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Microscopic Model of Anomalous Low-Frequency Excitations in Inorganic Glasses: Molecular Dynamics Study of BeF_2

Steven A. Brawer
University of California Lawrence Livermore National Laboratory, Livermore, California 94550

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In molecular-dynamics simulations of BeF_2 glass, it is observed that a few percent of the ions are capable of displacements of the order of 1 Å in 10 ps at temperatures lower than 300 K. It is shown that these ions are located at well-defined defect sites in the glass. The activation energy for such motion is between 0.03 and 0.2 eV. Ions making large displacements often return to their starting points after a few picoseconds (periodic motion). It is suggested that such mobile ions are responsible for the low-temperature anomalous properties of glass.

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Many inorganic glasses have anomalous thermal, acoustic, and dielectric properties at temperatures ranging from a few millidegrees to 100 K.[1] The measured anomalies are of two types. In a number of glasses at temperatures above 10 K, including BeF_2 and silica, there is a broad, strong acoustic absorption associated with activated hopping over potential barriers of height a few hundred to about 1000 K.[1,2] At temperatures below a few degrees Kelvin (where vitreous silica has been studied most extensively), the situation is different. There, the specific heat, thermal resistance, and negative thermal expansion are all unusually large and have anomalous temperature dependencies. There is considerable saturable acoustic absorption at all frequencies below 35 GHz. Phenomenologically, the excitations producing these very-low-temperature anomalies are two-level systems (TLS) with energy separations ranging from 0 to at least 35 GHz.[3-6]

The experimental results indicate that an atom, or group of atoms, is somehow loosely bound and so moves about relatively freely, presumably over distances greater than 0.5 Å, encountering potential barriers that are small compared to the activation energy for fluorine diffusion (> 2 eV).[1,3-5] Thus, for instance, TLS[3,4] and activated hopping can both result from some ions in double-well potentials with barrier heights ranging from a few hundred to a few thousand degrees Kelvin.

It is my intention to present a microscopic model of these anomalous excitations for the case of BeF_2 glass. Since, to my knowledge, no very-low-temperature experiments have been performed on BeF_2, this note serves as a prediction that effects similar to those found in SiO_2 will be found in BeF_2 glass. (Computer simulations are more realistic for ionic BeF_2 than for partially covalent SiO_2.)

BeF_2 glass was simulated by the molecular-dynamics (MD) technique.[7] Be^{2+} and F^- ions interact with a Coulomb potential (evaluated as the Ewald sum) and a Born-Mayer (exponential) repulsion. The repulsive parameters are as in Busing.[8] The system consists of 390 ions in a box of length 17.24 Å (density of 1.98 g/cm^3). The Verlet[7] algorithm was used with a time step of 0.002 ps.

The fluid was initially started from random initial conditions at 10 000 K and slowly cooled to a range of temperatures between 33 and 3300 K. For temperatures above 1300 K considerable topological changes in the fluid structure occurred over times greater than 20 ps, computed with use of Brawer's methodology.[9] (A time of 20 ps is a reasonably long computer run.) At temperatures of 1000 K and below, fluids were metastable since relaxation times were so long that topological changes rarely occurred over 20 ps. Thus, on a time scale of 20 ps, the glass transition region is between 1000 and 1300 K.[10]

Glasses were formed by lowering the temperature of an initial equilibrated fluid configuration to temperatures from 33 to 900 K while integrating the equations of motion for 4-6 ps.

Computer simulation of BeF_2 yields a fluid whose structural properties are those commonly attributed to BeF_2 made in the laboratory.[11,12] Most Be are fourfold coordinated by F in approximate tetrahedra, and most F are twofold coordinated by Be with widely varying Be-F-Be angles. The peaks of the calculated radial distribution functions (RDF) agree with experiment.[11]

Central to our discussion is the observation of a number of threefold- and fivefold-coordinated Be ions and threefold-coordinated F ions in the simulated glasses. We label these ions *defects*. Defects are *always* observed in simulated glasses.[9,13] The exact number of such defects depends on the radius of the Be coordination sphere, which we take as 2.4 Å, the location of the first minimum of the Be-F RDF. It is convenient to use the terminology that a Be-F pair are *bonded* if they are within 2.4 Å of each other. Bonded here means *proximity* (see Ref. 9). With this, the determination of a defect as a Be (F) ion with coordination number different from 4 (2) is unambiguous.

