Fragile-strong transitions and polyamorphism in glass former fluids

E. A. Jagla
Centro Atómico Bariloche, Comisión Nacional de Energía Atómica
(8400) S. C. de Bariloche, Argentina

A simple model of a glass former fluid, consisting of a bidisperse mixture of penetrable spheres is studied. The model shows a transition from fragile to strong behavior as temperature is reduced. This transition is driven by the competition between the two mechanisms that contribute to diffusivity in the model: collective rearrangement of particles (responsible for the fragile behavior), and individual particle motion (which gives rise to the strong behavior at low temperature). We also observe a maximum of diffusivity as a function of pressure that can be interpreted within the same framework. The connection between this behavior and polyamorphism is addressed.

I. INTRODUCTION

The dependence of single particle diffusivity $D$ (or alternatively viscosity $\eta$) on temperature is the main indicator that allows to classify glass formers as "fragile" or "strong". For strong glass formers (such as SiO$_2$) $D(T)$ is well fitted by an Arrhenius plot, indicating that there is a well defined value of the energy barriers which are relevant to diffusion. For fragile glass formers, diffusion is the result of collective rearrangements of the position of particles. As temperature is reduced, the size of the correlated clusters increases, and $D$ decreases more rapidly than the Arrhenius form. There is evidence that some materials show a fragile behavior at high temperatures, whereas $D(T)$ crosses over to a strong behavior at low temperatures. Water is an example. The microscopic mechanism that originates this behavior is not well understood.

Some materials display the phenomenon of polyamorphism, namely, the existence of different amorphous (solid) configurations at very low temperatures. One well known example is, again, water. In this case the two different amorphous states transform into each other through a first order transition when pressure is applied at low temperatures. Polyamorphism has been numerically found in a model for SiO$_2$ and in some tetrahedrally coordinated materials: Si, Al$_2$O$_3$-Y$_2$O$_3$, and others.

One route to the appearance of polyamorphism is the possibility of two different local arrangement of particles, of different density. If this is the case (and this will depend on the interaction potential between particles), external pressure can make the structure collapse from the most expanded configuration to the densest one, near some typical pressure $P_{cr}$. It has been recently shown in a simple model of spherical, purely repulsive particles with these characteristics, that the dependence of density on pressure at very low temperatures has an anomalously rapid increase (in other words, that the isothermal compressibility has a maximum) for pressures around some crossover value $P_{cr}$ at which the two local environments become equally stable. We will call this a ‘weak’ form of polyamorphism. If some kind of attraction between particles is added, this weak polyamorphism may transform (depending on the details of the attraction) in a true polyamorphic first order transition between two different amorphous structures. The interaction potential used in [7] to obtain two different local environments consists of a hard core at distance $r_0$ and a shoulder that extends up to some other distance $r_1 > r_0$. Interparticle distances $r \sim r_0$ are favored at high $P$, whereas at low $P$, $r \sim r_1$ is preferred.

There is an intimate relation between (weak) polyamorphism and fragile-strong transitions. We will show in this paper that a model within the class of those discussed in Ref. [7], displays (weak) polyamorphism and has a transition from fragile to strong behavior when $T$ is reduced. The model also exhibits a maximum in $D$ as a function of pressure, which is well known to occur, for instance, in water. All these phenomena are consequences of the existence of two different local environments available for the particles, and the two qualitatively different mechanisms that contribute to the diffusivity in these systems, as explained below.

II. THE MODEL

We studied a model similar to that of Ref [7], with hard core radius $r_0 = 0$. In this way, particles are penetrable, and can overlap. A bidisperse system is considered, to avoid crystallization. Particle $i$ is characterized by the value of $r_1$, which is taken from a bimodal distribution, i.e., $r_1 = r_a$, or $r_1 = r_b$, with equal probability. The interaction potential between particles $i$ and $j$ takes the form

$$V^{ij}(r) = \varepsilon_0(1 - r/R)(R/\bar{r})^3 \quad \text{for} \quad r < R$$
$$V^{ij}(r) = 0 \quad \text{for} \quad r > R$$

(1)

where $R = r_1 + r_1$, $\bar{r}$ is the average radius of the particles, and $\varepsilon_0$ sets the energy scale. In all the results to be
presented, we use \( r_a = 0.4375\bar{r} \), and \( r_b = 0.5625\bar{r} \). Temperature will be given in units of \( \varepsilon_0/k_B \), and pressure in units of \( \varepsilon_0/\bar{r}^3 \).

We used standard Monte Carlo techniques, in the NPT ensemble. The system is given the dynamics of the Monte Carlo evolution, and diffusivities are calculated using this as the temporal evolution. At each time step the position of a single particle is modified to a new position which is randomly chosen within a sphere of radius 0.06 \( \bar{r} \) centered at the original position. This trial movement is accepted according to the Metropolis rule. The update step corresponds to a sweep over all particles.

