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On the origin of the boson peak

Giorgio Parisi

Dipartimento di Fisica, Sezione INFN, SMC and INFM unità di Roma 1, Università di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185 Rome, Italy

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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 remnant of this transition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The aim of this paper is to show that the presence of a boson peak is essential to the present-day approach to glasses (Angell 1995). When we increase the temperature, the inherent structures (ISs) lose their stability: this happens at the dynamical transition point, i.e. at the mode coupling transition point T_c (Götze 1989). In contrast to what may happen in other materials, this lost of stability occurs because a finite proportion of the population of eigenvalues of the harmonic spectrum migrate from the positive region to the negative region (Kurchan and Laloux 1996, Cavagna 2001, Broderix *et al* 2000, Angelani *et al* 2000). In their journey, these eigenvalues have to traverse the small-ω region and, when they do so, they produce the boson peak.

The existence of the boson peak it thus unavoidable and this explains its ubiquity. However, detailed computations are needed to obtain its properties in a 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 describes some of the progress that has recently been made in this direction (Grigera *et al* 2001, 2002a, 2002b, 2002c)

In the next section of this paper, I will describe the general theoretical framework that lies behind these computations. In the following section I will introduce generalized inherent structures (GISs) (minima and saddles) and I will discuss their properties. In the fourth section I will compute, within a simplified model, the spectrum of the oscillations around the GISs and I will show how they are related to the boson peak. In the following section I will show how more precise computations can be carried out within 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 for the relevance of the GISs.

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 the Kauzmann entropy crisis and it should happen 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 (Götze 1989) and in that 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 dynamical transition temperature T_c at a higher value (for a recent review, see Cugliandolo 2002, Parisi 2002). Here the viscosity is divergent as a power law in $T - T_c$. This idealization is not so bad in the real world: activated processes are strongly depressed and the viscosity may increase by many orders of magnitude (e.g. 6) before reaching the region where activated processes become dominant.

As 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 work 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 which is proportional to ω^2) at low temperature in the low-ω region (Benassi *et al* 1996, Masciovecchio *et al* 1996, 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 the present approach) is that the sound velocity is linear in the region of the boson peak, with the result that these low-energy excitations do not appear at low momenta.

The boson peak is present in many materials: some example experimental data for silica are shown in figure 1.

3. Generalized inherent structures

An IS is a minimum of the Hamiltonian of the system that is near to an equilibrium configuration (Stillinger 1995a, Kob *et al* 2000, DeBenedetti and Stillinger 2001). We can associate with an equilibrium configuration an IS as the nearest minimum. In the same spirit, a 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 to a very good approximation, at temperatures lower than T_c, practically all GISs are also ISs (i.e. all stationary points of the Hamiltonian are also minima of the Hamiltonian), so the two definitions practically coincide in this region. Only for $T > T_c$, starting from an equilibrium configuration, is the associated GIS not an IS, and then 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 states); if λ is an eigenvalue of the Hessian of the Hamiltonian, the frequency ω is given by

$$\omega \propto \sqrt{\lambda}. \tag{1}$$

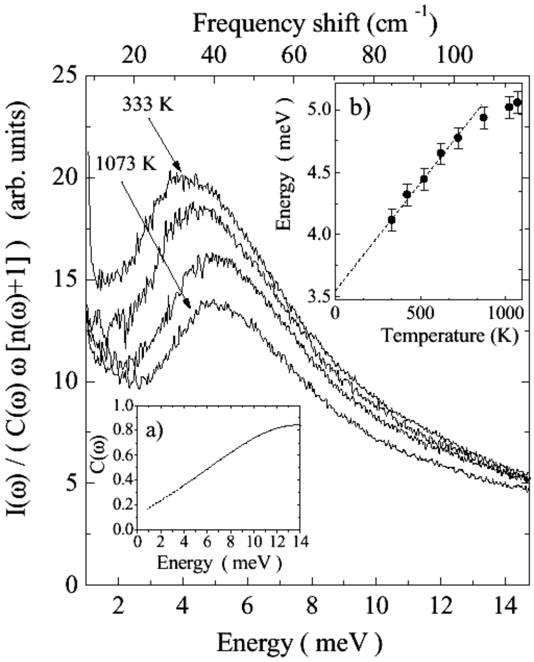

Figure 1. Examples of RS spectra taken for silica (Masciovecchio *et al* 1996). The data correspond to the reduced Raman intensities divided by $C(\omega)$ and shown in inset (a). In inset (b), the energy position of the maximum intensity at each temperature (•) is reported together with its linear fit in the low-temperature region.

