On the origine of the Boson peak

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Abstract. We show that the phonon-saddle transition in the ensemble of generalized inherent structures (minima and saddles) happens at the same point as the dynamical phase transition in glasses, that has been studied in the framework of the mode coupling approximation. The Boson peak observed in glasses at low temperature is a remanent of this transition.

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1. Introduction

The aim of this paper it show that the presence of a Boson peak is a necessity in the present days approach to glasses (Angell 1995). When we increase the temperature the inherent structures loose they stability: this happens at the dynamical transition point, i.e. at the mode coupling transition $T_c$ (Göetze 1989). In variance to what may happens in other materials this lost of stability is due to the fact a finite part of the population of eigenvalues of the harmonic spectrum migrates from the positive region to the negative region (Kurchan and Laloux 1996, Cavagna 2001, Broderix et al 2000, Angelani et al ). In they journey these eigenvalues have to traverse the small $\omega$ region and, when they do so, they produce the Boson peak.

The existence of the Boson peak it thus unavoidable and this explains its ubiquitous presence. However detailed computations are needed to obtain its properties in quantitative way; in particular one would like to show that no anomalies in the sound velocity are present at the frequency of the Boson peak. This paper presents some of the progresses that have recently done in this direction (Grigera et al 2001, Grigera et al 2002a, 2002b, 2002c).

In the next section of this paper, after the introduction, I will describe the general theoretic framework that stays behind these computations. In the next section I will introduce generalized inherent structures (minima and saddles) and I will discuss their properties. In the fourth section I will compute in a simplified model the spectrum of the oscillations around the generalised inherent structures and I will show how they are related to the Boson peak. In the next section I will show how more precise computations can be done in a more realistic models using the theory of Euclidean random matrices. In the last section I will present some conclusions. Finally in the appendix I will review some of the theoretical reasons that justify the relevance of the generalized inherent structures.

2. The general framework

It is usually believed that in the real world fragile glasses have only one thermodynamic transition with divergent viscosity (at temperature $T_K$). This transition cannot be observed directly because the time required for thermalization is too long. This transition is believed to be related to Kauzmann entropy crisis and it should happens just at the point where the configurational entropy becomes zero. The viscosity is supposed to diverge as $\exp(A/(T - T_K))$ and the specific heat should be discontinuous.

However in the idealized world of mean field theories, (Kirkpatrick et al 1989), both in the framework of the mode coupling theory (Göetze 1989) or of the equivalent replica approach (Mézard et al 1987, Parisi 1992), if activated processes are strictly forbidden (Franz and Parisi 1997), there is a second purely dynamics transition $T_c$ at higher temperatures (for a recent review see Cugliandolo 2002, Parisi 2002). Here the viscosity is divergent as a power law of $T - T_c$. This idealization is not so bad in the
real world: activated processes are strongly depressed and the viscosity may increase of many orders of magnitudo (e.g. 6) before reaching the region where activated processes become dominant.

As it happens in many cases, slow relaxation is related to the existence of zero energy modes and this statement is true also in the mode coupling theory. This statement can be easily verified in spin models where the mode coupling theory is exact and simple computations are possible.

Summarizing, this qualitative description can be easily verified in models where the mean field approximation is exact. In glass forming liquid, the picture is essentially sound (provided that we correct it by considering the existence of phonons).

The aim of this note is to show that, if the previous picture holds, there is a Boson peak at low temperatures. The Boson peak is a bump in the density of vibrational states (divided by the Debye density of states that is proportional to $\omega^2$) at low temperature in the low $\omega$ region (Benassi et al 1996, Masciovecchio et al, Sette et al 1998, Engberg et al 1999, Fioretto et al 1999, Hédoux et al 2001). One of the remarkable and puzzling features of the Boson peak (that is explained by present approach) is that the sound velocity is linear in the region of the Boson peak, so that these low energy excitations do not appear at low momenta.