Previous studies of related potentials [10] have shown that they display some ‘anomalous’ behavior, such as a line of maximum density and compressibility in the \( P-T \) diagram, and regions of anomalous melting in the \( P-T \) plane. These anomalies match those of real materials (such as water, SiO\(_2\), etc.) where polymorphism and fragile-strong transitions are observed or expected. We will concentrate here in the fluid phases of the model (see [10] for a discussion of the crystalline phases which are non-trivial) focusing on the behavior of diffusivity \( D \).

This is calculated from the long time behavior of the distance traveled by the particles, \(<(r(t) \to \infty) - r(0))^2 >= 6Dt\), where \( r(t) \) is the position of the particle at time \( t \). The reported values always correspond to an average over all particles in the system. \( D \) will be given in units of \( \bar{r}^2/t_0 \), where \( t_0 \) is the time corresponding to one Monte Carlo step. The number of Monte Carlo steps which are necessary to get good statistics greatly depends on the parameters \( P \) and \( T \). As much as \( 5 \times 10^7 \) steps were simulated for the lowest temperatures reported. The results correspond to a system of 200 particles, with periodic boundary conditions.

### III. RESULTS

We start showing results indicating the existence of weak polymorphism in the model. In Fig. [1] we see the evolution of the density \( \rho \) of the system and the corresponding values of isothermal compressibility \( K_T \equiv \rho^{-1} \partial \rho/\partial P \) at \( T = 0 \) and \( T = 0.03 \). Each point was obtained by an independent simulation at fixed pressure, and reducing temperature. There is a rather abrupt raising in density and a maximum in \( K_T \) around \( P \sim 1.3 \) at \( T = 0 \). The maximum becomes smoother and its position moves to slightly higher pressures at higher temperatures. The existence of this maximum is easy to understand. At low pressures (and low temperatures) the system behaves as a set of hard spheres, overlapping of particles in the same spatial position is highly improbable due to energetic reasons. Upon increasing external pressure, a value \( P_{cr} \) is reached beyond which it is energetically more favorable to accommodate particles in pairs, at each spatial position. The change of stability between ‘singed’ and ‘doubled’ local configurations is responsible for the maximum in \( K_T(P) \) around \( P_{cr} = 1.3 \). This is consistent with the form of the radial distribution function \( S(r) \), plotted in Fig. [2] for \( T = 0.03 \), at different values of \( P \), where we see the rapid increase of weight around \( r \sim 0 \) (indicating the appearance of ‘doubled’ particles) when crossing \( P_{cr} \). This is the evidence for weak polymorphism in the model.

![Fig. 1.](image1)

**Fig. 1.** Pressure dependence of the density \( \rho \) and isothermal compressibility \( K_T \), at \( T = 0 \) and \( T = 0.03 \). Lines are guides to the eye.

![Fig. 2.](image2)

**Fig. 2.** The radial distribution function at \( T = 0.03 \), for three different values of \( P \). There is a rapid increase of weight at distance \( r \sim r_0 = 0 \) for \( P \sim P_{cr} \). The three peaks around \( r = \bar{r} \) originate in the bidispersity of the system.

Next, we show results for single particle diffusivity as a function of pressure \( D(P) \), at different values of \( T \) in Fig. [3]. We see clearly a maximum in \( D \) at \( P \sim P_{cr} \). The origin of this maximum can be understood in the following way. For pressures much lower (larger) than the crossover value \( P_{cr} \) mostly singled (doubled) configuration of particles exist. For \( P \sim P_{cr} \), both singled and doubled particles coexist in the sample. Moreover, local rearrangements in which one particle of a doubled
pair moves onto some nearby singled particle are possible. This diffusion mechanism (which is illustrated in Fig. 3) is available only for \( P \sim P_{cr} \), and produces an enhancement of diffusivity in this pressure range.

The third set of results concerns the temperature dependence of diffusivity. In a standard glass former (i.e., pure hard spheres, or Lennard-Jones particles) diffusivity occurs via rearrangements of clusters of particles. As temperature is reduced, the size of the typical cluster that can rearrange increases, producing the typical temperature dependence of diffusivity of fragile glass formers. This mechanism is present in our system, and is basically the only one active for \( P \) much larger or lower than \( P_{cr} \). But for \( P \sim P_{cr} \) the mechanism discussed in the previous paragraph is also available. Since this is essentially a single particle mechanism (with a well defined activation energy), it account for a contribution to diffusivity which is basically Arrhenius-like. The total diffusivity is the combination of the ‘fragile’ part plus this ‘strong’ part. At large temperature the fragile part dominates. On reducing temperature the fragile contribution decreases much more rapidly, and leaves the strong contribution to be the main part at very low temperatures. In Fig. 4 we see the results for \( D(T) \) in our system, at three different values of \( P \). There is, in fact, a crossover between a fragile behavior at high temperature and a strong behavior at low temperature. The fragile part of these curves can be fitted by a Vogel-Fulcher law

\[ D \sim D_0 \exp(A/(T - T_0)) \]