Defects are present in the simulated fluids in thermal equilibrium. The number of defects in the fluid decreases as the temperature is lowered and increases as the temperature is raised, provided that the temperature is above the glass transition region so that the fluid can relax. (This shows that such defects are not pecuilar metastable structures trapped during cooling.) In addition, when a fluid at $T > 1300$ K is quenched to a glass ($T < 900$ K) over a time scale of 5 ps, the quench is so rapid that the fluid does not remain in thermal equilibrium, and the number of defects does not decrease appreciably during the quench. As a result, *the defect structure of the parent fluid is frozen into the glass quenched from that fluid.* The fraction of defects in a glass as a function of the fluid temperature from which the glass was quenched (the *fictive temperature*) is given in Table I. As expected, the lower the fictive temperature, the fewer is the number of defects.

It turns out that even below the glass transition region some ions are capable of moving distances of 0.5-1 Å in times of 1-10 ps. The presence of defects is important because virtually all such atomic motion occurs at defect sites. To show this, I have computed the coordination number (CN) of those ions involved in a "bond-breaking

TABLE I. P_c, the probability that a Be has coordination number c, and F_c, the probability that a fluorine has coordination number c, vs T_f, the fictive temperature (the temperature of the parent fluid quenched to the glass) for simulated BeF_2 glass. T_f is given in degrees Kelvin. Glasses are at 300 K.

T_f	3334	1668	1501	1334
P_5	0.153	0.108	0.078	0.055
P_3	0.091	0.038	0.012	0.008
F_3	0.050	0.035	0.031	0.023
F_1	0.012	0	0	0

event." Let a Be-F pair *break a bond* if the pair are initially within 2.4 Å for at least 0.03 ps, and then if they are separated later by a distance larger than some R_m for at least 0.03 ps. (R_m is typically 2.4–4.0 Å.)

Consider now the set "A" of all F ions involved in a bond-breaking event during some time interval, typically 1–20 ps. (Each F in set A was originally bonded to some Be, and separates from it by at least a distance R_m during the run.) We may compute the CN of each F in set A when it is a distance r from the Be to which it was originally bonded, and then find the distribution of coordination numbers for all F in set A. In this way, we get $P_f(n, r)$, the probability that a F in set A (i.e., undergoing bond breaking) has exactly n Be neighbors when it is a distance r from the Be to which it was originally bonded. For a given F, different values of r are different points in the same trajectory. $r<2.4$ Å describes coordination before bond breaking begins.

The quantity $P_f(n, r)$ is shown in Fig. 1 for a run of 1-ps duration at 300 K, starting from a well-equilibrated initial configuration, and $R_m = 3.5$. If B is the set of Be ions involved in bond breaking, then $P_b(n, r)$ is the equivalent quantity averaged over the set B, and this also is shown in Fig. 1.

Figure 1 shows that *the ions involved in bond breaking at low temperature are defects.* For Fig. 1, I have used a glass quenched from a fluid at 1660 K. A total of five bonds were broken for this run, for $R_m=3.5$. For $R_m=3$, about 2–3 times more bonds are broken than for $R_m=3.5$. The results of Fig. 1 are typical of all temperatures below the glass transition region. Thus, at 1000 K, some 90% of the F involved in bond breaking are threefold coordinated, and about 90% of Be ions are fivefold coordinated. Even at 33 K, several F ions (typically 1–4) are found to move 0.5–1 Å away in 1 ps from the Be ions to which they were originally "bonded." While simulation at 33 K is not physically realistic, since quantum effects dominate in real systems, still the result shows that small activation energies are involved.

It is clear then that, for temperatures below 1000 K, and over times of 1 ps or greater, ion motion over distances of 0.5–1 Å occurs at defect sites. The activation energy for such motions was estimated by making runs at a series of temperatures. At each temperature, that fraction of those Be-F ions, initially bonded, which separate by a distance of 3.0 Å or greater after a time of 3 ps, was calculated. The results are shown in Fig. 2, for two glasses with fictive temperatures of 1660 and 1300 K.

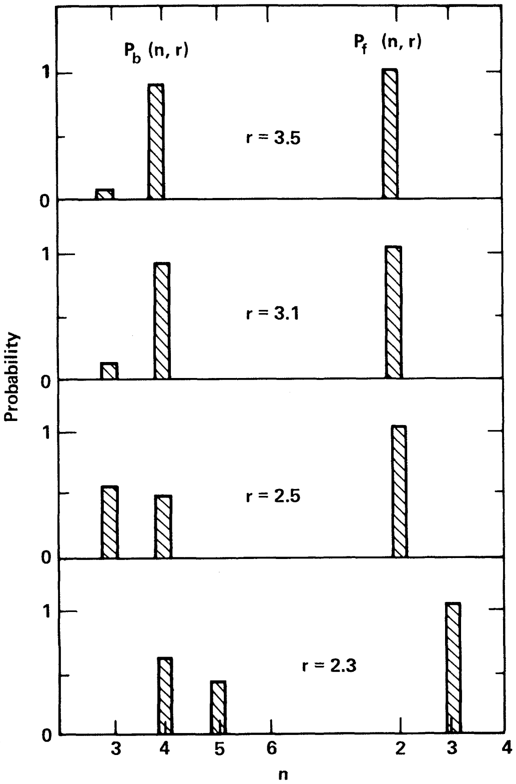

FIG. 1. Distribution of coordination numbers for ions involved in bond breaking at 333 K. $P_b(n, r)$ is the probability that a Be has exactly n F neighbors averaged only over those Be ions involved in bond breaking. P_f is similar for F, with Be neighbors. r is the distance between separating Be-F pairs. The calculation of P_f and P_b is discussed in the text.