The Boson peak is present in many materials: an example of the experimental data in silica is given in fig. 1.
3. Generalized inherent structures

An inherent structure (IS) is a minimum of the Hamiltonian of the system that is near to an equilibrium configuration. (Stillinger 1995, Kob et al 2000, Debenedetti and Stillinger 2001). We can associate to an equilibrium configuration an inherent structure as the nearest minimum. In the same spirit a generalized inherent structure (GIS) is the nearest stationary point of the Hamiltonian (i.e. a point where the forces on all the particles are equal to zero (Cavagna 2001)).

It seems that with a very good approximation at temperatures lower than $T_c$ practically all GIS’s are also IS’s (i.e. all stationary points of the Hamiltonian are also minima of the Hamiltonian) so that the two definitions practically coincides in this region. Only for $T > T_c$ starting from an equilibrium configuration the associated GIS is not an IS and it has a higher energy (Broderix et al 2000, Ruocco et al 2000).

A relevant property of a GIS is its vibrational spectrum (and the associated density of state); if $\lambda$ is an eigenvalue of the Hessian of the Hamiltonian, the frequency $\omega$ is given by

$$\omega \propto \sqrt{\lambda}.$$

A crucial quantity is the fraction of negative eigenvalues (i.e. imaginary frequency) that will be denoted by $K$. If $K = 0$ the GIS is an IS.

Generalized inherent structures are a powerful theoretical tool for many reasons.

- At high temperature (i.e. at $T > T_c$) inherent structures are not relevant: they are quite far away from the equilibrium configurations. On the contrary, also when you increase the temperature, you can find saddles that are not too different from the equilibrium configurations (Cavagna et al 2002).

- Saddles are the natural continuation at higher temperature of the inherent structures at low temperature and we may expect the the properties of the two different ensembles join smoothly at $T_c$.

- The most spectacular result is that the fraction of negative eigenvalues $K$ vanishes for the saddles when we approach $T_c$. This property can be analytically proved in the framework of the mean field approach (Cavagna et al 2002) and it is an empirical fact that it is satisfied with reasonable good approximation in all the models where explicit computations have been done (Broderix et al 2000, Ruocco et al 2002, Grigera et al 2002a).

The comparison of the spectrum of the instantaneous normal modes with that of the saddles is spectacular and is shown in fig. 2. The fraction of negative eigenvalues ($K$) of the saddles vanishes nearly linearly at $T_c$ while the instantaneous normal modes do not display any interesting behaviour at this point. This behaviour of the fraction of negative eigenvalues of GIS’s can be be used in many different ways.

- The numerical computation of $K(T)$ can be used as a diagnostic tool to compute the value of $T_c$. 

The dynamical correlation time of the system (neglecting hopping) is divergent just at the point where $K(T) = 0$. It makes sense to try to relate in a quantitative way the properties of the spectrum around the saddles and the dynamical quantities (a similar effort would be hopeless for the instantaneous normal modes).

We can use the fact that the properties of the inherent structures at $T < T_c$ smoothly join with those of the saddles at $T > T_c$ to predict the behaviour of the inherent structures at low temperature.

Here I will explore this third feature and I will show how one can derive in this framework the existence of a Boson peak.

4. Exact non realistic computations of the spectrum

It is well known that soluble models are not realistic and realistic models are not soluble. However the study of soluble models can give us some enlightens on the behaviour in a
realistic model. This is particularly true in this case: many properties of the GIS’s are very similar in realistic models and in the soluble cases.

The simplest model where we can investigate the properties of the GIS is the $p$-spin spherical model (Kirkpatrick et al. 1989). This model is the most unrealistic one. It has the advantage that, in spite of the fact that nearly everything can be computed analytically, it has a quite rich behaviour (both $T_c$ and $T_K$ are well defined) and the mode coupling equations for the dynamics are exact.