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

GISs constitute a powerful theoretical tool for many reasons:

- At high temperature (i.e. at $T > T_c$) ISs are not relevant: they are quite far away from the equilibrium configurations. In contrast, when you increase the temperature, you can also 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 ISs at low temperature and we may expect the properties of the two different ensembles to 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 to a reasonably good approximation in all the models for which explicit computations have been carried out (Broderix *et al* 2000, Ruocco *et al* 2000, 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 figure 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 GISs can 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.

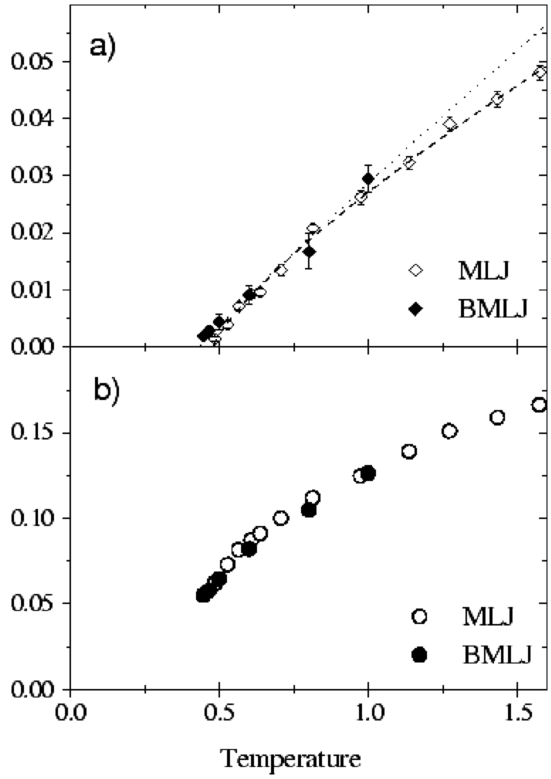

Figure 2. The temperature dependence of the fraction of negative eigenvalues of the Hessian calculated at the inherent saddle configurations, $n_s/3N$ (a), and at the instantaneous configurations, $n_i/3N$ (b). Open and closed symbols relate to two different choices of Lennard-Jones potentials (Angelani *et al* 2000).

- 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 pointless for the instantaneous normal modes).
- We can use the fact that the properties of the ISs at $T < T_c$ smoothly join those of the saddles at $T > T_c$ to predict the behaviour of the ISs 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 insight into the behaviour in a realistic model. This is particularly true in this case: many properties of the GISs are very similar in realistic models and in the soluble cases.

The simplest model in which 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

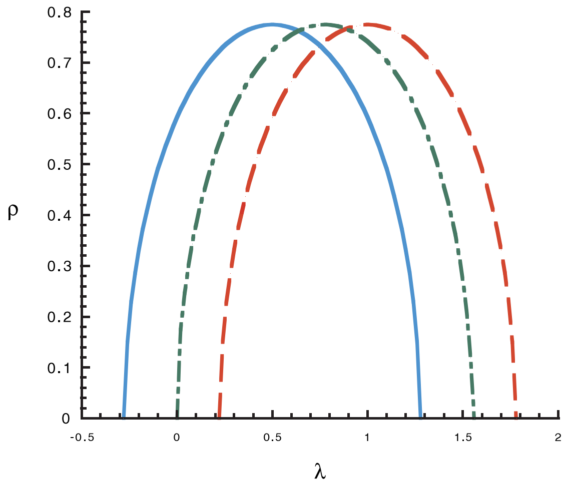

Figure 3. The qualitative behaviour of the spectral density for the GISs in the mean field approximation above T_c (full curve), at T_c (dot–dashed curve) and below T_c (dashed curve) as functions of the eigenvalue λ).

