

**M. I. Klinger.** *Low-temperature properties of nonmetallic glasses.* During the last 20 years an experimental discovery was made of the unusual behavior of low-temperature thermal, acoustic and dielectric properties of nonmetallic glasses, which is not typical for crystals and other amorphous solids and in this sense it is anomalous. Thus, the heat capacity  $C$  increases linearly with the temperature  $T$ , while the heat conductivity  $\chi \propto T^2$  at very low temperatures  $T \lesssim 1$  K, while at moderately low  $T$  ( $5 \text{ K} \lesssim T \lesssim 50\text{--}60 \text{ K}$ )  $C/T^3$  has a "hump", and  $\chi \approx \text{const}$  ("plateau"). These low-temperature properties are universal for all (nonmetallic) glasses and have their own characteristic nature, and in this sense provide a fundamental marker for this class of substances. The so-called "standard tunnelling model" (STM) has been proposed to interpret such phenomena. This model is based on two hypotheses<sup>1,3,4</sup>: 1) there exists a small fraction  $c^{(2)}$  ( $\ll 1$ ) of atoms having two close (both in energy and in space) equilibrium positions – a two-well potential with an asymmetry (a difference in the siting of the wells)  $\Delta \ll \hbar\omega_0$  and a tunnelling amplitude  $J \approx \hbar\omega_0 \exp(-\lambda) \ll \hbar\omega_0$ , with the frequency of oscillation in the well being  $\omega_0 \approx \omega_D$ ; 2) the density of the distribution  $P(\Delta, \lambda)$  of random values of  $\Delta$  and  $\lambda$  is uniform  $P(\Delta, \lambda) \approx P_0 = \text{const}$ . At sufficiently low energies the motion of the atoms between the wells is determined by tunnelling. As a result of this tunnelling states arise (two-level systems) – excitations with a low energy  $\mathcal{E} \ll \hbar\omega_0$  which are regarded as being responsible for the properties of the glasses at all the low  $T \ll \hbar\omega_0/k_B \approx \hbar\omega_D/k_B$ . In particular, a prediction was made of a possible dependence of the

heat capacity on the duration of the experiment. Within the framework of this model and the analogy with "two-level system–spin 1/2" it was possible to interpret many properties of glasses, but primarily at very low temperatures  $T \lesssim 1$  K. A comparison of the relationship between the model and experimental data has made it possible to estimate the fraction of atoms participating in the appearance of these excitations with an energy  $\mathcal{E} \lesssim 0.1 \text{ MeV}$ ,  $c^{(2)} \sim 10^{-5}$  and the characteristic energy  $\bar{b}$  of their binding to the low frequency acoustic phonons which turned out to be anomalously large,  $\bar{b} \sim 1 \text{ eV} \gg \hbar\omega_D$ .<sup>1</sup> This had been one of the problems of the STM. Other unsolved serious problems of the STM touched first of all on the nature and properties of the excitations with energies in the range  $5 \text{ K} \lesssim \mathcal{E}/k_B \lesssim 50\text{--}100 \text{ K}$  ( $5 \text{ K} \lesssim T \lesssim 50\text{--}100 \text{ K}$ ) and in general on the nature of the universality of the nonphonon low-energy excitations determining the properties of the (nonmetallic) glasses at  $T \lesssim 100 \text{ K} < \hbar\omega_D$  (cf., Ref. 2).

In this report we discuss the "soft configurations model" (SCM) – a set of concepts which enable one to give a general theoretical description of the universal nonphonon low-energy atomic dynamics and the corresponding elementary excitations which determine the low-temperature properties of glasses noted above. Incidentally the STM turns out to be a special case of this model and the problems of the STM can be solved in a natural manner. Moreover, the SCM enables us to give also a theoretical description of localized electron states and the anomalous electron properties determined by them of glasslike semiconductors in their correlation with

the atomic-dynamic properties (cf., Ref. 2). The basic picture in this model is as follows. Spatial fluctuations of random local atomic configurations in an amorphous system give rise to a small but finite fraction  $c_a$  ( $\ll 1$ ) of atoms the motion of which takes place in unusual, relatively easily rearranged local configurations which are called "soft". In a soft configuration the elastic coupling of the atoms with their surroundings is weak and the role played by the anharmonicity of interatomic couplings becomes more prominent. It is just because of this that the typical most probable potentials of atoms in soft configurations are significantly anharmonic and can be described by an expression of the form<sup>2</sup>

