Tunneling in real structural glasses: A universal theory

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We present a universal theory that describes the low-temperature properties of real structural glasses. The key ingredient is a mapping of real and possibly complex glasses on Lennard-Jones glasses. A dimensional analysis allows us to find a general explicit expression that relates the tunneling parameters [density of tunneling systems (TS's), coupling constant between TS's and heat bath] to material constants. Experimental evidence is presented, and the relation to recent numerical calculations on the NiP system is discussed.

In the low-temperature regime ($T < 1$ K), properties of glasses like specific heat and thermal conductivity can be understood by the phenomenological standard tunneling model (STM).[1-3] This model assumes that glasses contain large numbers of tunneling systems (TS's) which act as low-energy excitations. The microscopic origin of the TS's are double-well potentials (DWP's) in the configuration space of the glass. Each TS is described by its asymmetry Δ and its tunneling matrix element Δ_0. Within the STM it is assumed that the distribution of TS's is of the form $P(\Delta,\Delta_0) = n_{\rm eff}/\Delta_0$ where $n_{\rm eff}$ is a measure for the number of TS's per unit volume and unit energy. The STM contains two adjustable parameters: on the one hand $n_{\rm eff}$, on the other hand the deformation potential $\gamma_{l,t}$, which describes the coupling of TS's to longitudinal and transverse phonons, respectively.[4] We will denote them *tunneling parameters*. For reasons of simplicity we will only discuss the transverse case. No general theory now exists which allows a calculation of the tunneling parameters for glasses on the basis of its material constants. In fact, since glasses are chemically very heterogeneous it has been strongly doubted that the values of the tunneling parameters can be explained by a *single all-embracing theory.*[3]

In recent years the surprising phenomenological relation

$$C_t \equiv \frac{n_{\rm eff}\gamma_t^2}{\bar{v}^2\rho} \approx {\rm const} \tag{1}$$

has been stressed, which holds for a number of different glasses.[5] ρ is the density and $\bar{v}$ the average velocity of sound. This relation can be easily derived in a strong-coupling picture in which the phonon-mediated interaction between TS's is the dominating energy scale.[5-7] However, for the specific case of amorphous NiP we have shown that the assumption of a strong-coupling between TS's is questionable.[8,9] For the more realistic weak-coupling picture one would naively assume that no correlation exists between tunneling parameters of chemically very different glasses. However, the experimental observation, expressed in Eq. (1), implies that despite the chemical heterogeneity some common properties determine the tunneling regime. Guided by this observation we propose a universal theory for structural glasses. The key ingredient is a mapping of real glasses on generalized

Lennard-Jones (LJ) glasses. The molecular units of the glass are identified as pseudoatoms and the parameters of the LJ glass are chosen such that it has the same macroscopic properties as the original glass.

The following arguments support the physical relevance of this mapping. It is generally believed that the TS's of structural glasses correspond to local microscopic rearrangements.[3] In the general case molecular units are the smallest units which are mobile with respect to adjacent units. Therefore it is natural to identify the molecular units as the basic unit which is responsible for tunneling in glasses. This picture has been experimentally verified for a-SiO$_2$ where the transition between two local energy minima occurs via individual rotation of a few SiO$_4$ tetrahedra.[10] In the case of polymers one might argue that monomers along a chain cannot change their relative distance so that they cannot be considered as independent pseudoatoms. However, in our analysis of NiP we observed that adjacent atoms tend to minimize their relative distance change during the motion from one energy minimum to the other;[9] therefore, the distance constraint along the chain only mildly influences the validity of the pseudoatom picture. Of course, a true justification of this mapping can only be achieved via comparison of quantitative predictions of this theory with experimental data.

The Hamiltonian of a monatomic LJ glass can be written as

$$H = \frac{m}{2}\sum_i \left[\frac{\partial}{\partial t}{\rm r}_i\right]^2 + \hat{B}\sum_{i,j} g_{\rm pot}(|{\rm r}_i - {\rm r}_j|/a) . \tag{2}$$

$\{{\rm r}_i\}$ denote the coordinates of the atoms, m the mass, a the nearest-neighbor equilibrium distance, and $\hat{B}$ the energy scale. The dimensionless potential function $g_{\rm pot}$ may be of the standard 6-12 form. However, the exact form of $g_{\rm pot}$ and possible numerical factors do not enter our theory. m is chosen as the average mass of the molecular units, a as their average equilibrium distance, and $\hat{B}$ as a measure for the average energy scale of their interaction. $\hat{B}$ will be specified further below. This mapping is complicated by the fact that in contrast to conventional LJ glasses the coordination number n of the pseudoatoms in general is smaller than 12. Therefore we will use the expression *generalized* LJ glass. It is fully determined by

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the parameters m, n, a, and $\hat{B}$.

