The liquid-glass transition of silica

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We studied the liquid-glass transition of SiO$_2$ by means of replica theory, utilizing an effective pair potential which was proved to reproduce a few experimental features of silica. We found a finite critical temperature $T_0$, where the system undergoes a phase transition related to replica symmetry breaking, in a region where experiments do not show any transition. The possible sources of this discrepancy are discussed.

I. INTRODUCTION

According to the behavior of their transport coefficients, supercooled liquids were classified in fragile and strong liquids. Close to the experimental glass temperature $T_g$, where the system is no longer able to equilibrate on experimental time scales, the viscosity $\eta$ in strong liquids seems to be in a good agreement with the Arrhenius law $\exp(A/T)$, while in the fragile ones it is more correctly described by the Vogel-Fulcher-Tamman law $\exp(A/(T - T_0))$. As the dramatic slowing down of dynamics prevents to achieve equilibrium below $T_g$, the critical temperature $T_0$ can only be inferred by extrapolating at lower temperatures the available equilibrium data. However, this fitting procedure is hardly conclusive, as the viscosity changes of 14 order of magnitude in a small window of temperatures.

In such a classification silica (SiO$_2$) should belong to the class of strong liquid, though deviations from the pure Arrhenius plot above $T_g$ have been recently observed, supporting speculations about a fragile-strong transition at temperatures higher than $T_g$, that for silica is known to be $\sim 1446K$.

The amorphous network observed in supercooled silica has been recently shown to arise in molecular dynamics simulation when using the effective two body potential recently in-
roduced by van Best, Kramer and Van Santen\textsuperscript{6} (BKS). However, due to the limitations of numerical simulations, the transport coefficients of BKS silica were studied only in a regime of temperature well above $T_g$, hence the equilibrium behavior at low temperature is still an open issue. Controversial results indeed arose when the available data were extrapolated at lower temperatures and the possibility that the BKS potential rather implies a fragile behavior cannot be ruled out. As a matter of fact, fitting data with a VFT law yields $T_0 = 2525K$, while the power law fit $\eta \propto (T - T_c)^6$, motivated by the predictions of mode-coupling theory\textsuperscript{8}, yields the dynamical temperature $T_c \simeq 3300K$\textsuperscript{9,10,11}. On the other hand, the Arrhenius behavior seems to be recovered taking into account only the few data available at the lowest temperatures, suggesting the possibility of a fragile-strong transition at $T_c$. Furthermore, the study on the configurational entropy $S_c$\textsuperscript{12}, shows that the Adam-Gibbs relation $\eta \propto 1/T S_c$ is verified over 4 decades and suggests that the fragile-strong transition might be related to a change of the energy landscape properties at low temperatures.

Since the reliability of the BKS potential in describing the low temperature behavior of the viscosity of silica is still far from being established, we believe it is instructive to apply the replica approach\textsuperscript{13,14,15,16} to this case, looking for a possible critical temperature $T_0$ from a different route, namely as the point where the system undergoes a thermodynamic transition\textsuperscript{17} related to a replica symmetry breaking\textsuperscript{18}.

II. CORRELATED LIQUID PHASE

Let us assume that the glassy dynamics is the signature of the partitioning of the whole phase space in an exponentially large number $\mathcal{N}(f)$ of free energy minima (valleys in the following), whose exploration in the supercooled phase is still allowed due to hopping processes between them. The entropic contribution coming from the huge number of different valleys is called complexity:

$$\Sigma = \log \mathcal{N}(f)/N$$  \hspace{1cm} (1)

The ‘valleys’ must be thought as somewhat more complicated objects\textsuperscript{14} than the basins of the ‘inherent structures’\textsuperscript{19,20}, as their number can be badly different\textsuperscript{21}.

Generally speaking, a valley is stable against both an infinitesimal displacement of an extensive number of particles and a finite rearrangement of a non-extensive number of them. It has been argued\textsuperscript{22} that the complexity in a finite dimensional system should be thought
as a time-dependent quantity. The thermodynamic approach\cite{14,15,16} rather assumes that the valleys are metastable states with a macroscopic time-life, whose existence is limited to the region below $T_c$, as suggested by the analogy with generalized (mean field) spin glasses\cite{23}.

We shall exploit this assumption in order to make predictions about the supercooled phase, the glass temperature and the glass phase.

