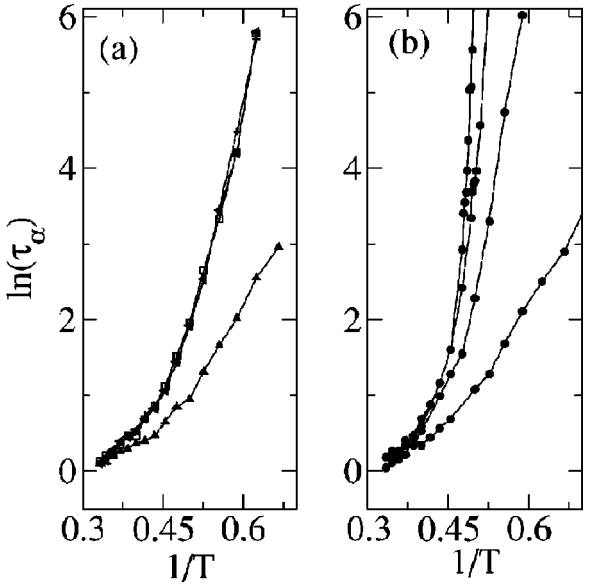


FIG. 5. Arrhenius plot of $\tau_\alpha$ for the $5-$state clock model and for lattice sizes $L=5,10,15,20$ (from right to left): $Q=0.006\,25$ (a) and $Q=0$ (b).

are worth noting: first, such a super-Arrhenius behavior 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]; second, the crossover occurs in the vicinity of the critical point of the unfrustrated system; thirdly, the departure from Arrhenius behavior, i.e., the fragility, becomes more marked as frustration decreases. To our knowledge, such a "tunable" fragility that provides a description over the whole spectrum of glass-forming behavior, from strong to very fragile, is shown by no other microscopic model.

The competition of interactions acting on very different length scales can thus generate fragile glass-forming behavior similar to that observed in actual supercooled liquids. In the FLDT [2], this behavior is attributed to the proximity of the critical point $T_c^0$ of the unfrustrated system, a critical point that is avoided in the presence of frustration. Avoided critical behavior [2,9] results in the appearance at $T$'s below $T_c^0$ of domains whose size is limited by the frustration. These domains are responsible for the nonexponential character of the relaxation and the super-Arrhenius, activated $T$ dependence of $\tau_\alpha$. Scaling arguments predict, for instance, that the effective activation free energy for the $\alpha$ relaxation behaves as [2]

$$E_\alpha(T)=E_\infty, \quad T>T^* \tag{2}$$

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

where $E_\alpha(T)=T\ln(\tau_\alpha(T)/\tau_\infty)$, with $\tau_\infty$ a characteristic high-$T$ time, $B\propto Q^{-1}$, and $T^*$ is close to $T_c^0$. The existence of a crossover in the vicinity of $T_c^0$ is indeed supported by the Monte Carlo results. More quantitatively, we have compared the above prediction with the simulation data. In doing so,

one must remember that the range of $\tau_\alpha$'s spanned by our data is limited, as in most simulations of glass-forming systems, and is far less than the 15 decades observed experimentally in supercooled liquids. The high-$T$ parameters $\tau_\infty$ and $E_\infty$ are independently obtained by an Arrhenius fit to $\tau_0(T)$ [see above, where $\tau_\infty/\tau_{0,\infty} = -\ln(0.1)$ due to the definition of $\tau_\alpha$ and $\tau_0$], and one is left with two adjustable parameters, $B$ and $T^*$, for each frustration (and each model). The resulting curves are shown in Fig. 4 for the five-state clock model. For all models the agreement between theory and simulation is good. As predicted by the theory, $T^*$ is found close to $T_c^0$ (e.g, $T^*/T_c^0 \simeq 1.14-1.20$ for the five-state clock and $1.04-1.12$ for the Ising model) and the super-Arrhenius parameter $B$ varies roughly as $Q^{-1}$ [7]. (As already stressed, small frustration $Q$ implies large super-Arrhenius character and large fragility.)

