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Feedback interaction between anharmonic and harmonic modes in glasses

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Abstract. The vibration spectrum of a metastable glassy state contains mainly two types of excitations: harmonic (phonons) and anharmonic modes (AM), some of which are double-well potentials. The AMs are treated in terms of the catastrophe theory. Two possible representations of the potential of the AMs are discussed. The double-well potentials correspond to only a minor part of the AMs, while the major part corresponds to soft anharmonic vibrations that are experimentally observed as a shift of the density of vibrational states towards lower frequencies.

Strong feedback interaction between the anharmonic and harmonic modes results in the appearance of higher-rank AMs, making a hierarchy in which the higher-rank AMs are responsible for stability of the corresponding lower-rank AM. A simple two-level hierarchy simulating the relaxation process of the glassy state is considered. The characteristic activation energy for this process decreases with temperature.

1. Introduction

The problem of the glassy state may be tackled from several directions, most interesting among which would seem to be the two outlined below.

First, the glassy state may be taken as it is and its properties studied without trying to go into the problem of glass formation. It is by now well established that all glasses contain a certain amount of the double-well potentials (DWP). This means that there are entities (atoms or groups of atoms) that can occupy at least two positions separated by a potential barrier. Transitions between these positions play the dominant role in many kinetic phenomena observed in glasses (see, e.g., the collection of reviews edited by Phillips (1981)).

The DWPs are believed to give rise to structural defects (SD), proposed by Anderson and Bömmel (1955) in order to describe kinetic phenomena in glasses at relatively high temperatures (above 10–20 K). At low temperatures (below 10 K) these phenomena are connected with the two-level systems (TLS) proposed by Phillips (1972) and Anderson *et al* (1972). The transitions in the SDs occur because of the thermal activation, while in the TLSS the most important role is played by tunnelling. (That is why they are often also called tunnelling modes.) A more elaborate theory of the tunnelling processes at relatively high temperatures (above 10–20 K) is presented in the Fleurov and Trakhtenberg (1986).

An intriguing question is the physical nature of the DWPs. Several models are now proposed (see, e.g., Phillips 1981, Cohen and Grest 1980). A simple model for the stretched Si–O–Si bond was considered in several papers (Vukčević 1972, Fowler and Edwards 1980, Fleurov *et al* 1985). A more complicated approach is presented by Chen *et al* (1987).

The Si–O–Si model may be considered as a useful toy-model that allows one to investigate various situations and derive important consequences that can hold also in more general cases. Karpov *et al* (1982, 1983) (see also a review by Klinger (1983)) proposed treating the DWPs in glasses by using a catastrophe-theory approach. (A description of basic catastrophe theory can be found in Gilmore's book (1981).) The idea that the DWPs (or more generally, anharmonic modes) are catastrophes of the potential energy of the solid created a new understanding of low-frequency excitations in glasses. This approach will be used below, although in a somewhat modified form.

The second direction from which to approach the theory of glasses that we would like to distinguish is to endeavour to understand the glassification process and the problem of the stability of glasses. From the 'liquid side' of the glass transition this problem is addressed by Leutheusser (1984) (another version is proposed by Jacobs (1987)). It is shown that a non-linear interaction between the density fluctuations of the liquid can result in an arrest of the diffusion and, hence, glassification. A percolation approach to the same problem is developed by Cohen and Grest (1979). As for the structure of the phase space of the glass, an interesting paper by Jäckle (1981) should be mentioned. He considers a system in which the ergodic hypothesis is broken down and calculates the residual entropy of the glass.

A gap between these two directions may be seen. However, there are reasons to believe that one can find a link between the low-temperature properties of glasses and the glassification process that proceeds at rather high temperatures. The DWPs are understood to be a consequence of the degeneracy of the metastable glassy state created at the melting temperature (see, e.g., the discussions of Cohen and Grest (1980), Fleurov and Trakhtenberg (1986)). There are also some experimental indications for such a link. According to an interesting experimental finding of Reynolds (1979, 1980), Raychadhuri and Pohl (1981), and Reichert *et al* (1986), the density of the TLSS measured at low temperatures is a function of the glassification temperature T_g .

The problem of the appearance of the DWPs and their possible role in the stability of glasses will be addressed. The DWPs will be treated by means of the catastrophe theory (introduced in glasses by Karpov *et al* (1982, 1983)), which allows one to separate the coordinate of a local anharmonic degree of freedom, leaving other degrees of freedom harmonic. However, some of these harmonic degrees of freedom may be strongly coupled with the DWPs. A feedback mechanism caused by this coupling may result in a conversion of one (or several) harmonic modes into anharmonic ones.

This is how one arrives at a hypothesis of a hierarchy of anharmonic modes in which the anharmonic modes of the n th rank are induced by the anharmonic modes of the $(n - 1)$ th rank. On the other hand the anharmonic modes appear to be responsible for the stability of the n th rank anharmonic modes. Therefore, the anharmonic modes (DWPs, in particular) turn out to be not only an inherent property of the glass but also to provide a mechanism for ensuring the metastability of the glass. An example of a simple hierarchy containing only two ranks will be considered in more detail.

2. Harmonic and anharmonic modes in glasses

In this section the vibration spectrum of a disordered solid is considered. Contrary to that which pertains to a crystal, whose spectrum can be represented as a set of harmonic

vibrations (phonons), the spectrum of a disordered solid is distorted and contains a lot of anharmonic modes (AM)—in particular, DWPs. The consideration to be presented in the next two sections is based mainly on the results of Karpov *et al* (1982, 1983). However, some important differences will be emphasised.

In order to find the spectrum of the vibrations in the disordered solid at zero temperature ($T = 0$) one has first to calculate its total energy $U(\{R_i^\alpha\})$. It is the sum of all the interactions between the atoms constituting the solid. $\{R_i^\alpha\}$ is the set of the coordinates of these atoms. It represents the configuration space \mathbb{R} of the system; i is the number of the atom and α represents the Cartesian coordinate.

The equilibrium positions of atoms are determined by the equation

$$\partial U(\{R_i^\alpha\})/\partial R_i^\beta = 0. \quad (1)$$

There is at least one point in the configuration space \mathbb{R} where the equations (1) are satisfied and the energy $U(\{R_i^\alpha\})$ achieves its absolute minimum. It corresponds to a certain crystalline structure. However, the existence of metastable glassy states implies that there are additional solutions corresponding to local minima of the energy.

