Anharmonic soft modes in glasses

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The anharmonic localized soft modes in glasses and undercooled liquids found in recent numerical work are explained in terms of two stable structural minima of the small core of the mode, frozen on the low-lying saddle point of the core potential by the positive restoring forces of the surroundings, with a resulting restoring force of the whole mode close to zero. An example is the gliding triangle transition of six atoms from an octahedron to two edge-sharing tetrahedra proposed earlier for simple liquids, which has the participation ratio and the fourth order potential term of the numerical data. The description is extended to vitreous silica, where the structural transformation of the core involves coupled rotations of corner-connected SiO$_4$-tetrahedra and one can compare to soft potential fits of the low temperature anomalies.

The low temperature properties of glasses around 1 K differ dramatically from those of simple crystals [1]. Below 1 K, two level states, coupling strongly to external shear and compression, dominate the heat capacity and the thermal conductivity [1, 2]. Above 1 K, the vibrational spectrum shows a boson peak on top of the Debye density of sound waves [1, 3].

There are successful empirical models like the tunneling model [4] and its extension to include low barrier relaxations and soft vibrations, the soft potential model [5–8]. But what is tunneling or vibrating there, and why it couples so strongly to shear and compression, remains an open question. It is clear that these soft modes freeze in at the glass transition, when the sample is no longer able to jump freely from one stable structure to the next. From this point of view, an understanding of the glass transition is essential for the understanding of the low temperature anomalies.

The last three years brought two important new numerical developments. The first was the discovery of localized vibrational soft modes in glasses [9–12] with the vibrational density of states $g(\omega) \propto \omega^4$ (\omega frequency) predicted by the soft potential model [6–8] and exhibiting the strong positive fourth order term in the mode potential [9] which the soft potential model needs for a common description of tunneling states and vibrations. The second was the swap mechanism for simple liquids [13], which enables the numerical cooling of simple liquids down to temperatures which are even lower than the glass temperature of real liquids. The application of the swap mechanism to undercooled liquids revealed the central role of the soft localized modes for the understanding of the mode coupling transition [14].

The present paper focuses on a central unanswered question of both the soft potential model and the numerical findings, namely where the strong positive fourth order term in the soft mode potential comes from. The paper generalizes an earlier Eshelby explanation of the boson peak in metallic glasses [17].

An Eshelby transition is defined [18] as a structural rearrangement of a core region within the glass former which changes the elastic misfit between the core and the surrounding elastic medium. For large cores with large rearrangement barriers, irreversible Eshelby transitions have been considered as a possible mechanism of the highly viscous flow [15, 16]. Here, we focus on the low barrier side, with the smallest possible cores, where the core of the mode can be frozen on top of the barrier between two stable structures by the positive restoring forces from the surroundings. A well-studied example [17] is the gliding triangle transformation from an octahedron to two edge-sharing tetrahedra in simple liquids in Fig. 1.

In this simplest case, the configurational coordinate of the local rearrangement is itself a pure shear strain. The positive restoring forces from the surrounding elastic medium are equal (or very nearly equal, depending on the Poisson ratio [18]) to the negative restoring forces at the maximum of the local energy barrier. This fol-
lows from the Eshelby theory \textsuperscript{[18]} under the assumption that the negative curvature at the local structural energy maximum has the same absolute value as the positive curvature at the two minima. By freezing the gliding triangle in near to its energy maximum, one gets a soft mode.

The gliding triangle transformation is also connected to an old topological problem, namely the closest packing of spheres in three dimensions \textsuperscript{[19]}. Looking at Fig. 1, one realizes that this shear transformation is the one in which an octahedral interstitial hole between six atoms is created or destroyed. A hypothetical purely tetrahedral packing of spheres without octahedral holes would fill a fraction of 0.78 of the space with spheres, but the two closely packed crystal structures, fcc and hcp, fill only a fraction of 0.7408, because there is one octahedral interstitial hole per atom in these two structures, which is obviously necessary for the creation of a periodic structure.

One does not expect well-defined octahedral interstitial holes in a frozen simple liquid, because the gliding triangle can freeze in anywhere between its two energy minima, depending on the shear energy minimum of the surroundings. If it freezes in the middle, it will produce a soft mode with a quadratic potential term close to zero, because inner and outer contributions to the restoring force cancel.