For completing the mapping procedure we have to express n, $\hat{B}$, and a in terms of material constants. The value of n depends on the local structure of the glass. In principle, values of n can range between 4 and 12. In a-SiO$_2$ a single SiO$_4$ tetrahedron is surrounded on average by four other SiO$_4$ tetrahedra so that for a-SiO$_2$ the choice $n = 4$ is reasonable. We extend this choice to all glasses which contain a significant amount of a-SiO$_2$. The other extreme corresponds to a closed-packed structure for which $n = 12$ is appropriate. However, for most molecular crystals which are neither tetracoordinated nor closed packed typical values of n range between 6 and 8. In order to be specific, we choose $n = 6$ for all non-tetracoordinated and non-closed-packed glasses. As will be shown further below the final results hardly change if we take $n = 8$ instead of $n = 6$. The choice $n = 6$ corresponds to a cubic structure. The value of a can be obtained from m, ρ, and n via $\rho = r_n m / a^3$, where r_n depends on n. For a closed-packed structure ($n = 12$), a cubic ($n = 6$), and a tetracoordinated structure ($n = 4$) we have $r_{12} = \sqrt{2}/1.1 \approx 1.3$, $r_6 = 1/1.1 \approx 0.9$, and $r_4 = (3\sqrt{3}/8)/1.1 \approx 0.6$, respectively. The factor of 1.1 in the expression for r_n takes into account that amorphous solids are approximately 10% less dense than their crystalline counterparts. The energy scale can be conveniently expressed as $\hat{B} = m\bar{v}^2/n$. Since $m\bar{v}^2 \propto n$ for given LJ-glass parameters, $\hat{B}$ is independent of n.[9]

Our theory implies that the general nature of the TS's of different glasses are the same, except for different energy, mass, and distance scales. In what follows we will show that this observation allows us to obtain universal relations between the tunneling parameters and the material constants m, $\bar{v}$, ρ, and n. We exploit the simple but important fact that the dimensionless quantities

$n_{\text{eff}}\gamma_t^2 a^3/\hat{B}$ and $\gamma_t/\hat{B}$ can themselves only depend on dimensionless quantities. The only dimensionless quantities for the generalized LJ glass (parametrized by m, $\hat{B}$, a, n) are n and $\mu \equiv \hat{B}a^2 m/\hbar^2$. First, we discuss the dependence of the tunneling parameters on n. It has readily been shown that $\gamma_t^2 \propto n$.[9] Not so obvious is the dependence of n_{eff} on n. In our recent work we observed that typical TS's are strongly localized in configuration space and may be mainly described by the motion of a single or only a very few atoms.[8] Therefore it is natural to assume that the number of TS's is proportional to the number of atoms. Furthermore, the energy variations during the motion of a single or a few adjacent atoms are on average proportional to the number of nearest neighbors so that the energy of a TS scales with n. The first observation can be formally expressed as $n_{\text{eff}} \propto r_n$, the second as $n_{\text{eff}} \propto 1/n$, so that $n_{\text{eff}} \propto r_n/n$. For the discussion of the dependence on μ we consider a set of LJ glasses with constant values of $\hat{B}$, a, and n and different values for m. Let d describe the distance between two energy minima in configuration space. In the limit $m \to \infty$, in general, tunneling is only possible for DWP's with vanishing values of d. The opposite holds for $m \to 0$. Since $\gamma_t \propto d$,[9,11] we have $\gamma_t[m \to (\infty, 0)] \to (0, \infty)$. The most simple function which fulfills these requirement is $\gamma_t \propto m^{-c} \propto \mu^{-c}$ with some positive constant c. We assume an analogous dependence for $n_{\text{eff}}\gamma_t^2$ with some different exponent.

Expressing $\hat{B}$, a, and μ in terms of ρ, $\bar{v}$, and m and taking into account the n dependence of n_{eff} and γ_t we finally obtain

$$n_{\text{eff}}\gamma_t^2 = \frac{b_1}{n}\rho\bar{v}^2\mu^{-c_1} \qquad (3)$$

and

TABLE I. Summary of the relevant data of 16 structural glasses taken from the work of Berret and Meissner together with the assumed coordination number n, the calculated effective mass μ, and the estimated values of $n_{\text{eff}}\gamma_t^2$ and γ_t. The chemical composition of the glasses can also be found in this work.