The vibration spectrum of the system in the vicinity of the absolute minimum is determined by the eigenvalues of the force matrix

$$\text{Det}(\partial^2 U/\partial R_i^\alpha \partial R_j^\beta - M_i \omega^2 \delta_{ij} \delta_{\alpha\beta}) = 0 \quad (2)$$

where M_i is the mass of the i th atom. All the solutions of equation (2) are certainly positive ($\omega^2 > 0$). The same holds for any local minimum. The number of solutions is $3N$, where N is the number of the atoms in the sample.

Two neighbouring minima are now considered. They are connected by a trajectory in the configuration space \mathbb{R} that passes at least once a saddle point of the energy $U(\{R_i^\alpha\})$. Equation (1) also holds at this saddle point, while equation (2) at this point has at least one negative eigenvalue.

The value of the total energy at this saddle point as compared to the energy at the minima determines the height of the potential barrier separating these two minima. The system passes with a certain probability from one minimum to another along this trajectory over the saddle point (thermal activation) or under it (tunnelling). This sort of motion corresponds, respectively, to either classical or quantum-mechanical motion of a small group of atoms.

Now one may consider the motion along this trajectory as a specific degree of freedom and arrive at the idea of the double-well potentials that can give rise either to TLSS or to SDs (see the discussions in Fleurov and Trakhtenberg (1986), Goldanskii *et al* (1989)). Since this trajectory is a single-parameter curve, one can transform the set of coordinates $\{R_i^\alpha\}$ diffeomorphically so as to distinguish the coordinate x_1 corresponding to the motion along the trajectory

$$\{R_i^\alpha\} \Rightarrow x_1, \{R_i^{(1)}\}. \quad (3)$$

The number of degrees of freedom in the set $\{R_i^{(1)}\}$ is $3N - 1$.

The energy of the system is a function $U(x_1, \{R_i^{(1)}\})$ of the transformed coordinates (3) and properties of these functions are studied. The splitting lemma and Thome's theorem of the catastrophe theory (see, e.g., Gilmore (1981)) enable one to represent this function in the form

$$U(x_1, \{R_i^{(1)}\}) = U^{(0)}(\{R_i^{(1)}\}) + A_1 f(x_1) \quad (4)$$

$$f_1(x_1) = \frac{1}{4}x_1^4 + \frac{1}{3}t^{(3)}x_1^3 + \frac{1}{2}t^{(2)}x_1^2 + t^{(1)}x_1 \quad (5)$$

where the parameters, $t^{(1)}$, $t^{(2)}$, and $t^{(3)}$ depend on the coordinates $\{R_j^{(1)}\}$. The parameter A_1 is an energy of the atomic order, while the other parameters are dimensionless. The set $\{R_j^{(1)}\}$ makes the control-variable space $\mathbb{R}^{(1)}$ for the A_{+3} type catastrophe characterised by the state variable x_1 . The latter is supposed to be dimensionless and measured in the interatomic spacings, a , i.e., $x_1 = (R_1 - R_1^{(0)})/a$. $R_1^{(0)}$ is a reference point. Generally one has to distinguish many anharmonic coordinates of the type x_1 . However, it is assumed that these do not interact with each other. Therefore one can deal with only one anharmonic coordinate in the representations (4), (5).

This holds best of all in the vicinity of a non-Morse critical point where all three derivatives of $f_1(x_1)$ over x_1 vanish:

$$t^{(3)}(\{R_j^{(1)}\}) = t^{(2)}(\{R_j^{(1)}\}) = t^{(1)}(\{R_j^{(1)}\}) = 0. \quad (6)$$

Equations (6) hold in a subspace $\mathbb{R}_c^{(1)}$ of the control variable space $\mathbb{R}^{(1)}$, which will be denoted as being below critical region.

Now there are two problems to be discussed. First, one may just assume without any additional explanation that the system is stabilised close to the critical region $\mathbb{R}_c^{(1)}$ and consider the properties of the anharmonic mode $f_1(x_1)$. Therefore, one assumes that the function $U^{(0)}(\{R_j^{(1)}\})$ has (quite by chance) a local minimum near the critical region, i.e.

$$\partial U^{(0)}/\partial R_j^{(1)} = 0 \quad (7)$$

for $\{R_j^{(1)}\}$ close to $\mathbb{R}_c^{(1)}$. The harmonic part of the vibration spectrum is determined by the equation

$$\text{Det}(\partial^2 U^{(0)}/\partial R_j^1 \partial R_i^1 - \tilde{M}_i \omega^2 \delta_{ij}) = 0 \quad (8)$$

where \tilde{M}_i is the reduced mass corresponding to the motion along the coordinate $R_i^{(1)}$. The number of the coordinates in equation (8) is $3N - 1$, compared with equation (2), which contains $3N$ coordinates. This first problem will be discussed in the § 3 of the present paper.

Secondly, one may ask the question whether there are any physical reasons for the system to have a local minimum just near the critical region $\mathbb{R}_c^{(1)}$? We shall see below in § 5 that these reasons may come from a strong interaction of the AM $f_1(x_1)$ with one (or several) harmonic mode(s) (8). Then the equation determining the local minimum becomes more complicated than (7).

3. Anharmonic modes

Properties of the AM $f_1(x_1)$ are considered assuming that the system is localised in the control-variable space $\mathbb{R}^{(1)}$ in the vicinity of the critical region $\mathbb{R}_c^{(1)}$. One may transform the function (5) by shifting the reference point,

$$x_1 \Rightarrow x_1 - b. \quad (9)$$

The constant b may be chosen in such a way as to eliminate one of the three lower order terms in (5). For example, the cubic term is eliminated if

$$b = \frac{1}{3}t^{(3)}. \quad (10)$$

The linear term can be also eliminated if b satisfies the equation

$$b^3 - t^{(3)}b^2 + t^{(2)}b - t^{(1)} = 0. \quad (11)$$

The elimination of the quadratic term, which can be carried out in a similar way, will not be considered here.