$$V(x) \approx V(0) + A \left[ \eta \left( \frac{x}{a_0} \right)^2 + \xi \left( \frac{x}{a_0} \right)^3 + \left( \frac{x}{a_0} \right)^4 \right], \quad (1)$$

where  $A \equiv k^{(0)} a_0^2/2$ ,  $a_0 \approx 1 \text{ \AA}$ ,  $\eta \geq 0$ ,  $\xi \geq 0$ , are anharmonic with respect to the only (its own for each random configuration) mode (coordinate)  $x$  of atomic motion. With respect to all the other modes ( $y$ ) the motion of such atoms, as well as the motion in general of the overwhelming fraction of atoms in ordinary ("nonsoft") configurations, reduces to standard small harmonic oscillations in single-well potentials  $V(y) \approx Ay^2$  with the force constant  $k \approx k^{(0)} \sim 30 \text{ eV/\AA}^2$  (Ref. 3) for values of  $\eta \approx 1$  and  $\xi^2 \ll 1$ . But for atoms in the soft configurations (1) the dynamics of which is the only one discussed below, not only is the asymmetry of the potential small ( $\xi^2 \ll 1$ ) but also the value of the random potential  $\eta$  is small  $|\eta| \ll 1$ , so that the (quasielastic) force constant is small  $0 < k \ll k^{(0)}$ , while the susceptibility to an external action is great. Such anharmonic potentials (1) are known as "critical", in particular due to their similarity to the well-known expressions for the thermodynamic potential in the Landau theory of phase transitions. The random parameters  $\eta$  and  $\xi$  describe the fluctuations of the atomic configurations. Depending on the ratio between them critical atomic potentials can be single-well potentials (almost harmonic ones) with the greatest concentration  $c_a^{(1)} \approx c_a$ , two-well potentials (with almost harmonic wells, but on the whole anharmonic ones), with a lowest concentration  $c_a^{(2)} \ll c_a^{(1)}$ , and "intermediate" strongly anharmonic ones, with an intermediate concentration  $c_a^{(3)}$ ,  $c_a^{(2)} \ll c_a^{(3)} \ll c_a^{(1)} \approx c_a$ . These three types of critical potentials of soft configurations are basically responsible for the appearance of three classes of low-energy nonphonon excitations with energy  $\mathcal{E} \ll \hbar\omega_D$  in nonmetallic glasses that determine their unusual low-temperature properties.

From this point of view glasses are distinguished from all amorphous solids by the fact that for atoms in soft configurations  $c_a$  attains the largest possible value compatible with the elastic properties of the glass,  $c_a \approx (c_a)_{\max}$ , and, consequently, the anharmonicity of the couplings is qualitatively essential. Different estimates yield the same scale  $(c_a)_{\max} \approx 0.1$ , i.e., approximately 10% of atoms in soft configurations in glasses.

In this theory the nonphonon low-energy excitations of nonmetallic glasses correspond to low excited states of a set of noninteracting (in zero-order approximation in terms of  $c_a \ll 1$  quantum anharmonic oscillators with the critical potential (1) for all possible values of  $\eta$  and  $\xi$  in the critical domain ( $|\eta| \ll 1$ ,  $\xi^2 \ll 1$ ). The majority of these excitations corresponds to harmonic motions of atoms basically in almost harmonic single-well potentials (1) — their energy  $\mathcal{E}$

has the greatest possible value  $\hbar\omega_D \gg \mathcal{E} > \mathcal{E}_b \approx 3\text{--}6 \text{ MeV}$ . These excitations are a part of the general set of local (quasi-local) harmonic oscillations of glass at energies  $\mathcal{E} \gg \mathcal{E}_b$ .

