Glass-like materials are nonequilibrium systems where the relaxation time may exceed reasonable time scales of observations. In the present paper a dynamic percolation model is introduced in order to explain the principal properties of glass-like materials near the dynamic transition. Here, contrary to conventional percolation problems, clusters are groups of particles dynamically correlated. Introducing a size dependent relaxation time and the scaling hypothesis for the distribution of dynamically correlated clusters the two step relaxation predicted by the mode coupling theory and observed in experiments is obtained.

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I. INTRODUCTION

In common second order transitions the new phase has as distinguish property the existence of long range order, leading to macroscopic structures like ferromagnetic domains. However, while it is believed that glass-like transitions are second order transitions, the glass-like state does not exhibit the conventional long range order but a short range order, at a mesoscopic scale, is preferred. The relaxation time of these systems becomes as long as, or longer than, the observation time and, therefore, the system cannot reach equilibrium within observation time. Thus, it is not clear if the glass-like transition is a true thermodynamic phase transition or a slow relaxation phenomenon, usually referred to as dynamic or freezing transition.

A major step toward resolving the dilemma would be the determination of an order parameter underlying the transition. The discovery of a diverging length associated with the glass-like transition, similar perhaps to the correlation length in a para-ferromagnetic transition would enhance our understanding of glass-like transitions and of the glassy state. From the structural point of view the glassy state is characterized by some local (quenched) disorder and frustrated bonds which inhibit the long range order and lead to the formation of clusters of mesoscopic sizes. Thus, any theory which try to explain the principal features of glass-like materials must take into account the existence of such clusters. In this direction several models have been proposed.

During the past few years a new theoretical approach, the mode coupling theory (MCT), has been developed which has motivated new experimental investigations. This theory provides a generalized kinetic equation approach to the density fluctuation dynamics in supercooled fluids. It predicts two step relaxation processes ($\alpha$ and $\beta$ relaxations). The $\alpha$ relaxation process exhibits a time scale which diverges at a crossover temperature $T_c$, which is somewhat above the calorimetric glass transition temperature $T_G$, and structural relaxation experiences rapid slowing down. On the other hand the time scale of the $\beta$ process is considerably shorter, does not diverge at $T_c$, and the $\beta$ process can therefore also be observed below $T_c$. These predictions are directly accessible to experimental verifications and have been tested for many glassforming materials.

Recently we have presented a fractal model which explains the hysteresis loss effect observed in supercooled liquids. The determinant influence of the fractal properties of the amorphous structure in the system dynamics was emphasized introducing a fractal distribution of cluster sizes. However, in that occasion, the nature and origin of this fractal clusters was not analyzed.

In the present paper a cluster model for the relaxation in glass-like materials is proposed following the general ideas presented in. As in previous works the relaxation of the system is obtained by superposition of independent relaxing clusters with a size dependent relaxation time. Nevertheless, in our model, differing from other formulations, a cluster exists through a series of relaxation processes giving rise to a dynamically correlated cluster (DCC). In this way the slow relaxation dynamics and other features of glass-like materials are explained. Results are compared with experimental data reported in the literature.

The paper is organized as follows. In section 2 the formation of DCC is analyzed. The main ideas and concepts about DCC and cluster dynamics are introduced. Then, the influence of the distribution of DCC on relaxation dynamics is investigated. It is obtained that the relaxation follows a two step process which may be identified with the $\alpha$ and $\beta$ processes. Comparison with experimental data and MCT predictions is presented in section 3. Finally the conclusions are given in section 4.

II. DYNAMIC PERCOLATION MODEL

A. DCC relaxation time

Molecular dynamics simulations of soft-sphere mixtures have revealed that in addition to the stochas-
tic jump motion of single atoms correlated jump motions, in which a cluster of several atoms jump at successive closed times by permuting their positions, take place. Similar results have been obtained in molecular dynamics simulations of water, a frustrated system with multiple random hydrogen bond network structure. Besides, Monte Carlo simulations of spin glasses also revealed the existence of such cooperative relaxation dynamics.

These results suggest that the cooperative motion of particles (atoms, spins, etc.) in glass-like materials does not take place as the motion of frozen clusters but as successive concatenations of single particle motions. Hence, in this sense, a cluster is formed through the perturbation propagation from one particle to its neighbors. This kind of cluster will be referred here as a dynamically correlated cluster (DCC). For short times only small clusters participate in the relaxation dynamics however, with increasing time, larger and larger clusters are incorporated.