The transformation (10) generates the unambiguous canonical form of the A_{+3} type catastrophe

$$f_1(x_1) = \frac{1}{4}x_1^4 + \frac{1}{2}\eta_1x_1^2 + t_1x_1 \tag{12}$$

to be used below, where

$$\eta_1 = \frac{1}{2}t^{(2)} - \frac{1}{6}t^{(3)2} \quad t_1 = \frac{2}{27}t^{(3)3} + \frac{1}{3}t^{(2)}t^{(3)} - t^{(1)}.$$

On the other hand, the transformation (11) is not necessarily unambiguous. If equation (11) has three real solutions then the catastrophe term

$$f_1(x_1) = \frac{1}{4}x_1^4 + \frac{1}{3}\bar{t}_1x_1^3 + \frac{1}{2}\bar{\eta}_1x_1^2 \tag{13}$$

may have three possible sets of real coefficients \bar{t}_1 and $\bar{\eta}_1$. It is quite clear that these three sets correspond to three different mathematical descriptions of the same physical object. Really, choosing $f_1(x_1)$ in the form (13), the first derivative df_1/dx_1 is always zero at $x_1 = 0$. Three real solutions of equation (11) imply that the function $f_1(x_1)$ describes a double-well curve. Such a curve has three points (one maximum and two minima) where the condition $df_1/dx_1 = 0$ holds. Three sets of the parameters \bar{t}_1 and $\bar{\eta}_1$ correspond to three possible choices of the reference point: $\bar{\eta}_1 < 0$ corresponds to the maximum and $\bar{\eta}_1 > 0$ corresponds to one of the minima.

Karpov *et al* (1982, 1983) (see also Klinger, 1983, 1985, 1987) considered two types of symmetric DWP. The type I DWP with $\bar{\eta}_1 < 0$ and $\bar{t}_1 = 0$ corresponded to the reference point in the maximum of the function $f_1(x_1)$, while the type II DWP with $\bar{\eta}_1 > 0$ and $\bar{t}_1^2 = \frac{2}{3}\bar{\eta}_1$ corresponded to the reference point in one of the minima. The shift

$$x_1 \Rightarrow x_1 \pm \sqrt{-\bar{\eta}_1}$$

transforms the type I into the type II DWP. The above discussion proves that these two types of DWP are merely different mathematical representations of the same physical entity and hence they are *identical*.

The function $f_1(x_1)$ of the form (12) is studied. It describes either a DWP or an anharmonic single-well potential (SWP). The extrema of the function $f_1(x_1)$ are determined by the equation

$$df_1/dx_1 = x_1^3 + \eta_1x_1 + t_1 = 0. \tag{14}$$

The Cartan formula (see, e.g., Korn and Korn (1968)) is applied to analyse this equation. The number of real solutions of the equation (14) is determined by the sign of the quantity

$$Q_1 = (\eta_1/3)^3 + (t_1/2)^2. \tag{15}$$

There are three real solutions if $Q_1 < 0$ and only one solution if $Q_1 \geq 0$. The equation

$$Q_1 = 0 \tag{16}$$

determines the separatrix in the (η_1, t_1) plane separating the SWP and the DWP regions (see figure 1).

The quantity Q_1 can be negative only if the parameter η_1 is negative and there is only one type of the DWP, as emphasised above. Another distinction between the representation (12) and (13) is that equation (13) always produces a DWP for any value of the asymmetry parameter \bar{t}_1 , provided only that $\bar{\eta}_1 < 0$ and even for positive values of $\bar{\eta}_1$ if $\bar{\eta}_1 < \frac{1}{4}\bar{t}_1^2$. A situation we believe to be more reasonable arises when using the

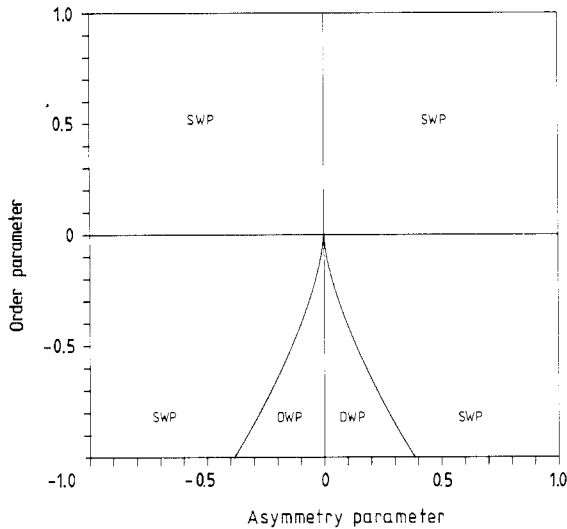


Figure 1. The separatrix in the (η_1, t_1) plane for the A_{+3} catastrophe separating the DWP and SWP regions.

potential (12). Then, increasing the asymmetry parameter t_1 (for $\eta_1 < 0$), a symmetric (at $t_1 = 0$) DWP first becomes asymmetric and then, after crossing the separatrix $Q_1 = 0$ (see figure 1), converts into an SWP. At positive values of η_1 the DWPs do not exist at all.

In the DWP region the three solutions of equation (14) are

$$\begin{aligned}
 x_I &= 2\sqrt{-\eta_1/3} \cos(\alpha/3) \\
 x_{II,III} &= -2\sqrt{-\eta_1/3} \cos(\alpha/3 \mp \pi/3)
 \end{aligned}
 \tag{17}$$

where

$$\alpha = \cos^{-1}[-(t_1/2)(-3/\eta_1)^{3/2}].$$

In the symmetric case, when $t_1 = 0$, one has $\alpha = \pi/2$ and $x_{III} = 0$, $x_I = x_{II} = \sqrt{-\eta_1}$. Therefore, the maximum of the function $f_1(x_i)$ is at the point x_{III} , while two minima are at the points x_I and x_{II} .

When the absolute value $|t_1|$ of the asymmetry parameter increases, two of the three solutions tend to fuse at the separatrix $Q_1 = 0$ (figure 1) and then become complex. If $t_1 < 0$, then these are x_{II} and x_{III} , if $t_1 > 0$ then these are x_I and x_{III} . The DWP converts into an SWP at the separatrix ($Q_1 = 0$) and its minimum lies at the point

$$x_{\min} = \pm 2\sqrt{-\eta_1/3}.
 \tag{18}$$

The sign in the equation (18) is opposite to the sign of the asymmetry parameter t_1 .