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 ISs, the GISs and the instantaneous normal modes can be computed exactly (Biroli 1999, Cavagna *et al* 2002); they have a semicircular shape (see figure 3) whose edges are a function of the temperature. The value of the lowest eigenvalue is particularly relevant for the physics and it is shown in figure 4.

If we look at the spectrum of the oscillations around the ISs, 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 may be unexpected; however, it is a necessary consequence of the fact that at T_c the ISs 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 not present (e.g. a crystal).

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

- Does this effect produce an excess of modes only in the low-momentum 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 not?
- The boson peak is something that appears at low temperatures; the effect that 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 these questions, it is necessary to carry out some explicit computation within more realistic three-dimensional models and this will be done in the next section.

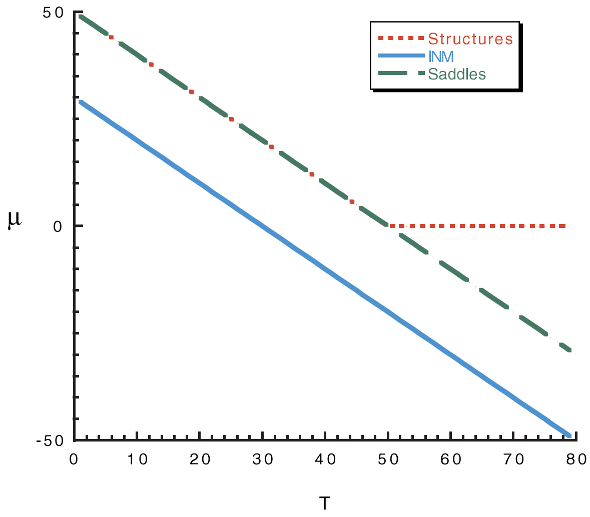

Figure 4. The qualitative behaviour of the threshold as a function of the temperature in the mean field approximation for the GIS normal modes (dotted line), for the instantaneous normal modes (full line) and for the IS normal modes (dashed line).

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

$$M_{i,k} = \delta_{i,k} \sum_j V''(x_i - x_j) - V''(x_i - x_k). \tag{2}$$

The points x are chosen randomly with a given probability distribution:

- If the points x are extracted with the equilibrium probability distribution at a temperature β, 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. For a 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[1].

This approach can be successful only if we are able to 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.

[1] A technical remark: in many ensembles the matrix M has tails of localized eigenvalues that may extend 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–saddle transition is no longer exactly sharp. This is not a surprise, because the dynamical transition point T_c is also not defined with infinite precision. The dynamical transition becomes sharp if activated processes are neglected, and the phonon–saddle transition becomes sharp if localized modes (in the low part of the spectrum) are neglected. These two approximations are related, but I cannot discuss this point further for reasons of space.

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):

(i) One first identifies a soluble limit (jellium) where the density of the particles is very high or equivalently the range of the forces goes to infinity.
(ii) The corrections to the jellium limit can be computed in a systematic way as an expansion in powers of the inverse of the density. This expansion can be expressed in a diagrammatic way.
(iii) It is possible to resum a given class of diagrams (very similar to those of the CPA) and to arrive at some kind of integral equation of the form

$$G(p,\omega)^{-1} = G_0(p,\omega) + \int \mathrm{d}k\, W(p,k)^2 G(p,\omega) \tag{3}$$

where G is the Green function[2] and is equal to the average of the resolvent, i.e.

$$G(p,\omega) = \overline{\sum_{j,k} R(j,k|\omega^2)\exp(\mathrm{i}p(x_j - x_k)}, \tag{4}$$

where the resolvent is given by

$$R(j,k|\lambda) \equiv \left(\frac{1}{\lambda - M}\right)_{j,k}. \tag{5}$$

(iv) These integral equations can be solved numerically. For a suitable choice of the parameters, one finds a phonon–saddle transition[3]. Fortunately it is also possible to derive some analytic results near the transition and to obtain the values of critical exponents.

Numerical and analytic studies show that there is an anomaly in the spectrum that has a shape very similar to that of the boson peak. These studies have been done for an unrealistic potential; the computation for a realistic potential is under way and should be ready soon (Grigera *et al* 2002c).

The main result (which 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; there is only marginal hybridization of these states with the acoustic branch (however, this hybridization influences the values of the critical exponents).