Let us denote a characteristic physical quantity of the \( i \)-th DCC particle by \( x_i \). It may be the displacements around an equilibrium position in ordinary glasses, the magnetic moment in a spin glass, or other. \( x_i \) will be random variable following certain distribution, with zero mean value and variance \( \langle x_i^2 \rangle = \delta^2 \), \( \delta \) being a typical value of fluctuations. Moreover, let \( \tau_0 \) be a characteristic time scale of the fluctuations in \( x_i \).

The different DCC configurations will be then characterized by the sum

\[
x = \sum_{i=1}^{s} x_i ,
\]

where \( s \) is the number of particles in the cluster, \( 1 \leq s < \infty \). In general the fluctuations \( x_i \) are correlated but, in a first approximation, they may be considered independent. In such an approximation the central limit theorem tells us that, for large \( s \), \( P_s(x) \) the limit distribution of the sum in equation 1 follows a Gaussian distribution with variance \( \delta^2 s^{1/2} \), i.e.

\[
P_s(x) = \frac{1}{\sqrt{2\delta^2 s}} \exp \left( - \frac{x^2}{2\delta^2 s} \right) .
\]

\( P_s(x) \) represents the relative number of microstates or configurations associated to a value of \( x \), for a cluster of size \( s \). The entropy of this 'temporally isolated' subsystem is thus given by

\[
S_s(x) = k \ln P_s(x) = -\frac{k}{2\delta^2 s} x^2 + \text{const}.
\]

and the force associated to an entropy change

\[
f_s(x) = T \frac{\partial S_s}{\partial x} = -\frac{kT}{\delta^2 s} x = -c x .
\]

Now, from the kinetic point of view, the relaxation of the DCC may be reduced to the Brownian motion of a harmonic oscillator with generalized coordinate \( x \), under the elastic force in equation 4 and with diffusion coefficient \( D = \delta^2 / \tau_0 \). In this mean field approach the normalized relaxation is given by

\[
\phi_s(t) = \frac{\langle x(t) \rangle}{\langle x(0) \rangle} = \exp \left( - \frac{t}{\tau_s} \right) ,
\]

with the size dependent relaxation time

\[
\tau_s = \frac{kT}{Dc} = \tau_0 s .
\]

Thus, in this mean field approximation the relaxation time of a DCC is proportional to its size and a perturbation of the equilibrium state relaxes exponentially towards equilibrium. As will be seen, the existence of a broad distribution modifies the relaxation rate.

### B. Relaxation dynamics

Let \( n_s \) be the cluster numbers, i.e. the number of DCC with size \( s \) per unit lattice. We assume that, in spite of the dynamic nature of the clusters, the scaling assumption about the cluster number still holds. Therefore, if the system is close to percolation \( \tau(1 - T/T_c) \sim 0 \) the scaling assumption establishes that

\[
n_s = s^{-\tau} f(\epsilon|s^\sigma|) ,
\]

where \( \tau \) and \( \sigma \) are scaling exponents and \( f(x) \) is a cutoff function \( f(z \ll 1) \approx 1 \), and \( f(z \gg 1) \ll 1 \). Thus, the averaged normalized decay will be given by

\[
\phi(t) = \sum n_s \phi_s(t) \sum n_s .
\]

Close to percolation the sum is dominated by the contribution of large cluster and we may substitute the sum by an integral. Thus, substituting equations 7 and 7 in equation 8, with the variable change \( z = t/\tau_s \), it is obtained

\[
\phi(t) = \frac{\int_0^{\tau_0} dz \int_0^{\tau_0} dz \phi(t/\tau_s) z^{-\sigma}}{\int_0^{\tau_0} dz \int_0^{\tau_0} d\phi(t/\tau_s) z^{-\sigma}} ,
\]

where \( \tau_s = \tau_0 \epsilon^{-1/\sigma} \) and \( a = \sigma - 2 \).

The first thing we note from this expression is the existence of two characteristic times \( \tau_0 \) and \( \tau_s \). The former is a characteristic time for the microscopic motion while the last one is the characteristic time of the largest clusters with size \( s \sim \epsilon^{-1/\sigma} \).

