Quantitative investigation of the mean-field scenario for the structural glass transition from a schematic mode-coupling analysis of experimental data

V. Krakoviack* and C. Alba-Simionesco†
LCP, UMR 8611, bâtiment 490, Université Paris Sud, F-91405 Orsay

Abstract

A quantitative application to real supercooled liquids of the mean-field scenario for the glass transition ($T_g$) is proposed. This scenario, based on an analogy with spin-glass models, suggests a unified picture of the mode-coupling dynamical singularity ($T_c$) and of the entropy crisis at the Kauzmann temperature ($T_K$), with $T_c > T_g > T_K$. Fitting a simple set of mode-coupling equations to experimental light-scattering spectra of two fragile liquids and deriving the equivalent spin-glass model, we can estimate not only $T_c$, but also the static transition temperature $T_s$ corresponding supposedly to $T_K$. For the models and systems considered here, $T_s$ is always found above $T_g$, in the fluid phase. A comparison with recent theoretical calculations shows that this overestimation of the ability of a liquid to form a glass seems to be a generic feature of the mean-field approach.

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*E-mail: krako@lcp.u-psud.fr
†E-mail: chalba@lcp.u-psud.fr
Despite considerable experimental and theoretical efforts, understanding the dynamics of supercooled liquids and the related phenomenon of glass transition remains a challenging problem of classical statistical mechanics [1].

Recently, Kirkpatrick et al. [2,3] conjectured that generalized spin-glass models with discontinuous one-step replica symmetry breaking (1RSB) transitions [4] (like the spin-glass with $p$-spin interactions ($p > 2$) or the $q$-state Potts glass ($q > 4$)) could be relevant models for the description of the structural glass transition. Essentially two points substantiate this analogy. Firstly, when considered in the mean-field limit where the interactions between spins have infinite range, the generalized spin-glasses display a (static) 1RSB transition to a spin-glass phase at a temperature $T_s$ that is accompanied by the vanishing of the configurational entropy similar to the entropy crisis at $T_K$ hypothesized by Kauzmann for glassforming liquids [5]. Secondly, in the same mean-field limit the study of the Langevin dynamics of such models shows that a dynamical transition takes place at a temperature $T_d$ greater than $T_s$. Above $T_d$, the time evolution of the spin correlation function is given by a non-linear equation of the same type as those occurring in the ideal mode-coupling theory (MCT) for the glass transition of simple liquids, where they describe the time evolution of density fluctuations [6], and $T_d$ coincides with what is called the critical temperature $T_c$ in the context of MCT. Below $T_d$, the systems display a nontrivial free-energy landscape that in finite-range models could lead to slow activated dynamics, as described for instance by the Adam-Gibbs theory [7].

Mean-field models and their extensions to finite-range systems could thus provide a consistent framework for the study of the liquid-glass transition, a framework in which the mode-coupling approach finds a natural place and that catches important aspects of the glass phenomenology. This approach has recently been very fruitful: first-principle studies based on the replica method have been proposed for simple liquid models [8,9], and computer simulation studies of the out-of-equilibrium dynamics of simple liquids [10] show aging behaviors qualitatively similar to the one displayed by generalized spin glasses [11].

A question remains, however, elusive. Indeed, it is known that the dynamical transition predicted by the ideal MCT is not experimentally observed: it is 'avoided' because of ergodicity restoring processes not accounted by the theory. In general, it is thought to be replaced by a smooth crossover regime where the dynamics changes qualitatively [3]. Because of the similarities between the ideal MCT and the dynamical aspects of the mean-field theory, the same breakdown is expected in the latter when more realistic systems with finite-range interactions are considered. Its influence on the other aspects of the mean-field picture described above is unknown, but the static transition is usually assumed to survive and the dynamical freezing is expected to occur only at the static transition [3]. This issue clearly deserves further investigation.

In this Letter, as a step in this direction, we propose a quantitative study of the above mean-field scenario for real supercooled liquids. By quantitative, we mean that we will extract from experimental data values for the two characteristic temperatures introduced within the mean-field approach and discuss these values in relation with known properties of the investigated systems. At present, no definite method exists for such a work. We propose here to start from a phenomenological mode-coupling approach, the so-called schematic approach to experimental data [12], which is found to be particularly well suited for investigating the avoidance of the dynamical transition. Then, taking advantage of the
coincidence between the ideal mode-coupling equations and the dynamics of some mean-field generalized spin-glass models, the schematic calculation is rephrased in terms of an effective spin-glass Hamiltonian, whose study allows us to determine, for the glassforming liquids under investigation, the location of the two transitions predicted by the mean-field theory.