Glass	ρ (kg/m^3)	$\bar{v}$ (km/s)	m/m_p	γ_t (eV)	$n_{\text{eff}}\gamma_t^2$ (10^7 J/m^3)	n	μ (10^6)	$(\gamma_t)_{\text{est}}$ (eV)	$(n_{\text{eff}}\gamma_t^2)_{\text{est}}$ 10^7 J/m^3
a-SiO$_2$	2200	4.10	60	0.65	0.87	4	0.38	0.63	2.04
BK7	2510	4.19	64	0.65	1.19	4	0.43	0.68	2.33
As$_2$S$_3$	3200	1.69	246	0.17	0.15	6	1.89	0.24	0.20
LaSF-7	5790	3.95	287[a]	0.92	0.87	6	10.5	0.99	1.10
SF4	4780	2.48	118	0.48	0.65	4	0.51	0.42	1.47
SF59	6260	2.13	150	0.49	0.61	4	0.59	0.38	1.35
V52	4800	2.51	183	0.52	1.18	6	1.45	0.42	0.71
BALNA	4280	2.59	141	0.45	1.09	6	0.83	0.39	0.81
LAT	5250	3.10	215	0.65	1.51	6	3.21	0.61	0.91
a-Se	4300	1.17	474	0.14	0.10	6	4.30	0.18	0.096
LiCl-7H$_2$O	1200	2.50	21		0.55	6	0.011	0.17	0.90
Zn-Glass	4240	2.58	118	0.38	0.81	6	0.52	0.36	0.94
PMMA	1180	1.70	100		0.11	6	0.33	0.15	0.13
PS	1050	1.67	104	0.13	0.12	6	0.39	0.14	0.11
PC	1200	1.86	254	0.18	0.07	6	4.77	0.24	0.07
Epoxy	1200	1.66	300[b]	0.22	0.14	6	5.93	0.21	0.05

[a]See Ref. 12.
[b]Estimated.

$$\gamma_t = \frac{b_2}{\sqrt{n}} m\bar{v}^2 \mu^{-c_2} \tag{4}$$

with

$$\mu = \frac{r_n^{2/3}}{n} \bar{v}^2 m^{8/3} \rho^{-2/3} \hbar^{-2} . \tag{5}$$

$b_{1,2}$ and $c_{1,2}$ are adjustable parameters. We stress that Eqs. (3)–(5) which are the main result of this work follow from very general arguments.

In order to justify our approach we compare the above predictions with experimental data. A systematic data collection of all nonmetallic and nonsuperconducting glasses for which reliable tunneling parameters could be determined can be found in the work of Berret and Meissner.[4] The relevant experimental data of these glasses are summarized in Table I. $\bar{v}$ has been calculated via $3\bar{v}^{-3} = 2v_t^{-3} + v_l^{-3}$. In the cases from which only v_t or v_l were available we additionally used the empirical relation $v_t = v_l/\sqrt{(3.2)}$.[4] For the determination of m for a-Se we referred to Ref. 13. The $Se_x Ge_{1-x}$ semiconductors are know to form strongly connected networks.[14] Since for this case the mapping on a LJ glass is problematic, we have excluded them from our analysis. Indeed, it turns out that for these glasses the density of TS's is much smaller than predicted by our theory. For the determination of γ_t either the low-temperature attenuation (as done in Ref. 4) or the temperature for which $\bar{v}$ displays a maximum can be used.[3] For PMMA and LiCl-7H$_2$O the values of γ_t given in Ref. 4 differ by more than a factor of 2 from those we derived with the second method. Therefore we omitted both values.

The quality of the fits depends weakly on the chosen values of c_1 and c_2, respectively. Reasonable values are $c_1 = \frac{1}{3}$ and $c_2 = \frac{1}{4}$. For these values b_1 and b_2 were obtained via least-square fits. It turns out $b_1 = 0.16$ and $b_2 = 2.9$.