It is tentative to associate these characteristic times with the \( \beta \) and \( \alpha \) relaxation processes, respectively. Moreover, the distribution of cluster sizes is divided in two regions. The initial part which follows a power law decay and a second part with a sharp cutoff. The cutoff size is of the order of \( \epsilon^{-1/\sigma} \) with characteristic time \( \tau_s \). Hence, \( \tau_s \) divides the time scale in two regions where the relaxation function will show different behaviors. These two time scales are analyzed below.
1. β relaxation

For $t \ll \tau_c$ equation \[\beta\] is approximated by
\[
\phi(t) \approx a \left( \frac{t}{\tau_0} \right)^{-a} \gamma \left( \frac{t}{\tau_0}, a \right),
\]
where $\gamma(x, a)$ is the incomplete Gamma Euler function. Moreover, for $t \ll \tau_0$, using the series expansion of $\gamma(x, a)$ for small $x$, we obtain
\[
\phi(t) \approx 1 - \frac{a}{1 + a \tau_0} t \approx \exp \left( - \frac{a}{1 + a \tau_0} t \right),
\]
while for $t \gg \tau_0$, $\gamma(t/\tau_0, a) \approx \Gamma(a)$, resulting
\[
\phi(t) \approx \Gamma(1 + a) \left( \frac{t}{\tau_0} \right)^{-a}.
\]

Thus, the initial decay, due to single particle motions, is exponential. However, for $t \gg \tau_0$ cooperative dynamics leads to the formation of DCC, with power law distribution sizes, giving the power tail in equation \[\alpha\]. The fractal behavior in the distribution of DCC sizes leads to fractal properties in the time decay.

The imaginary part of the susceptibility $\chi''$ is related to the relaxation function through the equation
\[
\chi''(\omega) = \omega \mathcal{F} \left[ \phi(t) \right],
\]
where $\mathcal{F}$ denotes the real part of the Fourier transform. Then, for $\tau_0 \ll t \ll \tau_c$, using equation \[\alpha\] it is obtained
\[
\chi''(\omega) \approx a \sec \left( \frac{\pi}{2} (\omega \tau_0)^a \right).
\]
This frequency dependence corresponds with the β relaxation. The characteristic time for these time scale is $\tau_0$ which does not depend on $\epsilon$. Hence, if we assume that the divergences near $T_c$ are given by the percolative nature of the DCC, $\tau_0$ will not diverge at $T = T_c$ as it is expected for the β process.

2. α relaxation

Now let us investigate the influence of the cutoff in the distribution of cluster sizes in the long time ($t \gg \tau_c$) relaxation dynamics. In this case the form of the cutoff function $f(x)$ is determinant and cannot be ruled out. We will assume that this cutoff function is of the form
\[
f(x) = \exp(-x^{\theta_{\pm}}),
\]
where $\theta_-$ and $\theta_+$ stand for $\epsilon < 0$ and $\epsilon > 0$, respectively.

An asymptotic expansion, for $t \gg \tau_c$, of $\phi(t)$ defined in equation \[\beta\] with $f(x)$ in equation \[\alpha\] give the estimate
\[
\phi(t) \sim \exp \left[ - \left( \frac{t}{\tau_{c,\pm}} \right)^{\beta_{\pm}} \right].
\]

with
\[
\tau_{c,\pm} = c_{\sigma,\theta_{\pm}} \tau_c,
\]
\[
\beta_{\pm} = \frac{\sigma\theta_{\pm}}{1 + \sigma\theta_{\pm}}.
\]

$c_{\sigma,\theta_{\pm}}$ is a constant which does not depend on $\epsilon$ and, therefore, $\tau_{c,\pm}$ diverges as $t_c$ near $T_c$.

Equation \[\alpha\] is the well known Kolraush stretched exponential often used to fit the experimental data in the α relaxation process. Moreover, the characteristic time $\tau_{c,\pm}$ diverges at $T = T_c$ as it is expected for the α relaxation process.

3. Static viscosity

The static viscosity is related to the mean cluster size through the expression
\[
\eta = G\langle s \rangle = G\tau_0 \langle s \rangle,
\]
where $G$ is an elasticity modulus and $\langle s \rangle$ is given by
\[
\langle s \rangle = \sum s^2 n_s / \sum s n_s.
\]
For $T \approx T_c$ the mean cluster size defined in equation \[\alpha\] will diverge according to $\langle s \rangle \sim |\epsilon|^{-1/\sigma}$ and, therefore,
\[
\eta \sim \tau_c \sim \tau_{c,\pm} \sim \langle s \rangle \sim |\epsilon|^{-1/\sigma}.
\]

Hence, $\tau_{c,\pm}$ the characteristic time for the α relaxation process shows the same temperature dependence of the static viscosity.

III. DISCUSSION

The present model exhibits the two step relaxation predicted by the MCT. The exponent $a$ of the β process ($\chi'' \sim \omega^a$) is identified here with $a = \tau - 2$. Moreover, since $2 \leq \tau \leq 5/2$ as it is obtained in conventional percolation \[\alpha\] then $0 \leq a \leq 1/2$, which is in the range predicted by the MCT. On the other hand, the Kolraush stretched exponent of the α process, given by equation \[\alpha\], satisfies $0 \leq \beta_{\pm} < 1$ which is also the range predicted by the MCT. Moreover, the characteristic time of the α process has the same temperature dependence as the static viscosity, in agreement with the MCT.