The spectrum of the harmonic oscillations around the inherent structures, the generalized inherent structures and the instantaneous normal modes can be computed exactly (Biroli 1999, Cavagna et al. 2002): they have a semicircular shape (see fig. 3) whose edges are a function of the temperature. The value of the lowest eigenvalue is particular relevant for physics and it is shown in fig. 4.

If we look to spectrum of the oscillations around the inherent structures, we find that it has a gap at $T < T_c$ and this gap vanishes at $T_c$. Therefore at the dynamical transition there is an excess of low frequency modes with respect to what happens at lower temperatures. This result maybe unexpected; however it is a necessary consequence of the fact that at $T_c$ the inherent structures merge with the saddles and the saddles must have negative eigenvalues.

Skipping all the details we conclude that there is a population of modes whose eigenvalues decrease when we approach $T_c$ and these eigenvalues change sign when we cross $T_c$. This is a quite general phenomenon and it survives also in more realistic cases. It is clear that the modes that migrate at low temperature must produce an increase in the density of states at low energy with respect to what happens in other models where these modes are non present (e.g. a crystal).

It is quite natural to suppose that this excess of extra modes is the origine of the
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Boson peak. In order to prove the correctness of this intuition there are three crucial points that must be discussed:

- This effect produces only an excess of modes in the low momenta region or do we find a peak, after dividing by the Debye density?
- Do these modes produce an anomaly in the sound velocity, and if not, why?
- The Boson peak is something that appears at low temperatures, the effect I am speaking about happens near $T_c$. How can one use a property of the system near $T_c$ to deduce the behaviour in the low temperature region?

It order to be able to answer to the previous questions it is necessary to do some explicit computation in more realistic 3-dimensional models and this will be done in the next section.

5. Euclidean Random Matrices and the phonon-saddle transition

Generally speaking our task is to compute the spectrum of the second derivative of the Hamiltonian, i.e. the spectrum of the Hessian the matrix $M$ defined as

$$M_{i,k} = \delta_{i,k} \sum_j V''(x_i - x_j) - V''(x_i - x_k).$$

(2)

The points $x$ are chosen random with a given probability distribution.

- If the points $x$ are extracted with the equilibrium probability distribution at a temperature $\beta$, we get the instantaneous normal models.
- If the points $x$ belong to a random GIS, we get the spectrum of the GIS.
• If the points $x$ belong to a random IS, we get the spectrum of the IS.

We can generalize the problem by studying the behaviour of the spectrum of $M$ when we change the probability distribution of the points $x$'s. For general random distribution we have the so called problem of Euclidean random matrices (Mézard et al. 1999, 2001).

In general we can stay in one of the two phases: all the eigenvalues of $M$ are positive (phonon phase), a fraction of the eigenvalues of $M$ are negative (saddle phase). By changing the parameters of the distribution of $x$ we should go from one phase to another one ‡.

This approach can be successful only if we are able to put under control the general problem of Euclidean random models. The strategy for the study of the spectrum of these random operators consists in extending to topologically disordered systems the approach used in disordered lattice problems.

The first step consist in extending the usual CPA approximation of lattice systems to the present case. This can be done in a few steps (Grigera et al. 2001, 2002a, 2002b, 2003):

(i) One firstly identifies a soluble limit (jellium) where the density of the particles is very high or equivalently the range of the forces goes to infinite.

(ii) The corrections to the jellium limit can be computed in a systematic way as expansion in powers of the inverse of the density. This expansion can be expressed in a diagrammatical way.