The computation of the complexity $\Sigma(f, T)$ in a given thermodynamic state of the system (hereafter represented by its temperature $T$) can be settled by using the method proposed by Monasson\cite{13}, which amounts to compute the free energy of a system composed by $m$ identical clones (copies) of the original system.

In the liquid phase, upon introducing a suitable coupling, two arbitrary clones can be forced to stay in the same valley (\textit{correlated liquid phase}), but when the coupling vanishes they are always found to be in different valleys (\textit{uncorrelated liquid phase}). On the other hand, in the glass phase, the clones remain in the same valley even after sending the coupling term to zero\cite{14}. Generally speaking, one needs to compute the free energy density of the cloned system in its correlated liquid phase. The information on the complexity of the cloned system is obtained when one computes the analytic continuation of the correlated liquid free-energy density $\phi(m)$ to real values of $m$, by means of\cite{13}:

$$\frac{m^2}{T} \frac{\partial (\phi(m, T))}{\partial m} = \Sigma(m, T). \quad (2)$$

Given this very general framework, the aim is to compute the potential $\phi$, depending both on the standard thermodynamic parameters (temperature, density, chemical potential, etc..) and on the parameter $m$, once the pair potential $V(r)$ has been given. Three different ways to compute the free energy of a replicated system were introduced\cite{14,15,16}, each relying on a different set of approximations. The results shown in the following were obtained within a harmonic approach, which only requires the pair correlation functions $g(r)$ computed in the liquid phase. The position $x_i^{(a)}$ of the $a$-th clone of the $i$-th particle is written as $x_i^{(a)} = z_i + u_i^{(a)}$, isolating the centers of mass $z_i$. By assuming that the displacements $u_i^{(a)}$ are ‘small’ in the correlated liquid phase, the partition function (in $d$ dimensions) is:

$$Z_m = m^{Nd/2}N^d \sqrt{2\pi}^{Nd(m-1)} Z_{\text{liq}}(T/m) \left\langle \exp \left( -\frac{m-1}{2} \text{Tr} \log \mathcal{H}/T \right) \right\rangle_{T/m}, \quad (3)$$

where $Z_{\text{liq}}(T/m)$ is the partition function of the liquid phase at the temperature $T/m$ and $\mathcal{H}$ is the Hessian matrix of the system. The average $\langle \ldots \rangle$ is taken over the equilibrium
configurations of the variables \{z_i\}. Introducing the quenched approximation\[14\):

\[
\left\langle \exp \left(-\frac{m-1}{2} \text{Tr} \log \mathcal{H}/T \right) \right\rangle_{T/m} \sim \exp \left(-\frac{m-1}{2} \left\langle \text{Tr} \log \mathcal{H}/T \right\rangle_{T/m} \right)
\]  

(4)

the free energy \(\phi(m)\) is:

\[
\phi(m) = f_{\text{liq}}(T/m) + \frac{T}{2m} \left[(m-1) \left\langle \text{Tr} \log \mathcal{H}/T \right\rangle_{T/m} - d (m-1) \ln 2\pi - d \log m \right]
\]  

(5)

The computation of \(\left\langle \text{Tr} \log \mathcal{H}/T \right\rangle_{T/m}\) is simplified by treating the fluctuations of the diagonal term in the Hessian matrix in a perturbative way\[14,15,16\] which is correct in the high density limit, while the off-diagonal term can be taken into account non-perturbatively\[14,15,16\].

Let us briefly recall the scenario and the predictions of the theory:

- In the liquid phase the physical quantities are obtained in the limit \(m \to 1\). In that case formula (2) simply reads:

\[
\Sigma(T) = S_{\text{liq}}(T) - S_{\text{sol}}(T),
\]  

(6)

\(S_{\text{liq}}\) being the entropy of the liquid and \(S_{\text{sol}}\) the entropy of a disordered harmonic solid.

- If a temperature \(T_0\) where complexity vanishes actually exists, there the ergodicity is broken and the system undergoes the thermodynamic glass transition.

- Choosing as a suitable order parameter of the phase transition the correlation function between the different clones, the transition turns out to be discontinuous. Surprisingly enough from the thermodynamic point of view it is a second order phase transition, the heat capacity jumping downwards from liquid to crystal-like values.