Thus, our model seems to arrive to the same results obtained by the MCT, which have been extensively tested in light scattering and neutron scattering experiments.\[\alpha\] In order to perform a more accurate comparison let us investigate the behavior of $\chi''$ around the minimum between the α peak and the β process. This minimum
should be near the frequency $1/\tau_c$ since it marks the transition from the $\beta$ to the $\alpha$ process in our model. In this frequency range we will have the contribution of the $\beta$ process with relax according to $(t/\tau_0)^{-a}$ and of the $\alpha$ process relaxing as $\exp[-(t/\tau_{\alpha\pm})^{\beta_\pm}] \approx 1 - (t/\tau_{\alpha\pm})^{\beta_\pm}$. Thus, a gross estimate of the relaxation function in the time scale will be given by considering both contributions which, resulting

$$\phi(t) \sim |\epsilon|^{a/\sigma} \left[ \left( \frac{t}{\tau_{\alpha\pm}} \right)^{-a} - \left( \frac{t}{\tau_{\beta\pm}} \right)^{b} \right],$$

(22)

where $b = \beta_\pm - a$. Substituting this expression in equation (13) and assuming $a, b \ll 1$ it is obtained

$$\chi''(\omega) \sim |\epsilon|^{a/\sigma} \left[ a(\omega \tau_{\alpha\pm})^a + b(\omega \tau_{\beta\pm})^{-b} \right],$$

(23)

This expression constitutes an interpolation formula often used to fit the experimental data. The values of $a$ and $b$ obtained from the fit to experimental data are in general small, thus our supposition $a, b \ll 1$ is consistent with experiments. From this expression we obtain that the position of the minimum $\omega_{\text{min}}$ and the value of $\chi''(\omega)$ at the minimum $\chi''_{\text{min}}$ satisfies

$$\omega_{\text{min}} \sim |\epsilon|^{1/\sigma},$$

(24)

$$\chi''_{\text{min}} \sim |\epsilon|^{a/\sigma}.$$

(25)

If $a/\sigma = 1/2$ then we obtain the MCT prediction which is consistent with the light scattering data. However, under this assumption the static viscosity in equation (13) and assuming $a, b \ll 1$ it is obtained

$$\chi''(\omega) \sim |\epsilon|^{a/\sigma} \left[ a(\omega \tau_{\alpha\pm})^a + b(\omega \tau_{\beta\pm})^{-b} \right].$$

This sharp cutoff for large sizes may be attributed to frustration effects which destroy the long range order. The existence of frustration, which is an inherent property of glass-like materials, may lead to different critical exponents. The percolation problem including frustration effects (frustrated percolation) is a subject of recent study, and exhibits properties which are different from the corresponding unfrustrated case.

Finally we want to mention that other authors have used the idea of DCC, for instance the models by Domb et al, Cohen et al, and Chamberlin. However, these models do not analyze the properties of glass-like materials. However, the scaling assumptions are still valid, but with different scaling exponents. To obtain a good agreement with the experimental observations $\sigma\theta_\pm$ should take larger values which implies that, in glass-forming materials, the cutoff for larger DCC sizes is stronger than the one expected in conventional percolation.

IV. CONCLUSIONS

The complex dynamics of glass-forming materials was reduced to the formation of independent dynamic correlated clusters (DCC) with a size dependent relaxation time. The relaxation of the system was obtained as a superposition of exponential relaxations over the distribution of the DCC sizes. In this way we have obtained the two step relaxation process observed in supercooled liquids.

Our model contains as a particular case the MCT predictions, it is more simple and it is based in a very general principle, the scaling assumption for the distribution of DCC near $T_c$. Besides, the present model gives the correct temperature dependence for the Kolraush exponent $\beta$, while the MCT predicts a constant value in disagreement with the experimental behavior.

The comparison of our results with the experimental data for glass-materials suggest that the percolation critical exponent $\tau$ should be larger than the one obtained in conventional percolation theory. Moreover, the cutoff for larger DCC sizes should also be stronger. These results were attributed to the existence of frustration effects,
which inhibit the formation of long range order dynamic structures.

We conclude that the use of geometrical descriptions, the distribution of DCC size for instance, constitute an alternative approach to describe the dynamics of glass-like materials. The properties of these systems near the dynamic transition can be predicted using conventional tools of standard critical phenomena such as the scaling hypothesis.

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