(iii) It is possible to resum a given class of diagrams (very similar to those of the CPA) and to arrive to some kind of integral equation of the form

$$G(p, \omega)^{-1} = G_0(p, \omega) + \int dk W(p, k)^2 G(p, \omega)$$

where $G$ is the Green function § and it is equal to the average of the resolvent, i.e.

$$G(p, \omega) = \sum_{j, k} R(j, k | \omega^2) \exp(ip(x_j - x_k)) ,$$

and the resolvent is given by

$$R(j, k | \lambda) \equiv \left( \frac{1}{\lambda - M} \right)_{j, k} .$$

‡ A technical remark: in many ensembles the matrix $M$ has a tails of localized eigenvalues that may extend up to infinity or very far away. In this situation the phonon phase is impossible. In the following we are going to neglect the existence of these localized modes whose fraction is often very small. If we take care of the existence of localized modes the phonon-saddles transition is no more exactly sharp. This is not a surprise because also the dynamical transition $T_c$ is not defined with infinite precision. The dynamical transition becomes sharp if activated processes are neglected and the phonon-saddle transition become sharp if localized modes (in the low part of the spectrum) are neglected. These two approximations are related but I cannot discuss more this point for reasons of space.

§ The Green function is related to the usual structure function by the relation: $S(p, \omega) \propto p^2 \omega^{-1} \text{Im} G(p^2, \omega + i0^+)$. 

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(iv) These integral equations can be numerically solved. For a suitable choice of the parameters one find a phonon saddle transition. Fortunately is also possible to derive some analytic results near transition and to obtain the value of critical exponents.

Numerical and analytic studies show that there is an anomaly in the spectrum that has a shape very similar to the Boson peak. This has been done for unrealistic potential and the computation for realistic potential is going on and should be ready soon (Grigera et al 2002).

The main result (that was unexpected, at least by me) is that near the transition nothing happens in the small momentum region. The sound velocity is regular in the region of frequency of the Boson peak. The states relevant for the transition have simultaneously high momentum and low energy region; there is a only marginal hybridization of these states with the acoustic branch (however this hybridization influences the value of the critical exponents).

It is quite possible that high order correction do not affect the critical exponents; however this system behaves in a very different way from the other phase transitions that I have studied in the last thirty years and I can hardly make a reliable guess before further investigations.

It is reasonable to suppose that these properties are universal and they are also present in the phonon-saddle transition for the generalized inherent structures as function of the temperature. However we must remark that the relevant parameter on which we expect a smooth behaviour is not the initial temperature, but the energy of the final generalized inherent structure: when the temperature change from 0 to \( T_K \) the properties of the generalized inherent structures (energy and spectrum) should hardly change, they should change by a little amount when we go from \( T_K \) to \( T_c \) and they should strongly change when we go from \( T_c \) to a very large temperature. In other words, due to the fact that the ration \( T_c/T_K \) is not very far from 1, the inherent structures should change of a little amount when we go from \( T_c \) to 0. In other word the energy of the IS structure at zero temperature is not very different from the energy of the IS at the critical temperature. In this sense 0 temperature is near to \( T_c \) and therefore the behaviour of the system in the critical region is relevant also at low temperature.

More detailed predictions can be done, but I cannot discuss them for reasons of space.

6. Conclusions

Let me try to summarize in a very crude way the scenario that is emerging.

In pure mean field models the excitation around a generalized saddle point form a band of delocalized states (let us call then glassons in absence of a better name). When

\[ \text{The leaned reader who is concerned by the fate of localized states, should notice that localized states are not be present in this CPA approximation.} \]
we cross the dynamical transition the lower edge of the glassons goes from negative eigenvalues (imaginary frequency) to positive eigenvalues (real frequency).

In realistic models we have both the glasson band and the usual phonon band. The low momenta structure function is dominated by the phonons and glassons decouple in this region. As far as the two bands superimpose it is not possible to separate them in a sharp way because there is always an hybridization among them, however it is convenient to think of them as two separate entities. At the dynamical point the lower edge of the glasson band becomes zero. At the low temperatures the glasson band develops a gap and when we look to the total density of states divided by $\omega^2$, the opening of the glasson band shows up as the Boson peak. The small hybridization among phonons and glassons is crucial to determine the detailed behaviour of the Boson peak near the dynamical transition.

