



INSTITUT DE FRANCE
Académie des sciences

Comptes Rendus

Physique

Yannick Champion

Entropy of metallic glasses and the size effect on glass transition


Volume 24, Special Issue S1 (2023), p. 155-164

Online since: 8 February 2023

Part of Special Issue: From everyday glass to disordered solids

Guest editors: Jean-Louis Barrat (Université Grenoble-Alpes, France) and Daniel Neuville (Université de Paris, Institut de physique du globe de Paris, CNRS, France)

<https://doi.org/10.5802/crphys.130>

 This article is licensed under the
CREATIVE COMMONS ATTRIBUTION 4.0 INTERNATIONAL LICENSE.
<http://creativecommons.org/licenses/by/4.0/>



*The Comptes Rendus. Physique are a member of the
Mersenne Center for open scientific publishing*
www.centre-mersenne.org — e-ISSN : 1878-1535

of symmetry and periodicity at the atomic scale, glass materials are excluded. Even if local atomic arrangements and short range order have been observed (the random distribution of near-icosahedra in metallic alloys, octahedra in oxides, chains of polymers) using high level characterizations technics and simulations (X-rays absorption, NMR...), no generic structural rules are emerging.

It is arising from disorder in glass that descriptions might be most likely statistical in nature. In addition, disorder also implies that none of the atoms or groups of atoms are able to define relevant reference for spatial localization. This second requirement can be faced by forgetting atoms and characterizing the glass using its potential energy landscape (PEL) introduced by Stillinger [1] and still a leading formalism for the analysis of glass forming dynamics [2] or deformation [3]. The first requirement can be fulfilled by evaluation from this PEL of an appropriate entropy for the glass leading to characterization parameters or information parameters with analogy to the Shannon entropy of information [4]. Besides, it has been shown that the PEL can be divided following its various characteristic domains (basin of attraction, minima...) to form a network, suggested to allow thermodynamics properties to be calculated [5].

We used nano-indentation mechanical testing to probe the PEL in order to reveal the glass zones where (atomic) rearrangements are allowed [6] and evaluate the statistic of these events. From this analysis an apparent entropy is derived and analyzed with the objective of identifying a specific length scale characterizing the glass, as cell parameter is characterizing the crystal or the Burgers vector the dislocation. The work reported in this article originally focused on the description of metallic glasses. But, we shall see that the results and analyses can be generalized to interpret behaviors of oxides and polymers glasses. With some hindsight, this is little surprising. The various classes of glass exhibit different physical, chemical and mechanical properties due to difference in their atomic bonds and local atomic arrangement. But the common high degree of disorder, leads to similar dynamics with only difference in the length and time scales. The emblematic common characteristic is the glass transition temperature, T_g delimiting absence and large plastic yielding behavior. The entropic description presented is tested on the prediction of the size effect on the mechanical behavior (transition from localized to homogenous deformation) observed for metallic and oxide glass, as well as the on the T_g variation with film thickness in polymers.

2. Derivation of entropy

Among main features, metallic glasses exhibit nano-metric serrations observed in nano-indentation [7, 8] or nano-pillar compression tests [9]. A serration is the results of atomic displacement under stress effect and its magnitude is naturally assumed to be related to local specific potential energy in the PEL. Hence, the mechanical test should be able to probe the local structure of the glass, showing in the displacement extent (serration size) the capacity for local atomic rearrangement related to the local energy. It is well known that the occurrence of serration events is strain rate dependent [8]. Hence, the most relevant structural description obtained from the mechanical probing, necessarily requires that the time scale of experiment is lower than the timescale of the mechanisms controlling the serration formation. To an experimental point of view, testing must be performed in quasistatic conditions that is at the lower strain rate as possible.

Experiments were carried out on the $Mg_{65}Cu_{12.5}Ni_{12.5}MM_{10}$ alloy, prepared by electromagnetic melting of Mg, Cu, Ni and mischmetal ($Ce_{75}La_{25}$) in a cold crucible under controlled atmosphere [10]. The metallic glass was then produced by twin roll casting of the liquid alloy in He atmosphere into the form of a sheet with a thickness of about 400 μm , a width of about 3 cm and a length of about 30 cm. In the as cast conditions, the alloy surface roughness is very low,