It is quite possible that high-order corrections do not affect the critical exponents; however, this system behaves in a very different way to the other phase transitions that I have studied in the last 30 years and I can hardly make a reliable guess without further investigation.

It is reasonable to suppose that these properties are universal and that they are also present in the phonon–saddle transition for the GISs as a function of the temperature. However, we must remark that the relevant parameter for which we expect a smooth behaviour is not the initial temperature, but the energy of the final GIS: when the temperature changes from 0 to T_K, the properties of the GISs (energy and spectrum) should hardly change; they should change by a small amount when we go from T_K to T_c; and they should change substantially when we go from T_c to a very large temperature. In other words, due to the fact that the ratio T_c/T_K is not very far from 1, the ISs should change little when we go from T_c to 0. In other words, 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, zero temperature is near to T_c and therefore the behaviour of the system in the critical region is relevant also at low temperature.

[2] The Green function is related to the usual structure function by the relation $S(p,\omega) \propto p^2\omega^{-1}\,\mathrm{Im}\,G(p^2,\omega + \mathrm{i}0^+)$.
[3] The learned reader who is concerned about the fate of the localized states should notice that localized states are not present in this CPA approximation.

More detailed predictions can be made, but I cannot discuss them here 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 forms a band of delocalized states (let us call them glassons in the absence of a better name). When 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-momentum structure function is dominated by the phonons, and glassons decouple in this region. As long as the two bands superimpose, it is not possible to separate them in a sharp way, because there is always hybridization between 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 low temperatures, the glasson band develops a gap and when we look at the total density of states divided by ω^2, the opening of the glasson band shows up as the boson peak. The *small* amount of hybridization among phonons and glassons is crucial to determining the detailed behaviour of the boson peak near the dynamical transition.

The main conclusions of this analysis are the following:

- The boson peak is a remnant of the softening of the free energy landscape at the dynamical temperature and it is composed by modes that migrate at imaginary ω 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 dependence of the boson peak on the temperature (see the contribution by Angell (2003) to this Special Issue).
- In general, a boson peak is present in any system of matrices near a phonon–saddle transition. In the case of the GIS, the point where this phenomenon happens coincides with the dynamical transition.
- Quantitative analytic direct computations of the various properties of the boson peak are feasible and they will be carried out in the near future.
- A comparison of this fully microscopic approach with the results of the mode coupling theory should be possible (Götze and Mayr 2000); work in this direction is in progress.

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

Acknowledgments

I am happy to thank A Cavagna, I Giardina, T Grigera, V Martín-Mayor and P Verrocchio who have worked with me on these matters in the last two years.

Appendix

Here I would like to describe some of the reasons for which GISs are important.

The general idea is quite simple. Let us consider the free energy as a functional of the density $\rho(x)$ (i.e. $F[\rho]$). We expect that at $T > T_c$ the trivial solution $\rho(x)$ = constant will be the only solution of the stationary equations for the free energy that is relevant for thermodynamics. At low temperatures there are an exponentially 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:

- At 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 approaches T_c. These quasi-solutions are relevant for the dynamics (Franz and Virasoro 2000). 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 figure 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 equation (6). They are essentially minima: the spectrum of the Hessian is non-negative and it starts from zero. As 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 the system may travel from one minimum to another (Kurchan and Laloux 1996).
- At low temperature the minima become deeper, the spectrum develops a gap as shown in figure 3 and the minima are no longer connected by flat regions. If activated processes were suppressed, the system would remain forever in one of these minima. In the real world the system may jump (by decreasing in energy) until it reaches the region where the minima are so deep that the energy barriers among them diverge.

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 using a drawing in a two- or three-dimensional space.

This qualitative description can be easily verified within 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 in a more precise way, we face the difficulty that the free energy functional $F(\rho)$ is a mythical object whose exact form is not exactly known, and consequently the eigenvalues of its Hessian cannot be computed.

The GISs are the 'poor-man's substitute' for solutions (or quasi-solutions) of the stationary equations of the free energy. It can be checked within mean field theory (Cavagna *et al* 2002) that the two constructions are quite similar and it is therefore reasonable that this similarity remains in more realistic models. It remains however surprising that the whole picture can be transferred from mean field models to realistic models without too much alteration.

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