The second derivative of the potential represented by the function $f_1(x_1)$ (at $Q_1 = 0$) is

$$d^2f_1/dx_1^2|_{x_1=x_{\min}} = -3\eta_1.
 \tag{19}$$

Thus the frequency of the vibrations of a mass M in such a potential can be estimated as

$$\omega_1^2 = -3A_1\eta_1/Ma^2 \approx -\frac{1}{3}\eta_1\omega_D^2.
 \tag{20}$$

Here we use for the estimates

$$A_1 \approx \hbar^2/ma^2 \quad \hbar\omega_D \approx A_1(m/M)^{1/2}$$

m is the electron mass, ω_D is of the order of the Debye frequency. Therefore, at

the separatrix the asymmetry converts the DWP into an SWP with an anomalously low characteristic frequency (for small values of $|\eta_1|$). If, however, the asymmetry increases further on $[(t_1/2)^2 \gg (|\eta_1|/3)^3]$ then the second derivative becomes

$$d^2f_1/dx_1^2 \cong 3|t_1|^{2/3}$$

and the frequency is

$$\omega_1^2 \approx 3\omega_D^2 |t_1|^{2/3}. \quad (21)$$

Therefore, at large asymmetries ($t_1 \approx 1$) the frequency (21) increases and approaches the characteristic frequencies of the solid.

These observations are in agreement with the experimental findings of Buchenau *et al* (1984, 1986), who measured by neutron scattering a softening of the vibration spectrum in glasses as compared to that of the crystal. It is emphasised that the anharmonic SWPs were first discussed by Karpov and Parshin (1984, 1985) (see also Krivoglaz (1985)). They pointed out the role played by these in phonon scattering at temperatures around 10–20 K and proposed an interpretation of the well known plateau in the thermal conductivity of glasses. However, their analysis uses the representation (13) rather than (12), hence, the asymmetric SWPs appear only if $\tilde{\eta}_1 > \frac{1}{4}t_1^2$, while the representation (12) produces SWPs at a much weaker condition, $Q_1 > 0$.

Equation (12) predicts much higher density of soft SWPs than the equation (13). Really, the soft symmetric DWPs—regardless of the representation—are characterised by the value $\eta_1 \approx 0.1$ (Karpov *et al* 1982, 1983). However, even a small asymmetry, $t_1 \geq 0.1$, in the representation (12) converts these DWPs into SWPs. Therefore, assuming a more-or-less uniform distribution of the values t_1 and η_1 , one can say that the number of the SWPs is at least an order of magnitude higher than that of the DWPs. This estimate can be easily obtained from figure 1, since the area of the DWP triangle is less than 0.1 of the whole area.

4. Strong coupling between anharmonic and harmonic modes

In the above consideration two types of degrees of freedom were distinguished. They correspond to the AM described by the potentials of the type $A_1 f_1(x_1)$ (12) and a set of harmonic modes ((7) and (8)). A mode $f_1(x_1)$ corresponds either to DWP or to an anharmonic soft SWP, while all the remaining modes correspond to harmonic vibrations (phonons) of the glass. This separation is, however, not complete. It is based on the assumption that the anharmonic and harmonic modes do not interact. However, the parameters of the potential $A_1 f_1(x_1)$ depend on the phonon coordinates $\{\tilde{R}_j^{(1)}\}$. This interaction is able to cause changes in the harmonic part of the vibration spectrum because of the feedback mechanism to be considered below.

The complete treatment of the phenomenon assumes a proper account of the quantum character of the motion in the anharmonic potential $A_1 f_1(x_1)$. Here we would not, however, go beyond the framework of the classical approach, which is much simpler than the quantum-mechanical one and nevertheless leads to a quite reasonable qualitative understanding. The classical calculation also makes a good basis for the quantum calculation to be presented elsewhere.

First, the properties of the system described by the potential (4) at zero temperature ($T = 0$) are studied. The particle in the potential $A_1 f_1(x_1)$ is near its minimum (or near the lowest of the two minima in the case of a DWP). The total energy of the system is

$$U(\{R_j^{(1)}\}) = U^{(0)}(\{R_j^{(1)}\}) + U_{\text{anh}}(\{R_j^{(1)}\}) \quad (22)$$

where

$$U_{\text{anh}}(\{R_j^{(1)}\}) = A_1 f_1(x_1)|_{x_1=x_{\min}}. \quad (23)$$

The vicinity of the critical region $\mathbb{R}_c^{(1)}$ is considered. The contribution of the anharmonic mode (23) with $|\eta_1| \ll 1$ can be found for various asymmetries. For example, in the case of a symmetric DWP ($t_1 = 0$) one has

$$U_{\text{anh}}(\{R_j^{(1)}\}) = -\frac{1}{4}A_1\eta_1^2. \quad (24)$$

At the separatrix, $Q_1 = 0$, this contribution becomes

$$U_{\text{anh}}(\{R_j^{(1)}\}) = -\frac{2}{9}A_1\eta_1^2. \quad (25)$$

Far from the separatrix, where $(t_1/2)^2 \gg (-\eta_1/3)^3$,

$$U_{\text{anh}}(\{R_j^{(1)}\}) \simeq -\frac{5}{4}A_1 t_1^4/3. \quad (26)$$

This contribution (measured in atomic units) appears to be small, unless the asymmetry parameter, t_1 , approaches unity.

We are interested, however, not in the absolute value of this contribution but rather in its variation as a function of the harmonic coordinates $\{R_j^{(1)}\}$. The principal role here is played by the 'order' parameter η_1 , which varies very strongly near the critical region. This fact follows, for example, from the model calculation (Fleurov *et al* 1985) where it is shown that varying the coordinate R (the Si–O–Si distance) in the critical region by a value, δR , which is of the order of the zero-point amplitude, u ($u \ll a$) the barrier height of the DWP varies from zero to a value of an atomic order (see also Fleurov and Trakhtenberg 1986, Chen *et al* 1987). This property of the critical (soft) DWP is also connected with the anomalously large value of the deformation potential for the phonon-DWP coupling (Karpov *et al* 1982, 1983).