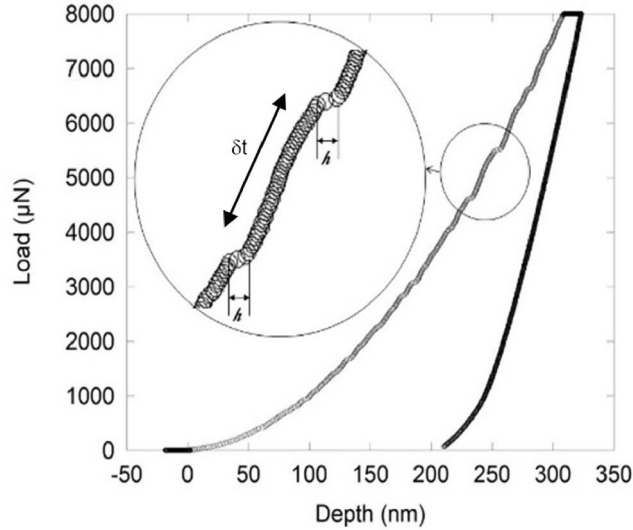


Figure 1. Nano-indentation curve showing serrations on the loading branch, also shown in the inset with the serration size, h and the waiting time between two successive serrations δt (data from [10]).

controlled by the imaging mode of the nano-indenter. An oxide is also formed at the surface with a thickness of about 2 nm negligible at the experimental indent depth considered for the analyses. Characterization of the amorphous alloys is reported in [10]. As cast sample containing free volume was investigated. Nanoindentation was performed with a TI 950 Hysitron Tribo Indenter equipped with a Berkovich tip (threefold symmetry pyramid). For each measurement, the load was applied at a loading rate of $4 \text{ mN}\cdot\text{s}^{-1}$ up to the maximum load of $8000 \text{ }\mu\text{N}$. Strain rate, $\dot{\epsilon} = dh/h dt$ (h is the indent depth and t is the time) is extremely high at the onset of the deformation and thus serrations are too small to be detected due to high strain rate effect. After about 100 nm indentation depth, the strain rate is nearly constant at a sufficiently low value of about 1 to 0.3 s^{-1} (nearly quasistatic conditions).

Figure 1 is an example of a nano-indentation curve, from the work of Thuriéau *et al.* [10], with the loading part showing serrations of size h and the waiting time δt , between two successive serrations (inset). The curve shows a plateau at the maximum load; this is a depth-time relaxation experiment at a constant load, used for evaluation of the activation volume of the deformation process (published elsewhere [10]). The nano-indentation test is ending by the unloading part. Serrations size and waiting times were automatically detected and measured using a tailor-made automated procedure based on the detection of slope discontinuities along the loading part of the indentation curves. The resolution in depth displacement is lower than 1 nm. 7980 serrations were measured from 320 indentation curves. The large dataset enables a relevant statistical analysis, containing in particular large size events having very low probability of occurrence.

To connect the serrations to the PEL structure, the glass is discretized in non-periodic regions of size l , called “clusters”, having various potential energy in the PEL. Figure 2 is a 2D scheme of a glass in such description, where black clusters are in favorable energy configuration for rearrangement under an external solicitation. The grey clusters depict the potential gradient around favorable ones. Under the applied shear stress, τ , atomic rearrangement is expected over a distance $h \approx k \times l$, corresponding to successive favorable and subsequent activated clusters (black and grey) one calls ligament. In that picture, the total number of clusters is very large ($n_c \gg 1$) and the probability to find a ligament (favorable clusters) is very small ($p \ll 1$). Such rare

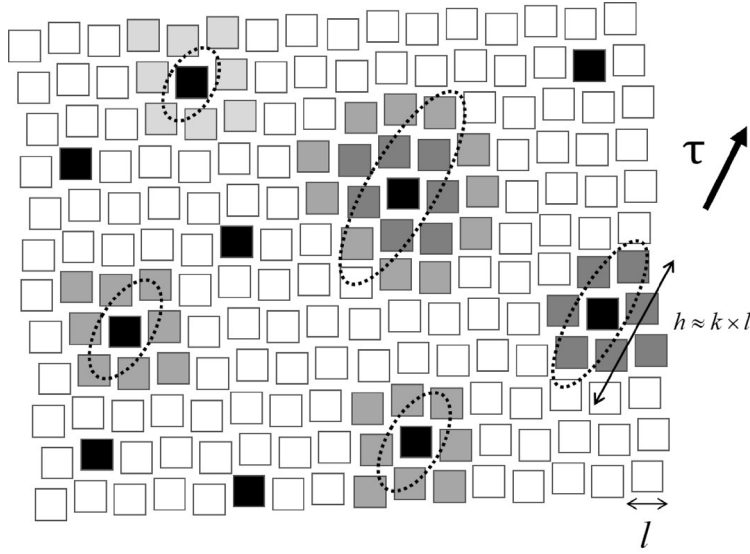


Figure 2. 2D scheme of the glass description in a PEL approach. The glass is divided in “clusters” of size l , formed in average of the same number but different atoms. Clusters are distributed over the PEL, where some (black) surrounded by various energetic gradient of clusters, are in favorable energy configuration for atomic rearrangement. An external shear stress sollicitation τ produces the rearrangement in the stress direction over various number of clusters, depending on the potential energy configuration.

event configuration is described by a Poisson distribution, with $P_k = \lambda^k e^{-\lambda} / k!$ the probability of finding ligaments formed of k clusters. $\lambda = p \times n_c$ is the average number of clusters giving the most expected ligament size $\bar{h} = \lambda \times l$. In this approach, the ligaments are associated to experimental serrations observed in the mechanical testing.