The analysis \textsuperscript{[17]} of the gliding triangle shear transformation to derive the parameters of the tunneling and the soft potential model will be generalized here to cases where the configurational coordinate of the transformation of the region is not a pure strain. Following \textsuperscript{[17]}, we describe the two structural minima of the core by a cosine potential and the outer restoring forces by a quadratic term in the mode coordinate \( y \)

\[
V(y) = v_4 (\cos y - 1 + y^2/2),
\]

where it is already assumed that the zero point of the outside forces coincides with the top of the core barrier and that one has perfect cancellation of the harmonic inside and outside terms, leading to the approximation

\[
V(y) = \frac{v_4}{24} y^4
\]

in the neighborhood of \( y = 0 \). Note that the creation energy of the mode is \( 2v_4 \), the height of the frozen saddle point for the core potential.

The crossover energy \( W \) between tunneling states and vibrations in the soft potential model is the zero point energy in this quartic potential, determined by the equality of potential energy and kinetic confinement energy. To calculate the kinetic confinement energy, one needs to know how many atoms move in the mode.

To characterize the atomic motion, let us consider the potential minima of the core at \( y_{1,2} = \pm \pi \), and denote by \( u_i \) the displacement of atom \( i \) with the atomic mass \( M_i \) between the two minima. For a given \( y \), the atomic displacement \( x_i = y u_i / 2\pi \), so the normal coordinate \( A \) of the mode (defined by the kinetic energy \( A^2/2 \)) is given by

\[
A^2 = \frac{y^2}{4\pi^2} \sum_{i=1}^{N} M_i u_i^2,
\]

where the sum extends over all atoms in the sample. The normal coordinate relates the atomic displacement vector \( \vec{x}_i \) to the normalized eigenvector \( \vec{c}_i \) of the mode

\[
\vec{x}_i = \frac{A}{M_i^{1/2}} \vec{c}_i
\]

where the sum over \( \vec{c}_i^2 \) for all atoms equals one.

According to the definitions of the soft potential model \textsuperscript{[8]}

\[
W = \frac{4\pi^2 \hbar^2}{296 \sum_{i=1}^{N} M_i u_i^2} = \frac{v_4}{24} y_0^4, \tag{5}
\]

where the left part defines \( y_0 \) by the equality of potential energy and kinetic confinement energy and leads to

\[
y_0 = 2^{3/4} 3^{1/4} \frac{W^{1/4}}{v_4^{1/4}}, \tag{6}
\]

and

\[
W = \frac{\pi^{4/3}}{6^{1/3}} \left( \frac{\hbar^2}{\sum_{i=1}^{N} M_i u_i^4} \right)^{2/3} v_4^{1/3}. \tag{7}
\]

For the gliding triangle soft mode of Fig. 1, \( v_4 = 3GV_a/4\pi^2 \) (\( G \) shear modulus, \( V_a \) atomic volume) as shown previously. But the normal mode determination of the previous paper \textsuperscript{[17]} in terms of a continuum approximation needs to be corrected.

Let us express the displacements in units of the atomic radius \( r_a \), where \( 2r_a \) is the nearest neighbor distance. The atomic volume \( V_a = 4\pi r_a^3/3p \), where \( p = 0.637 \) is the random close packing of spheres \textsuperscript{[19]}. The six inner atoms in Fig. 1 move by the distance \( r_a / \sqrt{2} \) between the two structural minima, corresponding to a shear angle of \( 1/\sqrt{2} \). The six atoms occupy a sphere with radius \( r_k = (6/0.637)^{1/3}r_a = 2.11r_a \). Outside, one has to assume a shear decreasing with \( 1/r^2 \), where \( r \) is the distance from the center of the sphere. But it does not start with \( 1/\sqrt{2} \) at \( r_k \), but rather with the additional factor \( r_{act}^2 / r_k^2 \), where \( r_{act} = r_a \sqrt{2} \) is the distance of the six atom cores from the center.

With this factor, the inner and outside kinetic energies are very nearly equal. This implies \( c_i^2 = 1/12 \) for the six core atoms. Calculating the contribution from the outside to the sum over \( c_i^2 \), one finds 0.03, so from the participation ratio the number \( N_p \) of atoms participating in the mode is

\[
N_p = \frac{1}{\sum_{i=1}^{N} (c_i^2)^2} = 14. \tag{8}
\]
For the normal coordinate $A$, the potential close to zero is $\chi_4 A^4$ with

$$\chi_4 = \frac{\pi^2}{32} \frac{G V_a}{M^2 r_a^4}. \tag{9}$$

In the simulation units [8], $G = 14$, $V_a = 1.22$ (so $r_a = 0.57$) and $M = 1$, so $\chi_4 = 49.9$. Fig. 2 compares the calculated gliding triangle values $N_p$ and $\chi_4$ to the numerical results [9,12]. From the comparison, one learns that the gliding triangle values are obtained from them is proportional to $N_p$. The same mean square change of the angle is to be expected perpendicular to the Si-O-Si plane, leading to a root mean square displacement of the oxygen of $\Delta x = 0.64 \text{Å}$ between the two minima.