While the data have considerable scatter, an estimate of the activation energy can be made. Figure 2 shows that the majority of sites has activation energies between 0.1 and 0.2 eV, while a few sites are still active below 500 K and have activation energies less than 0.1 eV. One gets similar results for different R_m and other time intervals.

Finally, I point out that in many cases the motion is quasiperiodic, in that some (but not all, during 10 ps) of the F are observed to become rebonded to the same Be from which they had separated in the past. The separation of several Be-F pairs versus time at 300 K is shown in Fig. 3. This typical result indicates the existence of at least two metastable equilibrium positions, quali-

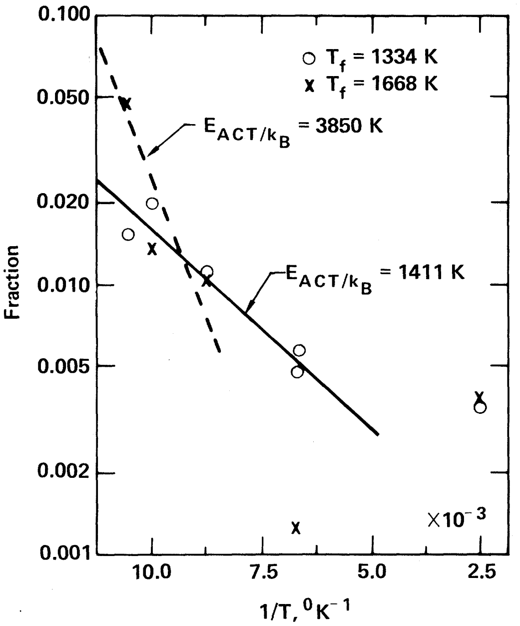

FIG. 2. Fraction of Be-F bonds broken after 3 ps vs inverse temperature, for glasses with fictive temperatures of 1667 and 1340 K. $R_m = 3.0$. k_B is Boltzmann's constant, and E_{act} is an effective activation energy.

tatively consistent with the double-well model of TLS.[3,4] One can also note from Fig. 3 that a bond breaking typically requires 0.1–0.5 ps to occur (that is, 0.1–0.5 ps for the F to go from 2.4 to 3 or 3.5 Å from the Be, see Fig. 3). This time seems to be of the same order of magnitude at 300 K and 1000 K. This is some 8–15 vibrational periods, and so the separation does not occur in a brief hop, and in this sense is more complex than the usual model of TLS might predict.

It is plausible that the defects observed in simulated BeF_2 can give rise to anomalous low-temperature properties (which, I predict, will be found in BeF_2). In the first place, the presence in the simulated glass of activated hopping over potential barriers less than 1000 K is consistent with sound absorption observed in BeF_2 above 10 K. As for the TLS, the existence of activation energies of order 0.2 eV, and the fact that the motions are quasiperiodic (indicating several metastable equilibrium positions), mean that the defects have the qualitative requirements for giving rise to TLS.[1,3,4] In addition, Table I indicates that in laboratory BeF_2, with fictive temperatures around 300 K, the number of defects will be much less than 1%, as expected based on results in other glasses.

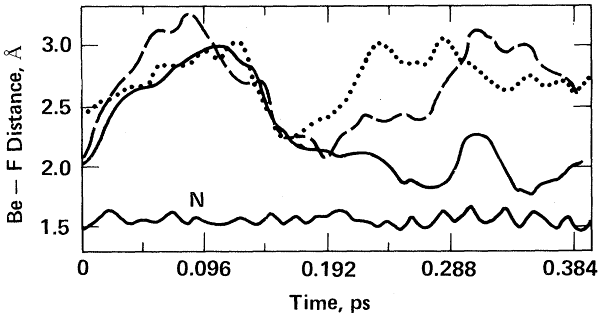

FIG. 3. Be-F distance vs time for four Be-F pairs, during a run at 300 K, for a glass with fictive temperatures of 1667 K. Curve N is the Be-F distance for "normal" Be-F ions, that is, ions not at defect sites.

It is tempting to use this same model for SiO_2, but because of the differences in interionic interaction between SiO_2 and BeF_2, no reliable extrapolation to partially covalent silica can be made at this point.

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