Schematic models are simple sets of mode-coupling equations \[ [13] \], which have proven to be useful in testing the MCT on realistic systems. Indeed, these models can be included within a fitting procedure of experimental data \textit{over a wide time or frequency range}, and they allow the calculation of effective mode-coupling parameters ('vertices') describing the dynamical evolution of a liquid with varying external conditions \[ [12,14–16] \]. A major interest of these models is that they catch the universal features of the mode-coupling equations, in particular the asymptotic scaling results valid near the dynamical transition, but are not reduced to them. They make possible to overcome the difficulties and uncertainties arising from the need for corrections to the asymptotic critical predictions of the theory and to take into account the \( \alpha \) relaxation as well as the regime of the high-frequency microscopic excitations. The price to pay is that these models are somewhat \textit{ad hoc} and might possibly display non-generic features.

We make use in this Letter of the results obtained from a previous study \[ [14] \] of the depolarized light scattering spectra of two so-called 'fragile' glassformers, CKN and salol \[ [17] \]. Only the facts relevant to our present calculation are reviewed here and the reader is referred to the corresponding paper for details. The basis of our study is the well studied generalized spin-glass models, the schematic calculation is rephrased in terms of an effective spin-glass Hamiltonian, whose study allows us to determine, for the glassforming liquids under investigation, the location of the two transitions predicted by the mean-field theory.

\[ \sum_{1 \leq i < j \leq N} J_{ij} s_i s_j + \sum_{1 \leq i < j < k \leq N} J_{ijk} s_i s_j s_k, \]

where the \( s_i \)'s are spherical spin variables and the couplings \( J_{ij} \) and \( J_{ijk} \) are independent Gaussian variables with zero means and variances \( \langle J_{ij}^2 \rangle = v_1/N \) and \( \langle J_{ijk}^2 \rangle = 2 v_2/N^2 \) \[ [18] \]. A remarkable property of these systems is that the correlation function of the Hamiltonian,
\[ \beta^2 \mathcal{H}[s] \mathcal{H}[s'] = N \left( \frac{v_1}{2} q_{s,s'}^2 + \frac{v_2}{3} q_{s,s'}^3 \right), \]

where \( q_{s,s'} = s \cdot s'/N = (\sum_i s_i s'_i)/N \) is the overlap between the spin configurations \( s \) and \( s' \), determines completely both their statics and dynamics \([19]\). With parameters \( v_1 \) and \( v_2 \) extracted from a fit of the dynamics, we are thus able to construct an effective generalized spin-glass model allowing us to investigate the mean-field scenario for the glassforming salol and CKN.

The phase diagram of the generalized spin-glass model described above is easily computed and is plotted on figure [1]. The dynamical-transition line separating the ergodic domain in the vicinity of the origin from the non-ergodic one in the vicinity of infinity has two branches: \( \{ v_1 = 1, \ v_2 \leq 1 \} \) corresponding to a continuous or type A transition and \( \{ v_1 = 2 (v_2)^{1/2} - v_2, \ 1 < v_2 \leq 4 \} \) corresponding to a discontinuous or type B one, respectively.

At the static level, by using the replica trick to average over the quenched disorder \([4]\), the model is exactly solved with a 1RSB ansatz, which leads to the following free energy density

\[ \beta f(q, x) = -\frac{v_1}{4} (1 - (1 - x)q^2) - \frac{v_2}{6} (1 - (1 - x)q^3) - \frac{1}{2x} \ln(1 - (1 - x)q) - \frac{x - 1}{2x} \ln(1 - q), \]

where \( q \), the mutual overlap between replicas lying in the same cluster, and \( x \), the cluster size, are variational parameters \( (0 \leq q, x \leq 1) \), with respect to which the free energy has to be maximized. Here again, the transition line between the replica-symmetric phase at small couplings and the 1RSB phase at large couplings has two branches: a continuous 1RSB transition line coincides with the continuous dynamical transition line, whereas a discontinuous 1RSB transition line is found beyond the dynamical discontinuous transition line. It corresponds to the appearance of a non-zero solution for \( q \) with \( x = 1 \) and its equation as a parametric function of \( q \) is given by

\[ v_1 = 2 \frac{2q^2 - 3q - 3(1 - q) \ln(1 - q)}{q^2(1 - q)}, \quad v_2 = 3 \frac{2q - q^2 + 2(1 - q) \ln(1 - q)}{q^3(1 - q)}. \]