A coordinate $x_2 = (R_2 - R_2^{(0)})$ is distinguished where $R_2^{(0)}$ is a reference point. It is also assumed for the sake of simplicity that only the coordinate x_2 in the control variable space $\mathbb{R}^{(1)}$ is strongly coupled with the AM, i.e. the inequality

$$d|\eta_1|/dx_2 \simeq a/u \gg 1 \quad (27)$$

holds for this in the nearest vicinity of the critical region. It is also reasonable to believe that the parameter t_1 does not depend strongly on any coordinate from the space $\mathbb{R}^{(1)}$, i.e.

$$(a/|t_1|)(\partial|t_1|/\partial R_j^{(1)}) \simeq 1 \quad (28)$$

for all $R_j^{(1)}$. It is also emphasised that the coordinate x_2 does not necessarily coincide with one of the coordinates of the set $\{R_j^{(1)}\}$. It is rather extinguished from this set by a new diffeomorphic transformation (cf (3)).

Now the question formulated in § 2 may be addressed: is the metastability of the system near the critical region $\mathbb{R}_c^{(1)}$ just a random event or are there some physical reasons for it? To answer this question one has to analyse the behaviour of the energy (4) (or (22)) near the critical region, carefully taking into account the contribution of the anharmonic mode, (24)–(26), to this energy.

The first derivative of the potential (22) is

$$\partial U/\partial x_2 = \partial U^{(0)}/\partial x_2 + \frac{1}{2}A_1 x_{\min}^2 d\eta_1/dx_2 \quad (29)$$

where the derivatives (28) are neglected and x_{\min} is the position of the lowest minimum of the function $f_1(x_1)$. x_{\min}^2 takes three values:

$$x_{\min}^2 = -\eta_1 \quad x_{\min}^2 = -\frac{1}{3}\eta_1 \quad x_{\min}^2 \approx |t_1|^{2/3} - \frac{2}{3}\eta_1 \quad (30)$$

for the three cases (24)–(26), respectively ($\eta_2 < 0$).

The factor x_{\min}^2 is positive and usually small since η_1 and t_1 are generally small. However, the derivative $d\eta_1/dx_2$ is negative and its absolute value is large (see (27)). Therefore, the second term in equation (29) representing the reaction of the soft anharmonic mode to the local distortion of the matter is *negative* and of *atomic order*. On the other hand, the first positive term in equation (29) gives the local reaction of the environment, which is also of atomic order. It is clear that for the large enough values of the derivative (27) one can always find a value R_2 close to its critical value ($\eta_1(R_{2c}), \ll 1$) where two terms in the equation (29) compensate each other and

$$\partial U/\partial x_2 = 0. \quad (31)$$

It is convenient to choose the reference point $R_2^{(0)}$ close to the critical point R_{2c} and to deal with small values of x_2 .

The minimisation of the energy (4) with respect to all the other coordinates from the space $\mathbb{R}^{(1)}$ that are not coupled with the AM can be carried out independently, so that equation (7) holds for these. Therefore, one can say that a sufficiently strong coupling of the AM with at least one variable x_2 may lead to an extremum of the total energy of the system close to the critical region $\mathbb{R}_c^{(1)}$.

In order to understand what type of extremum it is, one has to find the second derivative of the energy (22), i.e. the local compressibility of the matter

$$\partial^2 U/\partial x_2^2 = \partial^2 U^{(0)}/\partial x_2^2 + \frac{1}{2}A (d\eta_1/dx_2)(dx_{\min}^2/dx_2). \quad (32)$$

For above three cases (24)–(26) one has

$$\begin{aligned} dx_{\min}^2/dx_2 &= -d\eta_1/dx_2 & dx_{\min}^2/dx_2 &= -\frac{1}{3} d\eta_1/dx_2 \\ dx_{\min}^2/dx_2 &= -\frac{2}{3} d\eta_1/dx_2. \end{aligned} \quad (33)$$

It follows from the inequality (27) and equations (33) that the soft AM gives a large negative contribution to the second derivative of the energy making the latter also negative near the critical region

$$\partial^2 U/\partial x_2^2 < 1.$$

Therefore, the extremum is a 1-saddle point and the motion along the coordinate x_2 corresponds to the motion along the steepest descent path across the saddle. The situation would certainly become more complicated if more than one coordinate were strongly coupled with the anharmonic mode. Then a multidimensional consideration would be necessary.

A ‘negative local compressibility’ means a sort of local instability when the system tends to be distorted in such a way as to leave this saddle point in the energy relief. Therefore, we have again a double-well potential depending on the coordinate x_2 .

5. Anharmonic modes at finite temperatures

Now the feedback interaction between anharmonic and harmonic modes is examined at finite temperatures assuming, as before, a classical character of the motion. The Gibbs free energy, $G(\{R_j\})$, is to be considered instead of the energy $U(\{R_j\})$. Near the critical region it can be represented in the form

$$G(\{R_j^{(1)}\}) = G^{(0)}(\{R_j^{(1)}\}) - kT \ln Z \quad (34)$$

where

$$Z = B \int dx_1 \exp\{-\beta A_1 f(x_1)\} \quad (35)$$

$\beta = 1/kT$, k is the Boltzmann constant; the factor B in the equation (35) for the partition function Z stands for the contribution of the kinetic energy of the motion in the potential $A_1 f_1(x_1)$ and for the other degrees of freedom irrelevant to our problem. $G^{(0)}(\{R_j^{(1)}\})$ is the part of the free energy which does not depend on the 'anharmonic' coordinate x_1 . It is again assumed that there is a coordinate, x_2 , strongly coupled with the AM, and the behaviour of the free energy (35) is studied in the vicinity of the critical point R_{2c} :

$$\partial G / \partial x_2 = \partial G^{(0)} / \partial x_2 - \frac{1}{2} A_1 (d|\eta_1|/dx_2) \langle x_1^2 \rangle \quad (36)$$

and

$$\partial^2 G / \partial x_2^2 = \partial^2 G^{(0)} / \partial x_2^2 - \frac{1}{4} \beta A_1 (d\eta_1/dx_2)^2 (\langle x_1^4 \rangle - \langle x_1^2 \rangle^2) \quad (37)$$

where

$$\langle x_1^n \rangle = \int dx_1 x_1^n \exp(-\beta A_1 f(x_1)) / \int dx_1 \exp(-\beta A_1 f(x_1)). \quad (38)$$

Deriving equations (36)–(38), use is made of assumptions (27) and (28). It is also emphasised that, applying the functional integral representation for the partition function (35), the same equations (36) and (37) can be obtained where the classical averaging (38) should be, however, substituted by the quantum averaging.