We have thus found that our simulation data are compatible with an activated-type expression, $\tau_\alpha(T) \propto \exp[E_\alpha(T)/T]$ with $E_\alpha(T)$ given by the FLDT expression. [As discussed in Refs. [8,11], the data are also compatible with $E_\alpha(T)$ described by the entropic droplet/random-first-order transition approach (EDA) [10,11], which offers a unique opportunity for comparing these two alternative theories in more detail.] On the other hand, we have checked that they are poorly described by a power-law dependence, $\tau_\alpha(T) \propto |T - T_c|^{-\gamma}$, except of course when $Q=0$ [7]. In both the FLDT and the EDA, the slowing down of the relaxation and the nonexponential character are attributed to genuinely nonperturbative effects, such as heterogeneities (domains or droplets) and cooperative, activated processes. This is quite different than standard critical slowing down, as could occur if driven by the approach of a spinodal. In particular, the length scale associated with the slowing down is predicted to grow slowly with decreasing $T$, at a much slower rate than the relaxation time itself. To check this, we have performed a finite-size study of the five-state clock model for $Q = 0.006\,25$. As seen in Fig. 5(a), $\tau_\alpha(T)$ is indeed unchanged when one decreases the linear size of the system from 20 to 10; on the other hand, it is strongly altered when passing to $L=5$. This seems to confirm that any putative length scale associated with the strong slowing down is rather modest (of the order of 5 or so) over the whole $T$ range studied. For comparison, the same finite-size study for the unfrustrated ($Q=0$) model, showing the usual pattern associated with critical slowing down, is displayed in Fig. 5(b).

In summary, due to their properties (absence of quenched disorder, physical motivation in terms of structural frustration, three-dimensional, finite-range character, and tunable fragility), whose combination is found in no other models [12], the Coulomb frustrated systems appear as promising minimal theoretical models for describing the slowing down of relaxations in supercooled liquids.

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[1] M.D. Ediger, C.A. Angell, and S.R. Nagel J. Phys. Chem. **100**, 13200 (1996); G. Tarjus and D. Kivelson, in *Jamming and Rheology: Constrained Dynamics on Microscopic and Macroscopic Scales*, edited by A. J. Liu and S. Nagel (Taylor & Francis, London, 2001), p. 20; P.G. Debenedetti and F.H. Stillinger, Nature (London) **410**, 259 (2001).

[2] D. Kivelson, S.A. Kivelson, X.L. Zhao, Z. Nussinov, and G. Tarjus, Physica A **219**, 27 (1995); G. Tarjus, D. Kivelson, and P. Viot, J. Phys.: Condens. Matter **12**, 6497 (2000).

[3] D. Nelson and F. Spaepen, Solid State Phys. **42**, 1 (1989); J. F. Sadoc and R. Mosseri, *Geometrical Frustration* (Cambridge University Press, Cambridge, England, 1999).

[4] For a modulated ordered phase with icosahedral local order, see M. Dzugutov, Phys. Rev. Lett. **70**, 2924 (1993).

[5] M. Grousson, G. Tarjus, and P. Viot, Phys. Rev. E **64**, 036109 (2001).

[6] S.A. Brazovskii, Sov. Phys. JETP **41**, 85 (1975).

[7] M. Grousson, Ph.D. thesis, Université Pierre et Marie Curie, Paris, France, 2001.

[8] M. Grousson, G. Tarjus, and P. Viot, Phys. Rev. Lett. **86**, 3455 (2001).

[9] L. Chayes, V.J. Emery, S.A. Kivelson, Z. Nussinov, and G. Tarjus, Physica A **225**, 129 (1996); Z. Nussinov, J. Rudnick, S.A. Kivelson, and L.N. Chayes, Phys. Rev. Lett. **83**, 472 (1999).

[10] T.R. Kirkpatrick, D. Thirumalai, and P.G. Wolynes, Phys. Rev. A **40**, 1045 (1989).

[11] J. Schmalian and P.G. Wolynes, Phys. Rev. Lett. **85**, 836 (2000); **86**, 3456 (2001); H. Westfahl, J. Schmalian, and P.G. Wolynes, Phys. Rev. B **64**, 174203 (2001).

[12] See, e.g., P. Chandra, M.V. Feigelman, and L.B. Ioffe, Phys. Rev. Lett. **76**, 4805 (1996); S.J. Lee and B. Kim, Phys. Rev. E **60**, 1503 (1999); E. Marinari, G. Parisi, and F. Ritort, J. Phys. A: Math. Gen. **28**, 327 (1995); H. Yin and B. Chakraborty, Phys. Rev. Lett. **86**, 2058 (2001); G. Biroli and M. Mézard, *ibid.* **88**, 025501 (2002).