The main conclusion of this analysis are the following:

• The Boson peak is a remanent of the softening of the free energy landscape at the dynamical temperature and it composed by modes that migrate at imaginary $\omega$ at $T > T_c$.

• If activated processes were suppressed in the dynamics, the Boson peak would be infinite. In the same vein ultrafast quenching of the sample should give a very strong dependance of the Boson peak on the temperature (see Angell’s contribution to this conference).

• In general a Boson peak is present in any system of matrices near a phonon-saddle transition. In the case of the generalized inherent structure the point where this phenomenon happens coincide with the dynamical transition.

• Quantitative analytic direct computations of the various properties of the Boson peak are feasible and they will be done a next future.

• A comparison of this fully microscopic approach with the results of the mode-coupling theory should be possible (Göetze and Mayr 2000): work in this direction is in progress.

There still are many unclear points, conjectures that must be verified, connections with other theoretical results that must be established, but I believe that the basic scenario has been drawn and that it is essentially correct.

Appendix

Here I would like to describes some of the reasons for which generalized inherent structures are important.

The general idea is quite simple. Let us consider the free energy as functional of the density $\rho(x)$ (i.e. $F[\rho]$). We expect that at $T > T_c$ the trivial solution $\rho(x) = \text{const}$ is the only solution of the stationary equations the free energy that is relevant for the thermodynamics. At low temperatures there are an exponential large number of non-
equivalent solutions where the density has a non trivial dependence on \( x \). Skipping many details the situation should be the following:

- A temperature \( T > T_c \) there are no non-trivial relevant solutions of the equation
  \[
  \frac{\delta F}{\delta \rho(x)} = 0, \tag{6}
  \]
  however the dynamics is dominated by quasi solutions of the previous equations, i.e. by densities \( \rho(x) \) such that the left hand side of the previous equation is not zero, but vanishes when \( T \) approach \( T_c \). These quasi solutions are relevant for the dynamics (Franz and Virasoro 2001). One can compute the spectrum of the Hessian
  \[
  M(x, y) = \frac{\delta^2 F}{\delta \rho(x) \delta \rho(y)}. \tag{7}
  \]
  One finds that \( M \) has negative eigenvalues and its spectrum extends to the negative eigenvalue region and has qualitatively the shape shown in fig. 3. These quasi-stationary points of \( F \) look like saddles.

- At the transition point \( T = T_c \) the quasi stationary points becomes real solutions of the equations (6). They are essentially minima: the spectrum of the Hessian is non-negative and it arrives up to zero. As it can be checked directly, the existence of these nearly zero energy modes is responsible of the slowing down of the dynamics. The different minima are connected by flat regions so that the system may travel from one minimum to another (Kurchan and Laloux 1999).

- At low temperature the mimima become more deep, the spectrum develops a gap as shown in fig. 3 and the minima are no more connected by flat regions. If activated processes were suppressed, the system would remains forever in one of these minima. In the real world the system may jump (by decreasing his energy) until it reaches the region where the minima are so deep that the energy barriers among them diverges.

This picture is not so intuitive because it involves the presence of saddles with many directions in which the curvature is negative, and it is practically impossible to visualize it by making a drawing in a two or a three dimensional space.

This qualitative description can be easily verified in models where the mean field approximation is exact. In glass forming liquid, the picture is essentially sound (provided that we correct it by considering the existence of phonons). However, if we try to test it a more precise way, we face the difficulty that the free energy functional \( F[\rho] \) is a mythological object whose exact form is not exactly known and consequently the eigenvalues of its Hessian cannot be computed.

The generalized inherent structures are the “poor man” substitute of the solutions (or quasi solutions) of the stationary equations of the free-energy. It can be checked in mean field theory (Cavagna et al 2002) that the two constructions are quite similar and it is therefore reasonable that this similarity remains true also in more realistic...
models. It remains however surprising how the whole picture can be transferred from mean models to realistic models without too much to change.

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