The integrals (38) can be calculated at low temperatures using the steepest descent technique. For this one has to find the minima, x_I and x_{II} , of the function $f(x_1)$ as well as its values, f_I and f_{II} , and second derivatives, f_I'' and f_{II}'' , at these points (see § 3). Then

$$\begin{aligned} \langle x_1^2 \rangle = & \{(f_{II}'')^{1/2} (x_I^2 + 1/\beta A_1 f_I'') + (f_{II}'')^{1/2} [x_{II}^2 + 1/\beta A_1 f_{II}''] \exp[-\beta A_1 (f_{II} - f_I)]\} / \{(f_{II}'')^{1/2} \\ & + (f_I'') \exp[-\beta A_1 (f_{II} - f_I)]\} \end{aligned} \quad (39)$$

and

$$\begin{aligned} \langle x_1^4 \rangle - \langle x_1^2 \rangle^2 = & \{[4x_I^2/\beta A_1 f_I'' + 2/(\beta A_1 f_I'')^2] f_{II}'' \\ & + [4x_I^2/\beta A_1 f_I'' + 2/(\beta A_1 f_I'')^2] f_I'' \exp[-2\beta A_1 (f_{II} - f_I)] \\ & + (f_I'' f_{II}'')^{1/2} \exp[-\beta A_1 (f_{II} - f_I)] [(x_I^2 - x_{II}^2)^2 + (2x_I^2/\beta A_1) (3/f_{II}'' - 1/f_I)] \\ & + [1/(\beta A_1)^2] (3/f_I''^2 + 3/f_{II}''^2 - 1/f_I'' f_{II}'')\} \\ & \times [(f_{II}'')^{1/2} + (f_I'') \exp[-\beta A_1 (f_{II} - f_I)]]^{-2}. \end{aligned} \quad (40)$$

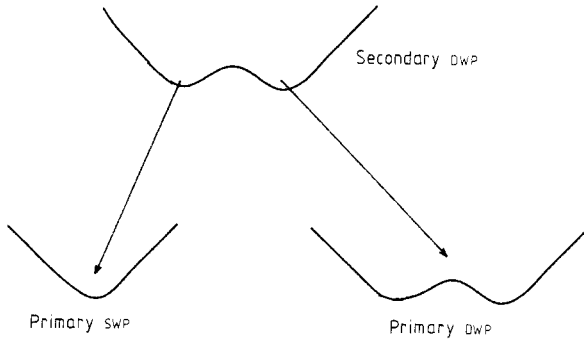


Figure 2. A scheme illustrating how the shape of the primary AM depends on the state of the secondary AM. Both modes are assumed to be double-well potentials.

The equations (39) and (40) hold if the anharmonic mode is a DWP: otherwise it has only one minimum and

$$\langle x_1^2 \rangle = x_1^2 + 1/\beta A f_1'' \quad \langle x_1^4 \rangle - \langle x_1^2 \rangle^2 = 4x_1^2/\beta A_1 f_1'' + 2/(\beta A_1 f_1'')^2. \quad (41)$$

Equations (41) also result from the equations (39) and (40) for a DWP in the limit $\beta A_1 f_{1,II}'' \ll 1$.

The third derivative of the free energy G can be also calculated:

$$\partial^3 G / \partial x_1^3 = \partial^3 G^{(0)} / \partial x_1^3 + \frac{1}{8} \beta^2 A_1^3 (d\eta_1/dx_2)^3 [\langle x_1^6 \rangle - 3\langle x_1^4 \rangle \langle x_1^2 \rangle + 2\langle x_1^2 \rangle^3]. \quad (42)$$

The cumulant $\langle x_1^6 \rangle - 3\langle x_1^4 \rangle \langle x_1^2 \rangle + 2\langle x_1^2 \rangle^3$ is zero in approximation (41). However, it gives a contribution to the asymmetry of the AM at finite temperatures.

6. Two-rank hierarchy

The above consideration leads us to the following conclusions. In order to create a soft AM with the coordinate x_1 (state variable) the system is to be distorted along another coordinate x_2 (control variable) until the critical value of the latter is achieved. A sufficiently strong feedback interaction between these two degrees of freedom may result in a saddle point in the potential relief for the motion along the coordinate x_2 . This saddle point corresponds in fact to the potential barrier separating the subcritical ($\eta_1(x_2) > 0$) and supercritical ($\eta_1(x_2) < 0$) regions. A DWP exists only in the supercritical region. If only two coupled modes are considered, then the system in the subcritical region is free to relax back to the crystalline state.

A system of two coupled AMS arranged in a hierarchical order is discussed below. The one with the coordinate x_1 is called the primary AM while the one with the coordinate x_2 is the secondary AM. The latter can be also described as an A_{+3} catastrophe whose potential is represented in the form

$$U(\{R^{(1)}\}) = U^{(1)}(\{R^{(2)}\}) + A_2 (\frac{1}{4} x_2^4 + \frac{1}{2} \eta_2 x_2^2 + t_2 x_2) \quad (43)$$

where η_2 and t_2 depend on the variables $\{R^{(2)}\}$ transversal to R_1 and R_2 .

The motion in the secondary AM is associated with a larger mass and is slower than in the primary AM. On changing the coordinate x_2 , the potential of the primary AM is changed (see figure 2). The transition from the right-hand well to the left-hand well in

the secondary DWP is accompanied by a conversion of the primary DWP into a normal single-well potential, which leads to a disappearance of the glassy feature. It is also clear that the barrier in the secondary DWP ensures its metastability. Studying the transitions in the secondary DWP one can obtain information about the relaxation of the glassy features.