- In the glass phase the eq. (2) at \(m = 1\) yields a negative complexity, which is meaningless. Since in the \(m - T\) plane one still finds out a critical line \(m^*(T)\) (lesser than 1) where \(\Sigma = 0\), the replica approach takes \(\phi(m^*, T)\) as the physical free energy.

Finally, it is interesting to note that the replica scenario shares many features with the old Adam-Gibbs-Di Marzio one\[17\].

III. RESULTS

We analytically studied the glass transition of \(SiO_2\), when the temperature is lowered and the density is kept fixed at the value \(\rho = 2.36 g/cm^3\), which is close to the experimental
density at ambient pressure. We studied the correlated liquid phase within the harmonic approach sketched in the previous section, describing the interactions by means of the BKS potential:

\[ V(r) = \frac{Q}{r} + A e^{-B r^2} - \frac{C}{r^6} + v_{sr}(r), \]  

(7)

where \( Q = q_s q e^2 \) with \( q_s = 2.4 \), \( q_o = -1.2 \), \( e^2 = 1602.19/(4\pi 8.8542) \) eV \( \cdot \) Å, the other parameter values being reported in Tab. (1). Since the potential has no lower bounds when \( r \rightarrow 0 \), we followed the procedure of numerical simulations adding a short-ranged \( 24 - 6 \) Lennard-Jones term, which does not affect the thermodynamic quantities.

In order to obtain the \( g(r) \) we resorted to standard theory of liquids. Among the others, the so-called Hypernetted Chain Approximation (HNC) turns out to be a rather reliable approach in describing fluids with electrostatic long range interactions such as silica. In the HNC free energy the infrared divergence due to Coulomb term is exactly canceled out by the resummation of the divergences of the virial expansion. Unfortunately, the HNC closure is not powerful enough to study the correlated liquid phase. As a matter of fact, a thermodynamic inconsistency between the two different routes for computing the compressibility makes the integral

\[ \chi_1 = \frac{\beta}{\rho} + \beta \int d^3r (g(r) - 1) \]

(8)

to increase far more rapidly than the quantity

\[ \chi_2 = \frac{1}{\rho} \left( \frac{dP}{d\rho} \right)^{-1} \]

(9)

when going to low temperatures. This prevented to study the whole correlated liquid phase, since it is not possible to obtain the \( g(r) \) in HNC approximation for temperatures below \( \sim 3200K \).

A very simple procedure to deal with this difficulty is to get the results at very low temperatures by extrapolating the ones obtained at the temperatures allowed within the HNC approach. Since such a procedure might appear not satisfactory enough, we have also chosen to utilize a different approximation interpolating between HNC and Mean Spherical Approximation (MSA) introduced by Zerah & Hansen (ZH), which retains the advantages of the HNC approximation extending its reliability at much lower temperatures, in such a way that no extrapolation is required. It is interesting to note that the extrapolated HNC results turn out to be very similar to the ones obtained by means of the ZH approach, as
we shall show. Finally let us point out that, since the short range behavior is ruled by the MSA closure while the long range one is still described by the HNC, the cancellation of the infrared divergence described above is unaffected by the interpolation.

More in detail, we considered the following integral equations for the $g^{\epsilon,\epsilon'}(r)$:

$$c^{\epsilon,\epsilon'} \rho^2 g_{\epsilon\epsilon'}(r) = \exp \left( -\beta V_{(R)}^{\epsilon,\epsilon'}(r) \right) \left( 1 + \frac{\exp \left\{ f^{\epsilon,\epsilon'}(r) \left[ w^{\epsilon,\epsilon'}(r) - \beta V_{(A)}^{\epsilon,\epsilon'}(r) \right] \right\} - 1}{f^{\epsilon,\epsilon'}(r)} \right)$$