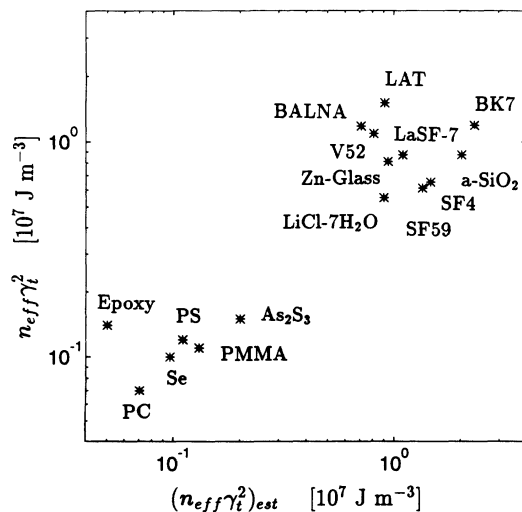In Figs. 1 and 2 and Table I the estimated values for

FIG. 1. The estimated vs the experimental values of $n_{\text{eff}}\gamma_t^2$ for 16 structural glasses.
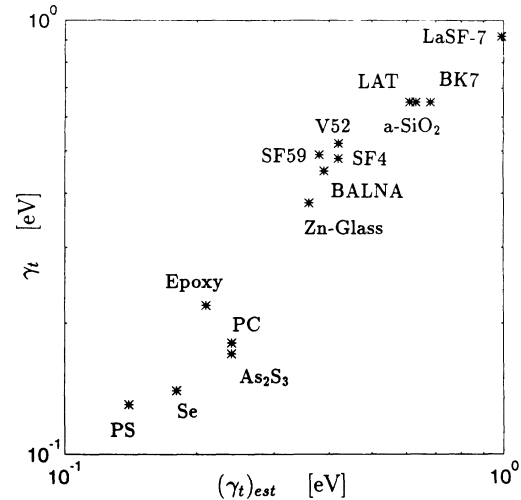

FIG. 2. The estimated vs the experimental values of γ_t for 14 structural glasses.

$n_{\text{eff}}\gamma_t^2$ and γ_t are shown together with the experimental values. All tunneling parameters can be estimated reasonably well. Interestingly, the scattering is larger in Fig. 1. Note that the m dependence of $n_{\text{eff}}\gamma_t^2 (\propto m^{8/9})$ is much stronger than that of $\gamma_t (\propto m^{1/3})$. Since our mapping is mainly expressed by the value of m (ρ, $\bar{v}$, n are already determined by the real glass) it is not surprising that estimates are better for quantities which only mildly depend on m. Choosing $n = 8$ instead of $n = 6$ changes $n_{\text{eff}}\gamma_t^2$ only by 25% and γ_t by 13%. Hence the uncertainty of our choice of n is very uncritical.

One might argue that the very good agreement between theoretical and experimental tunneling parameters is partly due to the introduction of two adjustable parameters. However, the adjustable parameters can be independently estimated by the method we presented in Refs. 8 and 9. We have to calculate n_{eff} and γ_t for LJ glasses in dependence of μ. For these numerical calculations we have to take into account that n_{eff} as well as γ_t are energy dependent.[8,9] A natural scale for E is the Debye temperature T_D.[13] For a comparison with experimental values it is therefore consistent to identify $n_{\text{eff}}(E = c_E k_B T_D)$ and the deformation potential $\gamma_t(E = c_E k_B T_D)$ with the corresponding experimental quantities n_{eff} and γ_t. We choose c_E such that for the specific example NiP we have $E/k_B = 1$ K. For the μ range of interest it turns out that, first, the use of the algebraic dependences on μ was a very good approximation and, second, the c_i correspond within 20% to the values found from the analysis of the experimental data. The proportionality constants in Eqs. (3) and (4) can be checked by comparison with the values of n_{eff} and γ_t we numerically obtained for NiP ($n_{\text{eff}} = 1.6 \times 10^{46}$ J^{-1} m^{-3}, $\gamma_t = 0.25$ eV).[8,9] Inserting $\rho = 8350$ kg m^{-3}, $\bar{v} = 2530$ ms^{-1}, and $m = 56 m_p$ into Eqs. (3)–(5) we obtain $n_{\text{eff}} = 1.5 \times 10^{46}$ J^{-1} m^{-3}, $\gamma_t = 0.25$ eV in very good agreement with the above values.[15] This comparison shows that our theory is consistent with the numerical calculations presented in recent work.[8,9] Stated differently, our

theory allows an estimation of the tunneling parameters of real glasses without a single adjustable parameter.

In summary, we have presented a universal theory which allows a reliable estimation of tunneling parameters for most structural glasses just on the basis of their average molecular mass, their density, their velocity of sound, and their coordination number. The main idea is to identify the molecular units as pseudoatoms. The adjustable parameter entering this theory can be independently determined from direct numerical calculations.

The theory implies that to a good approximation the distribution of TS's of different glasses are identical except for different energy, mass, and distance scales.

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