The 'order' parameter, η_2 , for the second rank DWP is determined by the 'local compressibility coefficient', k , of the medium. It is given by the equation (37) and contains two terms. The first term

$$k_0 = \partial^2 G_2^{(0)} / \partial x_2^2$$

represents the reaction of the environment. Its temperature dependence will be neglected below. The second, negative, term corresponds to the reaction of the first-rank AM. At $T = 0$ it is

$$k_{\text{DWP}}(0) = -A_1(x_1^2/f_1'')(d\eta_1/dx_2)^2. \quad (44)$$

The second rank DWP appears if

$$\eta_2 = k_0 + k_{\text{DWP}}(T) < 0. \quad (45)$$

Then the potential barrier for the motion along the coordinate x_2 (the asymmetry being neglected, $t_2 = 0$) is estimated as

$$V_b \cong \frac{1}{4}A_2\eta_2^2(T). \quad (46)$$

The absolute value $|\eta_2(T)|$ decreases with the increasing temperature and may become zero at a temperature T_0 determined by the equation

$$\eta_2(T_0) = k_0 + k_{\text{DWP}}(T_0) = 0. \quad (47)$$

Figures 3–5 show the temperature dependence of the value

$$K(T) = 2k_{\text{DWP}}(T)/[d\eta_1/dx_2]^2 = \frac{1}{2}\beta A_1(\langle x_1^4 \rangle - \langle x_1^2 \rangle^2)$$

which determines the temperature dependence of the AM contribution to the local compressibility of the matter. This quantity is calculated numerically for various values of the order parameter η_1 and the asymmetry parameter t_1 using equation (38).

Figure 3 shows that the largest contribution comes from nearly symmetric ($t_1 = 0$) DWP at low temperatures. The asymmetric AMs make an essentially weaker contribution, and for both of them the value of $K(T)$ decreases with temperature. The contribution of the AMs with the positive value of the order parameter, $\eta_1 = 0.1$, is depicted in figure 4. The value of $K(T)$ for the symmetric AM is negligible at low temperatures and increases with temperature remaining, however, small. The asymmetric AMs both for positive and negative order parameters, η_1 , behave more or less similarly. Figure 5 shows the temperature dependence of the value $K(T)$ for a larger negative value of the order parameter, $\eta_1 = -0.3$. Here one cannot find essential changes compared with figure 3.

The strongest effect, i.e. the largest negative value of the DWP compressibility $k_{\text{DWP}}(T)$, is observed at low temperatures for nearly symmetric DWPs ($\eta_1 < 0$, $Q_1 < 0$, see figure 3). Therefore, these contribute mainly to the creation of the secondary AM.

The barrier in the second-rank DWP decreases with temperature and may even disappear above a certain temperature T_0 ($\eta_2(T > T_0) > 0$). Then our model system is free to relax to the crystalline state, i.e. the hierarchy containing only two levels is *absolutely unstable* at $T > T_0$. This process simulates, in a rather simplified manner, the

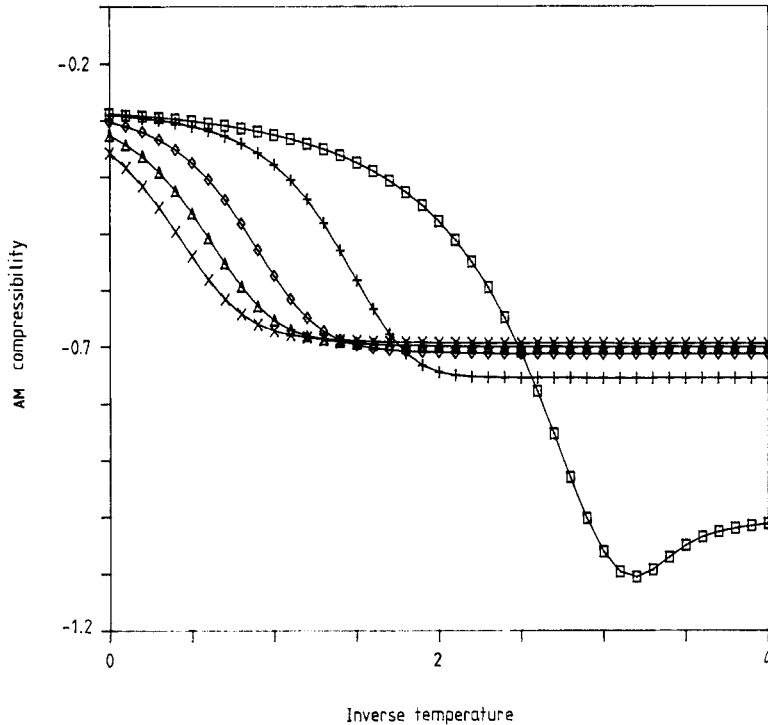


Figure 3. Temperature dependence of the function $K(T)$ determining the contribution of the AM with $\eta_1 = -1$ and several values of the asymmetry parameter, t_1 , to the local compressibility as a function of the inverse temperature in the units βA_1 . \square , $t = 0$; $+$, $t = 0.1$; \diamond , $t = 0.3$; \triangle , $t = 0.5$; \times , $t = 0.7$.

real crystallisation of the glass. At temperatures, $T < T_0$, the 'crystallisation' occurs because of the thermal activation over the barrier (46) and the characteristic relaxation time of the process is

$$1/\tau = (1/\tau^{(0)}) \exp\{-V_b(T)/KT\} \quad (48)$$

where the activation energy $V_b(T)$ depends on the temperature and becomes zero at $T = T_0^\dagger$. The relaxation rate in such a system deviates from the standard Arrhenius law. This deviation becomes especially strong at high temperatures when $V_b(T)$ essentially decrease.

7. Discussion

The model of a two-rank hierarchy discussed above is far from being a realistic model for the glass-crystal transition. Nevertheless it reflects some essential properties of the process. In order to make the model more realistic one has to consider a hierarchy containing a large number of levels. The mechanism considered above presents, in

[†] It must be emphasised that this temperature (if any) should not be considered as a direct analogue of the glassification temperature. The two-rank hierarchy is too primitive to describe a real glassification process and a multirank hierarchy is necessary. (See the next section.)

