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Low-temperature anomalies of glasses: What can we learn from computer simulations?

Andreas Heuer [a,*], Robert J. Silbey [b]

[a] *Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany*
[b] *Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

Abstract

We show that computer simulations can be used to obtain microscopic information about the nature of the soft modes which are believed to be responsible for the low-temperature anomalies. We derive the low-temperature properties from first principles. Furthermore, we obtain new information about the question as to how sensitively the anomalies depend on the microscopic structure.

1. Introduction

At low temperatures the disorder in structural glasses leads to anomalies at low temperatures like the dramatic increase of the specific heat as compared to the Debye contribution [1]. Most anomalies can be described by phenomenological models like the tunneling model [2, 3] and the soft potential model [4, 5]. In the tunneling model it is postulated that some adjacent units of the glass can switch collectively between two adjacent minima of the potential energy, hence giving rise to double-well potentials (DWPs) in the configuration space. However, only little is known about the microscopic origin of the DWPs. The goal of this paper is to show that computer simulations of model glasses can contribute in several ways to the understanding of the low-temperature properties.

2. Geometric properties of DWPs

In a recent paper [6] we presented an algorithm which analyses the potential surface in the high-dimensional configurational space of a model glass and systematically searches for adjacent minima. Such a pair of minima corresponds to a DWP. By applying this algorithm to a 3D [7] or a 2D [8] Lennard–Jones type model glass, we obtain very specific information about microscopic properties of DWPs. For example, we observe that the distance vector $\boldsymbol{r}_{ij}$ of two adjacent atoms i,j tends to be orthogonal to the vector $\boldsymbol{d}_{ij}$ which describes the relative change in position during a transition between both minima [7]. This observation is in agreement with intuition since, in this way, the difference in relative distance and hence in potential energy for both configurations is small. It indicates that additional microscopic constraints like constant distances between adjacent units would only mildly influence the nature of the DWPs. This is a first hint that the results of the simulations of LJ glasses are applicable to a larger class of glasses. The geometric information is also important for the estimation of the deformation potential $\gamma_{l,t}$ which describes the interaction of the soft modes with longitudinal and transversal phonons, respectively. Under the assumption that $\boldsymbol{r}_{ij}$ and $\boldsymbol{d}_{ij}$ are uncorrelated we may estimate $\gamma_{l,t}$; however, incorporation of the geometric correlations like the one described above yields dramamatically lower (by a factor of approximately 3) $\gamma_{l,t}$ and $\gamma_l^2/\gamma_t^2 = 2.4$, very close to the average experimental value of 2.5 [7]. Hence the geometric information is essential for a quantitative understanding of the deformation potential.

* Corresponding author.

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3. Density of soft modes

Since we employ a systematic search algorithm for DWPs, we also obtain information about the absolute number of DWPs. From our distribution of DWPs we can directly estimate the value of n_{eff}, which is the density of DWPs per volume and energy. Defining $C_{\text{l,t}}$ as $C_{\text{l,t}} \equiv n_{\text{eff}}\gamma_{\text{l,t}}^2/\rho v^2$ (ρ density, v velocity of sound) we obtain from our simulations $2\pi^2 C_{\text{l}} \approx 1/200$ [7]. This value is in reasonable agreement with typical experimental values of 1/150. The estimation of $C_{\text{l,t}}$ is confirmed by a more elaborate analysis for which the underlying statistics of the DWPs is taken into account (see below).

4. Temperature dependence of low-temperature observables

At low temperatures we are mainly interested in nearly symmetric DWPs. Unfortunately, from our simulations we mainly obtained very asymmetric DWPs, which are not relevant at low temperatures. Typical characteristics of DWPs are the potential height, the asymmetry and the distance between both minima. These parameters are strongly correlated, so that it is not possible to estimate the properties of nearly symmetric DWPs with sufficient accuracy. However, progress can be achieved if the potentials are parametrized in analogy with the soft potential model by a quartic polynomial, hence $E_{\text{pot}}(x) \propto (w_2x^2 + w_3x^3 + w_4x^4)$, where x is the variable along the reaction path of the DWP. It turns out that the w_i are statistically independent [6]. This observation dramatically increases the knowledge about the distribution of nearly symmetric DWPs, so that it becomes possible to numerically calculate the temperature dependence of observables like the specific heat $C(T)$ or the thermal conducitivity $\kappa(T)$ at low temperatures. Similar calculations have been performed in the framework of the soft potential model [9]. For example, it turns out $\kappa(T) \propto T^{1.85}$ [7], in close agreement with typical experimental values.