where $V_{(R)}^{\epsilon,\epsilon'}(r) \equiv V^{\epsilon,\epsilon'}(r) - V_{\min}^{\epsilon,\epsilon'}$ for $r \leq r_{\min}$ and zero otherwise, while $V_{(A)}^{\epsilon,\epsilon'}(r) \equiv V^{\epsilon,\epsilon'}(r) - V_{(R)}^{\epsilon,\epsilon'}(r)$. Moreover $w^{\epsilon,\epsilon'}(r) \equiv \int dr' h^{\epsilon,\epsilon'}(r-r') c^{\epsilon,\epsilon'}(r')$, where $c^{\epsilon,\epsilon'}(r)$ is the direct correlation function and $h^{\epsilon,\epsilon'}(r) = g^{\epsilon,\epsilon'}(r) - 1$. The interpolation is achieved by means of the function $f(r)$ (here the same for all the components). In the regions where $f(r) \sim 1$ the eq. (10) gives the well-known HNC equations, while the MSA ones are recovered for $f(r) \sim 0$. As we made the choice $f(r) = 1 - \exp(-r/\alpha)$ the interpolation depends only on the parameter $\alpha$. Its value can be suitably chosen in order to strongly reduce the difference between the two compressibilities.

We numerically solved the equations obtaining the pair correlation functions in two different cases. In the former we solved the HNC equations, corresponding to the $\alpha \to 0$ limit in eq. (10), while in the latter $\alpha$ has been chosen in such a way to reduce the difference $\chi_1 - \chi_2$. More precisely, we let $\alpha$ to take the constant value 0.7, which has been checked to be the average value minimizing the difference between the two compressibilities down to $\sim 4000K$. This solution of the integral equations in the $\alpha = 0.7$ case gave our $g_{\epsilon\epsilon'}(r)$ in the ZH approximation.

In order to solve the integral equations we discretized them, introducing a cut-off $L$ in the real space and a mesh size $a$. More in detail, we are showing results obtained when the cut-off in the real space has the value $L = 32$ Å, considering respectively 4096 points (HNC) and 2048 points (ZH), checking that they do not change significantly below $T_c$ when $L$ is doubled, though we still observe small scale oscillations on the correlation functions depending on the mesh size.

In figs. 1, 2, 3 we show the pair correlation obtained in the two different approximations, comparing them at two different temperatures ($4000K$, $2750K$) with numerical data previously published by Horbach and Kob. Let us note that the positions of maxima and minima are quite correctly reproduced but there is an error even larger than 10% which increases when lowering the temperature on the values of the first peak and of the first
minimum, though they roughly cancel out when considering the integral. Moreover the obtained $g(r)$ show the already mentioned small scale oscillations which are related to finite size effects in the momenta domain. Therefore the agreement with simulations seems to be not as good as in the previously considered cases\cite{15,16}.

As stated before, the HNC results at very low temperatures can only be inferred by extrapolating the high temperature ones. That procedure is simplified by the theoretical argument given by Rosenfeld & Tarazona\cite{28} yielding a $T^{-2/5}$ behavior for the entropy of the liquid (apart from the thermal contribution). Interestingly, also in the ZH approach we found a $S_{\text{liq}}$ depending linearly on $T^{-2/5}$ in the whole low temperatures region. On the other hand, the temperature dependence of the disordered solid entropy is well approximated by a
FIG. 3: The analytical $Si-O$ pair correlation functions compared with numerical data by Horbach and Kob.

FIG. 4: The liquid and solid entropies as obtained by extrapolating HNC results with the functions $a_{liq} + b_{liq} T^{-2/5}$ and $a_{sol} + b_{sol} \log T$ respectively. Here the thermal contribution and the correct normalization constant (giving $S = 0$ when the phase space volume is equal to $h^3$) are added to both of the entropies.

logarithmic behavior, as expected when only vibrations are taken into account. In fig. (4) we show both the entropies obtained by the HNC solutions and the results of the extrapolation procedure.

The main result of our work is presented in fig. (5), showing the complexity of the system in the liquid phase, computed both in the HNC and ZH approaches utilizing the eq. (6) when $\phi(m)$ is given by the eq. (5). As anticipated, the two curves gives roughly the same $T_0 \sim 2100K$ yielding a rather sound prediction, which should not strongly depend on the particular way chosen to describe the liquid phase.
FIG. 5: The complexity as obtained within the HNC and the ZH approximation respectively.

FIG. 6: The behavior of $m$ as function of the temperature in the glassy phase.