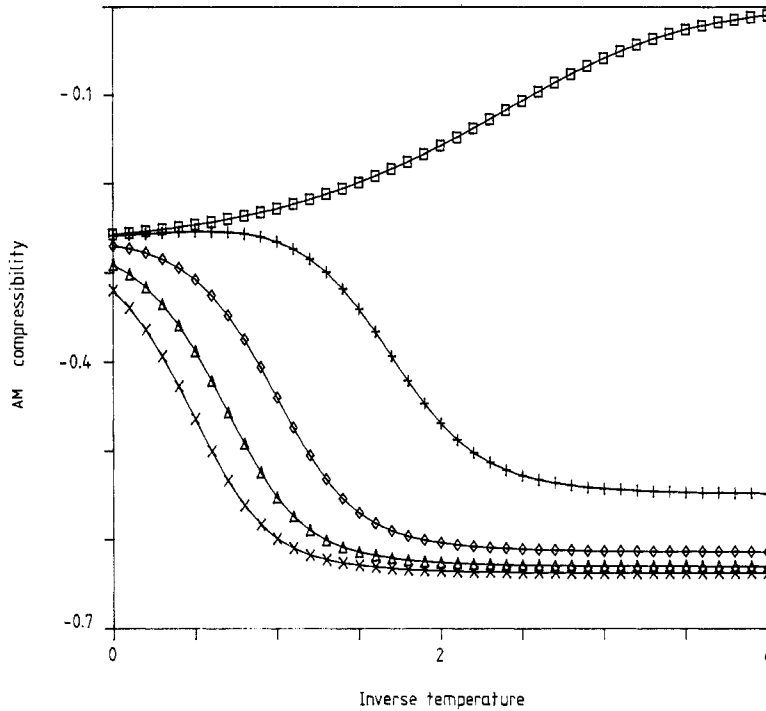


Figure 4. Temperature dependence of the function $K(T)$ determining the contribution of the AM with $\eta_1 = 1$ and several values of the asymmetry parameter, t_1 , to the local compressibility as a function of the inverse temperature in the units βA_1 . \square , $t = 0$; $+$, $t = 0.1$; \diamond , $t = 0.3$; \triangle , $t = 0.5$; \times , $t = 0.7$.

principle, such a possibility. Really, the potential (43) for the secondary AM may be treated in the same fashion as was the potential (12) for the primary AM. Then, if the second-rank AM interacts strongly with a harmonic mode, this harmonic mode would be converted into a third rank AM by the feedback mechanism described above.

The feedback mechanism leads to a hierarchy of the AMs which have two important features. First, each n th rank AM induces an appearance of an $(n + 1)$ th-rank AM. That is how the hierarchy is constructed. Second, each $(n + 1)$ th-rank AM creates a well (or wells) for the $(n + 1)$ th-rank control variable near the corresponding critical value. This ensures a metastability of the n th-rank AM.

It is now clearly realised that the hierarchy may provide a means of understanding the glass-liquid or glass-crystal transitions. Palmer *et al* (1984) demonstrated what possibilities are presented by the idea of a hierarchy of relaxations in glasses. In particular, they showed how such well known empirical laws as the Kohlrausch and Vogel-Fulcher laws follow from it. Pietronero (1986) considered a hierarchy of DWPs in which higher-rank DWPs controlled the relaxations of the corresponding lower-rank DWPs. Reichert and Schilling (1985) considered an exactly solvable one-dimensional model in which a hierarchy of the DWPs involving an increasing (with rank) number of atoms appeared. Our hypothesis of a hierarchy in which the same mechanism is responsible for both its appearance and its metastability seems to be very appealing and we hope to develop it further in future publications.

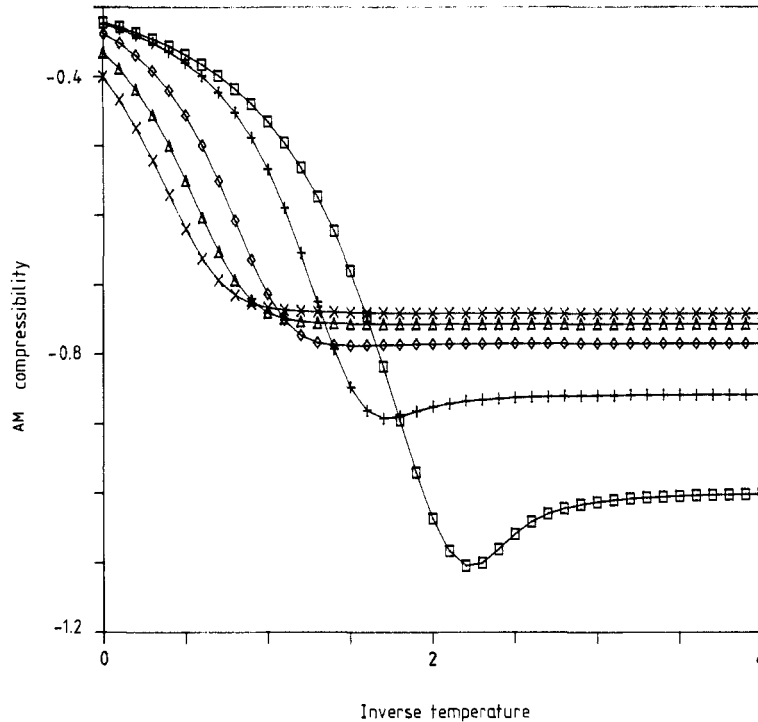


Figure 5. Temperature dependence of the function $K(T)$ determining the contribution of the AM with $\eta_1 = -0.3$ and several values of the asymmetry parameter, t_1 , to the local compressibility as a function of the inverse temperature in the units βA_1 . \square , $t = 0$; $+$, $t = 0.1$; \diamond , $t = 0.3$; \triangle , $t = 0.5$; \times , $t = 0.7$.

In its present form (see above) the model seems to be more applicable to the interpretation of the experimental findings of Kolesnikov *et al* (1988). Their Al-Ge samples are put under pressure and then rapidly cooled down to the liquid nitrogen temperature. The pressure induces an appearance of a soft AM that is revealed by neutron scattering. At low temperatures these glassy features become metastable. However, at room temperature they relax out within a day.

One may assume that the pressure induces local distortions which lead to an appearance of primary AMS. They are observed by neutron scattering to be soft modes. The feedback mechanism as described above results in the appearance of secondary AMS that are responsible for the low-temperature metastability of the primary AMS. The relaxation of these glassy features at room temperature is also qualitatively understood within this model. A quantitative treatment of this phenomenon has not yet been carried out. It is connected, in particular, with a lack of detailed experimental data on the time and temperature dependence of the kinetics of the process. However we believe that experiments will be done in the near future which will throw more light onto this interesting phenomenon.

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