for the diffusivity of fragile glass formers, but the whole curve cannot be fitted to a single expression of this type, as we see in the figure. Also to be noticed is the fact that the strong component of diffusivity at low temperature is maximized around \( P_{cr} \). So it is close to \( P_{cr} \) than the fragile strong transition is more easily observed. To compare with a more usual case, we made an independent simulation for particles with a strict hard core at \( R = r_1^2 + r_2^2 \). In this case the properties of the system depend only on \( P/T \) (or alternatively, on density), i.e., the system is athermal. But we still plot \( D \) vs \( T^{-1} \) at a fixed \( P = 1.2 \) to compare with the general case. The results are the symbols at the left of Fig. 5. In this case the whole curve can be nicely fitted by a Vogel-Fulcher law, the fragile behavior extending down to the lowest values of diffusivity that we can detect.

To get a visualization of the two different mechanisms for diffusivity we present the snapshots of Fig. 6. They show the projection of the positions of the particles onto a reference plane, and the displacements of the particles during a simulation of \( 5 \times 10^6 \) Monte Carlo steps. Panel (a) was obtained at \( P = 1.2, T = 0.012 \), in our system of particles interacting through \( (1) \). According to Fig. 3,
diffusivity has a strong behavior in this case. Panel (b) was obtained for the system with strict hard cores at distance $R$, at $P = 1.2, T = 0.039$. In this case diffusivity has a fragile behavior. Note that the overall values of $D$ in both cases (a) and (b) are comparable (see Fig. 3). However, the observable features of diffusivity are clearly different. In the fragile case (Fig. 6(b)) a cluster of particles (approximately delimited by the dotted line, note however that this is only qualitative, since the system is three-dimensional) has rearranged during the simulation time. This is consistent with the collective nature of the rearrangements in the fragile regime. For the strong case however, as Fig. 6(a) shows, we see that mostly independent motions of particles in uncorrelated positions of the sample have occur. This is the manifestation of the single particle character of diffusion in this case, and is consistent with the pictorial image of Fig. 4.

**IV. DISCUSSION AND CONCLUSIONS**

We have studied the relation between fragile-strong transitions and polyamorphism in a model glass former. We showed that if the system has a tendency to reach two different amorphous configurations when cooled down below and above some crossover pressure $P_{cr}$, then on general grounds we can expect maxima in the diffusivity $D$ as a function of $P$, occurring precisely around $P_{cr}$. In addition, $D(T)$ calculated at $P \sim P_{cr}$ is expected to have a fragile-strong transition when temperature is reduced.

This behavior is in fact expected in the wide class of tetrahedrally coordinated materials. In all these materials, there are two typical local arrangement of particles, one more expanded (corresponding for instance to the local structure of ice Ih in the case of water) and another more compact (corresponding to local arrangements in high pressure polymorphs of ice), which correlate with our two typical distances between particles in the model. Then we expect in all these cases fragile-strong transitions and maxima of $D(P)$ to be present. Real materials include in general some sort of attraction between particles. With this ingredient weak polyamorphism may develop into a true first order phase transition between two different amorphous phases. This is in fact what happens in water, which is the best known example in which a truly first order polyamorphic transition, a fragile-strong transition and maxima in $D(P)$ occur. In this case the two amorphous structures are separated by a first order line that is supposed to end in a critical point in the supercooled liquid region. The effects we have discussed (maxima in $D(P)$ and fragile-strong transitions) however do not require the existence of this critical point. Only weak polyamorphism is needed.

**V. ACKNOWLEDGEMENTS**

This work was financially supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

---

1. C. A. Angell, J. Non-Cryst. solids 131-133, 13 (1991).
2. G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965); C. A. Angell, Science 267, 1924 (1995).
3. C. A. Angell, J. Phys. Chem. 97, 6339 (1993); K. Ito, C. T. Moynihan, and C. A. Angell, Nature 398, 492 (1999); F. W. Starr, C. A. Angell, R. J. Speedy, and H. E. Stanley, LANL preprint cond-mat#9903451.
4. O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) 310, 393 (1984); 314, 76 (1995); O. Mishima, K. Takemura, and K. Aoki, Science 254, 406 (1991); O. Mishima, J. Chem. Phys. 100, 5910 (1994).
With this interaction potential, two particles at the same position get an energy $\varepsilon_0 (R/\bar{r})^3$. Since the energy per particle associated to the existence of an external pressure $P$ is $Pv \sim PR^3$, our choice is reasonable in order to obtain a single crossover pressure $P_{cr}$ (independent of the radius of the particle) at which particles overlap.

For a crystalline material, in which all particles are in equivalent positions the transition from singled to doubled configurations occurs at a well defined pressure (at $T = 0$). For our glassy system in which there are many inequivalent spatial positions, this transition is smooth, even at $T = 0$, as Fig. 1 shows.

At sufficiently high pressures, particles also overlap in triplets, etc. In the range of pressures we are working these configurations are extremely rare.