The presence of DWPs alone cannot explain the existence of the so-called bump in $C(T)/T^3$. In analogy with the soft potential model we postulate that at higher energies the density of soft modes is dominated by localized single-well potentials (SWPs). They lead to a dramatic increase of $C(T)$ with temperature. Their existence has been confirmed by simulations [10]. Due to the statistical independence of the w_i in the DWP regime, it is natural to assume that the distributions of the w_i are the same in the SWP regime. It is easy to check that E_{pot} describes SWPs if w_3 is small. With this natural extension we may also predict observables like the temperature $T_{C,\text{l}}$ for which $C(T)/T^3$ displays a minimum without adjustable parameters.

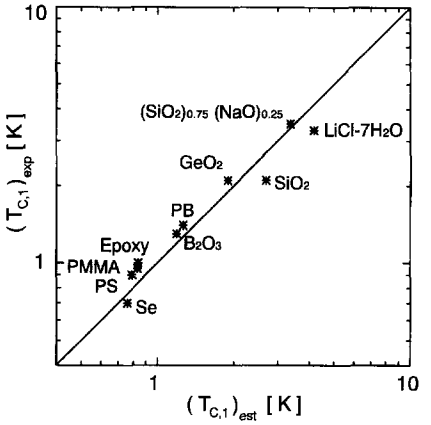

Fig. 1. A comparison of the estimated value of $T_{C,\text{l}}$ and the experimental values for different types of glasses. A single adjustable parameter has been used to scale the estimated data relative to the experimental data (see text).

5. Relation between low-temperature observables and material constants

As mentioned above, quantities like $T_{C,\text{l}}$ can be calculated for a given model glass. A LJ glass is fully determined by three material constants like T_{g}, v, and ρ. Hence it is possible to express $T_{C,\text{l}}$ in terms of these material constants. We obtain $T_{C,\text{l}} = cT_{\text{g}}^{-7/9}v^{20/9}\rho^{4/9}\hbar^{4/3}k_{\text{B}}^{-16/9}$ with $c = 1/125$ [11]. Note that only one exponent and the prefactor c have been derived from our simulations. All other exponents automatically follow from dimensional arguments. Although this relation only holds for LJ glasses, we have formulated it such that it can be applied also to different glasses like silicate glasses or polymers [12]. In Fig. 1 we compare the estimated values of $T_{C,\text{l}}$ with the experimental values for various glasses. We find a surprisingly good agreement. The overall scaling parameter c has been adjusted to be 0.01 and hence is close to the simulated value of 0.008. This means that practically without adjustable parameters we can predict the temperature dependence of quantities like the specific heat or the thermal conductivity for many structural glasses.

6. Sensitivity of the low-temperature parameters on the microscopic structure

Similiar correlations hold for quantities like $\gamma_{\text{l,t}}$ and $n_{\text{eff}}\gamma_{\text{l,t}}^2$ for which a good agreement with experimental data can be found, too [11]. This is a strong indication that the microscopic structure only mildly influences the low-temperature properties. Interestingly, no agreement can be found for the temperature T_{s} for which the sound absorption displays a maximum. The expected relation $T_{\text{s}} \propto T_{\text{g}}$

is dramatically violated among different glasses [e.g., $T_s/T_g(GeO_2) \approx 6T_s/T_g(SiO_2)$] [13]. This observation is supported by the fact that for B_2O_3 the value of T_s strongly depends on the OH-content whereas parameters like $C_{l,t}$ remain virtually unchanged [14]. It is known that the DWPs which are relevant for the peak of sound absorption have much higher potential heights than those relevant at lower temperatures. Our simulations show that the average value of the potential parameters w_i are approximately inversely proportional to the spatial extension of the DWPs, so that the DWPs relevant close to T_s are much more localized than those relevant at lower temperatures [11]. Therefore, for spatially extended soft modes the microscopic differences are averaged out yielding a scaling behaviour like that in Fig.1. Only for very localized soft modes is the energy scale dominated by the microscopic structure of the glass, yielding the strong material dependence of T_s/T_g.

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