However, of greatest interest here are the anharmonic excitations with lower energies  $\mathcal{E} < \mathcal{E}_b$ . It is essential that in this theory a new scale of vibrational energy  $w$  arises, which characterizes the soft anharmonic vibrations in soft configurations and which has the meaning of the scale of lowest energy of (quasi)local oscillations:  $w/k_B \approx 10\text{--}20 \text{ K} \sim 0.1 \hbar\omega_D$ .<sup>2</sup> Consequently, at very low energies  $\mathcal{E} \lesssim \mathcal{E}_a \approx 0.1 \text{ MeV}$ , the excitations cannot be vibrational and correspond to tunnelling two-level systems in "critical" two-well potentials which are to some extent similar to those postulated in the STM. The density of states  $n(\mathcal{E})$  increases weakly with  $\mathcal{E}$  deviating from the uniform density in the STM. Thus, STM turns out to be after some modification a special case of this theory at very low values of  $T \lesssim 1 \text{ K}$ . At moderately low energies  $\mathcal{E}_a < \mathcal{E} \lesssim \mathcal{E}_b \approx 3w$  the excitations are coupled with soft anharmonic oscillations basically in the "intermediate" critical potentials noted above. Their density of states, however, differs sharply from a uniform one, being of a nonmonotonic nature and having a singularity of the form  $\ln|\mathcal{E} - \mathcal{E}_c|^{-1}$  for  $\mathcal{E}_c \approx 2w$ .<sup>2</sup>

As far as the characteristic energy  $\bar{b}$  of coupling with phonons is concerned, it is anomalously large due to the soft nature of the configuration, not only for the tunnelling two-level systems with a very low  $\mathcal{E} \lesssim \mathcal{E}_a \approx 0.1w$  but also for soft anharmonic vibrational excitations with a moderately low energy  $\bar{b} \sim 1 \text{ eV} \gg \hbar\omega_D$  in agreement with experiment.

It is just these anharmonic excitations ( $\mathcal{E} \lesssim \mathcal{E}_b \approx 3w$ ) discussed above that are assumed here to be responsible for the properties of nonmetallic glasses at low temperatures  $T \lesssim 50\text{--}60 \text{ K}$ , which in fact are determined by the density of states of these excitations and their coupling with phonons (or photons) with frequencies  $\omega \lesssim \mathcal{E}_b/\hbar$ , at least in qualitative agreement with experimental data.<sup>2</sup> Thus, the characteristic peak in the inelastic scattering of neutrons by soft anharmonic vibrations in the case of inelasticity  $\Delta E \approx w$  predicted by theory was discovered in an independent experiment (cf., references in the review of Ref. 2). We note that the soft configurations being examined are also capable of determining the appearance of anomalous electron localized states and properties characteristic for semiconducting glasses.<sup>2</sup> Among other predictions of the theory are the dependences of the density of states of excitations  $n(\mathcal{E})$  and of the concentration  $c_a$  of atoms in soft configurations, and also of the parameter  $\bar{b}$  of coupling with phonons on the vitrification temperature  $T_g$  ( $c_a \propto \exp[(\vartheta/T_g)^\beta]$  for  $\vartheta = \text{const} \approx 300\text{--}600 \text{ K}$ ,  $\beta \approx 1$ ;  $\bar{b} \propto T_g^\gamma$ ,  $\gamma \approx 1$ ) and also on the hydrostatic pressure  $p$  ( $c_a \propto \exp(-p/p^{**} - (p/\bar{p})^2)$ ,  $p^{**} \approx 10^4\text{--}10^5 \text{ bar}$ ,  $\bar{p} \approx 10^4\text{--}10^5 \text{ bar}$ .<sup>2,5</sup> At high pressures,  $10^4 \text{ bar} \lesssim p \lesssim 10^5 \text{ bar}$ ,  $c_a$  decreases very rapidly with increasing  $p$  so that all the low-temperature properties described above, as well as the anomalous electron properties, are suppressed. As a result for  $p \approx p_c^* \sim 10^5 \text{ bar}$  one expects a quite sharp "elastic transformation" of a soft glass into a "hard" amorphous material while at  $p \approx p_c \sim 10^5 \text{ bar}$  of an almost diamagnetic semiconductor glass into a paramagnetic amorphous material.<sup>4</sup>

<sup>1</sup>Amorphous Solids, (Ed.) W. A. Phillips, Springer-Verlag, Berlin, Heidelberg, New York, 1981.