In the glass phase we want to focus on the predicted behavior of the thermodynamics parameter $m^*$ as a function of the temperature, shown in fig.(6). As explained before, $m^*$ has been found by maximizing the free energy (5) in the correlated liquid phase with respect to $m$. This thermodynamic parameter has a linear behavior, shared by all the glassy systems to our knowledge, ranging from fragile glasses\(^{15,16}\) to generalized spin glasses\(^{29}\), implying that the quantity $T/m^*$ remains nearly constant in the whole glassy phase. The analogy with generalized spin-glasses suggests that $m^*$ might be related to the relative height of the two-peaks equilibrium probability distribution of distances between replicas. Some numerical evidence for this quantity being non trivial was obtained\(^{30}\).
IV. DISCUSSION

The study of supercooled BKS silica, by means of the replica approach dealing with structural glasses introduced by Mézard and Parisi\cite{mezard1986}, which utilizes simple liquid theory in order to obtain the pair correlation functions, yielded a liquid-glass phase transition at a temperature $T_0 \sim 2100K$. This result is quite odd, since it contradicts the experimental result implying no thermodynamical transition down to the experimental glass temperature $T_g = 1446K$, hence a few comments are strongly required.

As it should be clear from the previous discussion on the behavior of viscosity in the BKS silica, our theoretical findings are not ruled out on numerical grounds\cite{10,12}, as MD simulations have not explored the region where temperatures are much lower than the Mode-Coupling one. Because of that a nearly-Arrhenius behavior (covering no more than two decades) has been observed only taking into account a few low temperature data, whereas a previous extrapolation of data\cite{6} was compatible with a divergence at a finite temperature $T_0$ larger than $T_g$. Therefore one could argue that the too large critical temperature found in this thermodynamic approach is nothing but an artifact of the BKS potential which is not completely faithful to the actual low temperature behavior of real silica.

On the other hand, as we have already stressed, the $g(r)$ obtained from approximate theory of liquids show some difference from the ones obtained by MD simulations utilizing the BKS potential. We want to recall here that both the approximations involved (HNC and ZH) satisfy the $T^{-2/5}$ behavior for the entropy of the liquid in the whole low temperature phase, while the claimed fragile-strong transition\cite{12} at $T_c$ points to the failing of this law. This discrepancy could be the source of a severe overestimation of the value of the actual critical temperature.

Hence we are led to consider 2100$K$ rather as a rough estimate of the actual glass temperature. As a matter of fact, experiments cannot rule out the possibility of a thermodynamic transition at a temperature lower than $T_g$.

Furthermore, it is worthwhile to note that the approximations involved in the computation of correlated liquid free energy are quite crude. This could lead to an overestimation of the critical temperature as well.

An intriguing issue is the possibility to gain an insight into the existence of a finite $T_0$ by means of measurements of the violation of the fluctuation-dissipation relation in off-
equilibrium experiments. It has been suggested the existence in structural glasses of an off-eq-
equilibrium regime, called 'aging', reached by a system driven out-of-equilibrium by letting it to suddenly cross the transition point.

It has been also argued that in the aging regime the fluctuation-dissipation relation could still be utilized to define an effective temperature $T_{eff}$ which does not depend on the age of the system\cite{31,32}. On very general grounds, it has been moreover conjectured the equivalence for disordered systems between the ratio $T/T_{eff}$ and the parameter describing the replica symmetry breaking, that at one step level is nothing but the function $m^*(T)$ computed in the thermodynamic approach\cite{33}. Of course, the existence of $T_g$ makes the experimental situation much more complicated, as for practical purposes the system falls out-of-equilibrium when crossing $T_g$. At the moment, it is unclear how to link an effective temperature measured between $T_g$ and $T_0$ to some purely thermodynamic computation.

Nevertheless, a few attempts on different systems have been already performed\cite{34,35} or are in progress\cite{36}, and we believe that even on silica those kind of experiments could be useful to clarify many open points.

V. ACKNOWLEDGMENTS

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2 \( T_g \) is defined as the temperature where the viscosity is \( 10^{13} \) Poise; we shall assume that the temperature \( T_0 \) in the VFT law is equivalent to the Kauzmann temperature\[17\]; \( T_c \) is the mode-coupling temperature\[8\].

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TABLE I: Parameters of the BKS potential

|       | A (eV)  | B (Å\(^{-1}\)) | C (eV · Å\(^{-6}\)) |
|-------|---------|----------------|----------------------|
| SiSi  | 0.0     | 0.0            | 0.0                  |
| OO    | 4.87318 | 2.76           | 175.0                |
| SiO   | 18003.7572 | 4.8732    | 133.5381             |