The restoring force for the harmonic vibration of the oxygen in one of the stable structural minima can be estimated from the frequency $6 \text{meV}$ of the lowest van-Hove singularity in the cristobalite crystal [25], which is essentially an oxygen motion [20] (note that here one should not take the lowest van-Hove singularity of quartz, where the Si-O-Si angle is smaller, and therefore the density is higher than the one in vitreous silica [23,27]). Then the harmonic restoring force constant for one oxygen atom is $D = 0.14 \text{eV/Å}^2$ and the $v_4$ of eq. 9 becomes

$$v_4 = D N_O \frac{\Delta x^2}{4\pi^2}, \tag{10}$$

where $N_O$ is the number of oxygens in the core of the soft mode.

With respect to the normal coordinate of the mode, one obviously needs as many stabilizing Si-O-Si connections outside the core as unstable ones inside to get the restoring force down to zero. Therefore the kinetic energy outside should again equal the one inside, so

$$\sum_{i=1}^{N} M_i u_i^2 = 2N_O M_O \Delta x^2. \tag{11}$$

Both quantities in eqns. 10 and eq. 11 are proportional to $N_O$, so the $W$ of eq. 7 which can be calculated from them is proportional to $N_O^{-1/3}$. Taking the $W/k_B$-value of 3.9 K, which one can determine in three independent ways from the low temperature anomalies of silica [8], one arrives at $N_O = 57$ oxygen atoms, about thirty SiO$_4$-tetrahedra moving in the core.

A cross-check of this calculation can be obtained from the coupling of the soft modes to the sound waves. To
do this, one ascribes the restoring force for the central oxygen displacement $x_{O,in-plane}$ in Fig. 3 to the double force $F$ required to achieve the displacements $\pm w_{ext}$ on the outsides of the two SiO$_4$-tetrahedra. Then the elastic dipole moment is

$$P_{xx} = 2F \frac{4}{3} r_{Si-O},$$

(12)

with a bilinear coupling energy $P_{xx} \epsilon_{xx}$ of the oxygen displacement to a longitudinal distortion in $x$-direction. Averaging over the possible directions of a propagating longitudinal sound wave, one obtains the factor $1/\sqrt{3}$. Summing the squares of $P_{xx}$ for all oxygens in the soft mode to obtain the square of the elastic dipole moment of the whole mode, a straightforward calculation results in $\Lambda_l = 0.3$ eV in the bilinear coupling $\Lambda_l \epsilon_l x$, where $\epsilon_l$ is the longitudinal distortion and $x = y/y_0$ is the normalized soft mode displacement of the soft potential model.

The soft potential fits of silica [3] do not allow to calculate $\Lambda_l$ separately, because they only provide an average coupling to longitudinal and transverse sound waves, expressed in a dimensionless $C = 2.6 \cdot 10^{-4}$. On the other hand, one knows from measurements of tunneling states [28] that, in vitreous silica, $C_l = C_t$. Therefore one can calculate $\Lambda_l$ from

$$C = \frac{P_s \Lambda_l^2}{W \rho v_t^2},$$

(13)

taking the density $P_s$ of soft modes, the density $\rho$ and the sound velocity $v_t$ from [8], resulting in $\Lambda_l = 0.54$ eV, in reasonable agreement with the estimated value.

In addition, the equality of $C_l$ and $C_t$ in silica supports the elastic dipole concept, because for an elastic dipole $\Lambda_l/\Lambda_t = \sqrt{3}$, in close agreement with the sound velocity ratio $v_t/v_s = 1.52$.

From eq. (13), one calculates a creation energy with $2\nu_b/k_B = 1923$ K, a factor of 1.3 larger than the glass temperature $T_g = 1473$ K. The ratio $2\nu_b/k_BT_g$ in silica is markedly lower than the one of 2.67 estimated [17] for the metallic glasses, helping one to understand why the boson peak compared to the Debye density of states is five times higher in silica [3] than in metallic glasses [29].

To conclude, the soft anharmonic localized vibrational and tunneling modes in glasses as well as their strong interaction with the sound waves and the strong positive fourth order term in their mode potential find a natural explanation in terms of the lowest saddle points of the energy landscape, frozen in with a restoring force close to zero by the harmonic restoring forces from the surroundings.

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