On figure [1] are also reported the effective vertices obtained from the experimental data for the two supercooled liquids. They display two different regimes with varying temperature. At higher temperatures, they vary linearly and show the apparent evolution of the liquids toward the dynamical transition expected from MCT. But, above the corresponding transition temperature, the vertices behavior changes: the transition is not reached, and the vertices follow the dynamical-transition line without crossing it. The first regime can be associated with the domain of validity of the ideal MCT, whereas the second one indicates the failure of the theory because of the putative onset of activated processes. Indeed, the MCT states that the dynamics is governed by vertices which are purely static quantities and thus change smoothly with external parameters. Even if in the case of schematic models the connection between the effective vertices and static quantities is somewhat obscured, it is reasonable to expect smooth variations of the fitted parameters with temperature. Accordingly, we concentrate in the following on the high temperature regime and its extrapolation to lower temperatures. Note that one can avoid the need for extrapolation using a low frequency cut-off for the lowest temperatures \([13]\).

With this method, we find the dynamical temperatures \( T_d = T_c = 257 \pm 5 \) K for salol and \( T_d = T_c = 388 \pm 5 \) K for CKN, in good agreement with previously determined values of
the mode-coupling transition temperature. By construction, the mode-coupling transitions of the liquids and the dynamical transitions of the effective disordered systems are identical.

We now turn to the static calculation. We are interested in the discontinuous 1RSB transition temperature, since it is thought to describe the entropy crisis associated with the resolution of the Kauzmann paradox. Indeed, as first pointed by Kauzmann, because the heat capacity of a supercooled liquid is substantially greater than that of the underlying crystalline solid, reasonable extrapolations of the liquid entropy below the glass transition seem to cross the entropy of the crystal at a non-zero temperature $T_K$. To solve this paradox, following Gibbs and Di Marzio [20], it is sometimes postulated that, below $T_g$, a second-order transition to an ideal glassy state should exist, at which the configurational contribution to the entropy of the liquid vanishes. This mechanism is precisely at work in the mean-field models at a discontinuous 1RSB transition. Between the dynamical and static transitions, one finds that the Gibbs measure is dominated by a number of states exponentially large in $N$, leading to a finite configurational entropy density (defined as the logarithm of that number of states divided by $N$). At the static transition, this configurational entropy density vanishes and stays zero in the low-temperature phase.

From the above analysis, we find $T_s = 242 \pm 5$ K for salol and $T_s = 376 \pm 5$ K for CKN. These values, which are very close to $T_d$, have to be compared with the experimental calorimetric glass transition temperatures ($T_g = 220$ K for salol, $T_g = 333$ K for CKN) and the empirically determined Kauzmann temperatures ($T_K = 175$ K for salol [21], no value for CKN because the crystalline phase is unstable): $T_s$ is found in both cases above $T_g$, i.e. still in the liquid phase! All these characteristic temperatures are plotted in figure 2 in the case of salol: the total configurational entropy decreases by only 10% between $T_d$ and $T_s$.

We have investigated the effect of minor modifications of the schematic calculation on our results, namely changing the expression of the calculated susceptibility as a functional of $\phi_0$ and $\phi_1$ (each can enter linearly or quadratically in the susceptibility expression) and/or changing the second memory function to $m_1(t) = r \phi_0(t) \phi_1(t)$. The resulting fits are all of equally good quality, and the corresponding vertex trajectories, although slightly different, agree with the previous values for both the two transition temperatures and the vertices at the dynamical transition. As these changes merely affect $\phi_1$, this consistency validates our assumption of neglecting it for building the effective model. For more drastic changes to the model, in which the $F_{12}$ equation is replaced by another one (for instance, we tried the $F_{13}$ and $F_{29}$ models where $m_0(t) = v_1 \phi_0(t) + v_3 \phi_0^3(t)$ and $m_0(t) = v_2 \phi_0^2(t) + v_9 \phi_0^9(t)$, respectively), we have not been able to fit satisfactorily the experimental susceptibilities. Indeed, the fitted curves failed to reproduce the location of the susceptibility minimum, its shape, or else the position of the $\alpha$-peak. As these features are crucial for the characterization of the dynamics within the MCT framework, the results, in qualitative agreement with those obtained with the $F_{12}$ model, do not appear reliable enough for quantitative purpose. The origin of this failure is in general unclear, but in some cases can be related to non-generic features of a given schematic model (for instance, the $F_{13}$ model displays an $A_3$ singularity very close to the calculated vertex trajectories). This limitation seems to be severe for our static calculation, as it is known from the study of mean-field models like spin-glasses with $p$-spin ($p > 2$) interactions [22] or the Potts glass [23], that the larger the asymptotic value of the correlation function at the dynamical transition, the larger the ratio $T_d/T_s$, and the $F_{12}$ model only allows for small values of the former. But we stress that, in our model, the
temperature enters in a different way, only through the effective vertices whose dependence comes out directly from the fitting procedure to dynamic light-scattering susceptibilities. There is, thus, no built-in closeness of $T_d$ and $T_s$ in our work. A related remark is the independence of our results with respect to changes in the way $\phi_0(t)$ enters the calculated susceptibility, thereby showing that its infinite time limit is not a sensitive parameter in the study.

Within our phenomenological implementation of the mean-field approach, we find thus that this theory seems to overestimate notably the tendency of a supercooled liquid to form a glass. This overestimation shows up at two levels ($T_d > T_g$ on one hand, $T_s > T_g$ on the other) with clearly different implications. As stated in introduction, this result is expected from the dynamical side of the theory, because of its closeness with the ideal mode-coupling theory, whose inadequacy at low temperature is well known, and of the need to take into account corrections to mean-field in finite dimension [3]. From this point of view, this conclusion is not new. What is more unexpected is that the obtained static temperature values are clearly located in the fluid domain and do not seem to be associated to any change of behavior of the studied systems. These results are thus inconsistent with the arguments prescribing that, going beyond mean-field, the real dynamical transition should occur at $T_s$ for finite dimensional systems [3].

Whether the found overestimation has to be ascribed to an inadequacy of our simple phenomenological approach or more fundamentally to the theory itself can not be answered here a priori. We can nevertheless remark that theoretical studies of simple liquid models based on the replica method [8,9] tend to support our observations and conclusions. Indeed, one finds in general that the location of the static transition agrees well with the glass transition found by computer simulation, i.e. obtained with large quenching rates and on short observation times. This agreement implies thus an overestimation of the ability of the liquids to freeze into a glass on a macroscopic time scale, as found in our calculation. Concerning the closeness of the dynamical and static transitions, our results can only be compared consistently with theoretical approaches allowing one to compute the locations of both transitions within the same framework. This is the case in the papers of Ref. [8] only, in which the transitions are found very close to each other, just as we find here.

To summarize, we have investigated a potential application of the mean-field scenario for the liquid-glass transition to real supercooled liquids by constructing an effective generalized spin-glass model whose dynamics reproduces the standard mode-coupling equations used in the ideal MCT of glassforming liquids. We have been able to determine from experimental data for two fragile glass-formers both the dynamical and static transitions, which are found to be rather close and both located in the liquid phase. This result, in qualitative agreement with recent theoretical studies, shows that the theory apparently overestimates the ability of a supercooled liquid to freeze into a glass, at least in its simple implementation considered here. Whether this deficiency could be cured by employing a more sophisticated (but yet unknown) version of the mean-field approach to real supercooled liquids or would require a non mean-field treatment accounting explicitly for activated dynamics remains an open question.

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REFERENCES

[1] C.A. Angell, Science 267, 1924 (1995) and references therein.
[2] T.R. Kirkpatrick and P.G. Wolynes, Phys. Rev. A 35, 3072 (1987); T.R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. 58, 2091 (1987); Phys. Rev. B 36, 5388 (1987); Phys. Rev. B 37, 5342 (1988).
[3] T.R. Kirkpatrick and P.G. Wolynes, Phys. Rev. B 36, 8552 (1987); T.R. Kirkpatrick, D. Thirumalai, and P.G. Wolynes, Phys. Rev. A 40, 1045 (1989).
[4] M. M´ezard, G. Parisi, and M.A. Virasoro, Spin glass theory and beyond (World Scientific, Singapore, 1987).
[5] W. Kauzmann, Chem. Rev. 43, 219 (1948).
[6] W. G¨otze, in Liquids, freezing and glass transition, J.P. Hansen, D. Levesque, J. Zinn-Justin Editors (North Holland, 1991); W. G¨otze and L. Sj¨ogren, Rep. Prog. Phys. 55, 241 (1992).
[7] G. Adams and J.H. Gibbs, J. Chem. Phys. 43, 139 (1965).
[8] M. M´ezard and G. Parisi, J. Phys. A 29, 6515 (1996); M. Cardenas, S. Franz, and G. Parisi, J. Chem. Phys. 110, 1726 (1999).
[9] M. M´ezard and G. Parisi, Phys. Rev. Lett. 82, 747 (1999); J. Chem. Phys. 111, 1076 (1999).
[10] G. Parisi, Phys. Rev. Lett. 79, 3660 (1997); J. Phys. A 30, L765 (1997); W. Kob and J.-L. Barrat, Phys. Rev. Lett. 78, 4581 (1997); Europhys. Lett. 46, 637 (1999); Eur. Phys. J. B 13, 319 (2000).
[11] L.F. Cugliandolo and J. Kurchan, Phys. Rev. Lett. 71, 173 (1993).
[12] C. Alba-Simionesco and M. Krauzman, J. Chem. Phys. 102, 6574 (1995).
[13] W. G¨otze, Z. Phys. B 56, 139 (1984); E. Leutheusser, Phys. Rev. A 29, 2765 (1984).
[14] V. Krakoviack, C. Alba-Simionesco, and M. Krauzman, J. Chem. Phys. 107, 3417 (1997).
[15] T. Franosch, W. G¨otze, M.R. Mayr, and A.P. Singh, Phys. Rev. E 55, 3183 (1997).
[16] A.P. Singh, G. Li, H.Z. Cummins, T. Franosch, M. Fuchs, and W. G¨otze, J. Non-Cryst. Solids 235-237, 66 (1998).
[17] G. Li, W.M. Du, A. Sakai and H.Z. Cummins, Phys. Rev. A 46, 3343 (1992); G. Li, W.M. Du, X.K. Chen, H.Z. Cummins and N.J. Tao, Phys. Rev. A 45, 3867 (1992).
[18] J.-Ph. Bouchaud, L.F. Cugliandolo, J. Kurchan, and M. M´ezard, Physica A 226, 243 (1996); S. Ciuchi and A. Crisanti, Europhys. Lett. 49, 754 (2000).
[19] S. Franz and G. Parisi, J. Phys. I (France) 5, 1401 (1995).
[20] J.H. Gibbs and E.A. Di Marzio, J. Chem. Phys. 28, 373 (1958).
[21] R. Richert and C.A. Angell, J. Chem. Phys. 108, 9016 (1998).
[22] A. Crisanti and H.-J. Sommers, Z. Phys. B 87, 341 (1992).
[23] E. De Santis, G. Parisi, and F. Ritort, J. Phys. A 28, 327 (1995).
[24] H. Fujimori, M. Oguni, private communication.
FIG. 1. Phase diagram of the generalized spin-glass model (continuous line: continuous dynamical and 1RSB transitions, dashed line: discontinuous dynamical transition, dotted line: discontinuous 1RSB transition) and effective vertices obtained from the MCT fit (open symbols: CKN, filled symbols: salol). Inset: evolution of the vertices with temperature. The superimposed straight lines are the linear fits used for the low-temperature extrapolations.
FIG. 2. Characteristic temperatures calculated within the mean-field scenario for salol, \( T_c = T_d \) and \( T_s \), represented on a configurational entropy plot (normalized to the entropy of melting \( \Delta S_m \)). Entropy data taken from Ref. [24]. Also shown are the calorimetric glass transition temperature \( T_g \), the melting temperature \( T_m \), and the extrapolated Kauzmann temperature \( T_K \). The predicted static transition \( T_s \) occurs well above \( T_g \).