The normalized distribution of experimental serrations, $P_e(h)$ is plotted in the Figure 3 and compared to a normalized Poisson distribution $P(h)$ with the fitting parameters: $\bar{h} = 3.47 \pm 0.03$ nm, $l = 0.64 \pm 0.03$ nm, which gives $\lambda \approx 5$. The waiting times, δt distribution (inset of Figure 3) is also consistent with the Poisson statistic and verifies $P(\delta t) = Ae^{-\lambda \delta t}$. It was reported that the activation volume controlling the shear band formation in this Mg glass is of the order of 3 atoms [10]. Similar value was reported by Schall and collaborators [11] and Ju and collaborators [12] for different materials. The present statistical analysis is consistent with that result, considering that an elementary displacement of the order of l , which is about two interatomic distances, needs a rearrangement of at least 3 atoms. It is much satisfactory to find analogy between cluster size used for the discretization of the glass and the activation volume controlling shear band formation, having a physical meaning.

For derivation of thermodynamic quantities, the previous analysis is linked to a statistical physic approach similar to that proposed by Gibbs and Adam [13] to describe glass viscosity. The probability to find a ligament formed of k clusters writes, $P_k = g_k e^{-u_k / k_b T} / Z$, where u_k is the energy of a ligament of k clusters in the PEL, g_k is a degeneracy factor, Z is the partition function, k_b is the Boltzmann constant and T is the absolute temperature. For the most probable ligament of λ clusters, it is arbitrarily chosen that $g_\lambda = 1$. Combining with the Poisson distribution, the free energy is obtained: $f = -k_b T \ln Z = u_\lambda - k_b T \ln(\lambda! / \lambda^\lambda e^{-\lambda})$, where the energy of the ligament, u_λ is unknown. From this quantity, a simple apparent entropy per ligament is derived:

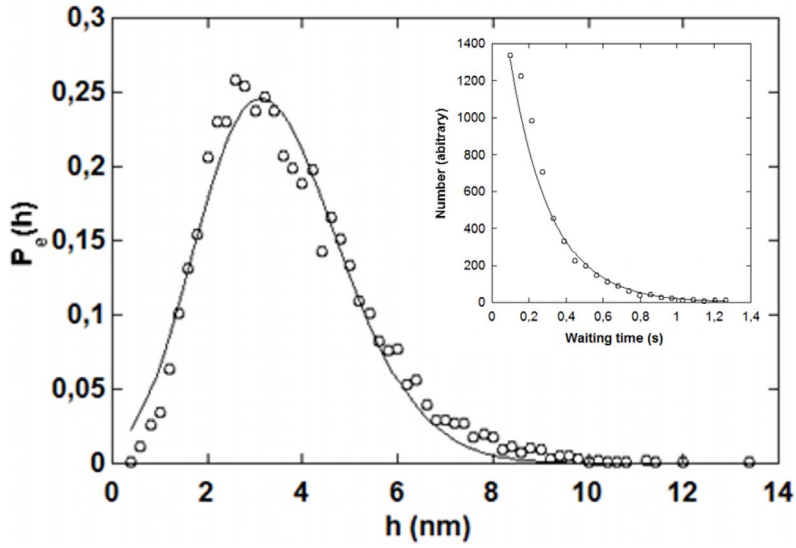


Figure 3. Normalized experimental distribution of serration sizes $P_e(h)$ (open dots) compared with the Poisson distribution $P(h)$. Distribution of waiting time, δt between successive serrations is shown in the inset.

$$s = k_b \ln \left(\frac{\lambda!}{\lambda^\lambda e^{-\lambda}} \right). \quad (1)$$

With analogy to the Shannon measure of information (information entropy), the value of relation (1) is a first step in a statistical description of the glass, which depends on the unique structural parameter λ related to the glass PEL.

3. The size dependence of the mechanical behavior in metallic glass

As a first attempt for validation, the entropic description is tested in regards to the size dependence of the mechanical behavior. Glasses (metallic, oxide, polymers) flows at high temperature allowing easy forming, but are brittle below the glass transition temperature. Of course, fundamental mechanisms for absence of macroscopic plastic deformation are distinct between these phases due to their difference in atomic bonds. However, in both cases the brittleness stems from the stress localization leading to formation of cracks in oxides and a shear bands in metals and polymers. It is then very intriguing to observe homogenous plastic deformation when glass sample is getting sufficiently small. The first evidence was reported by Taylor in 1949 using indentation on a borosilicate optical glass [14]. Since, mechanical tests on micro pillars reveal plasticity for diameter of sample of few micrometers [15]. For metallic glasses, the first evidence was reported by Volkert and collaborators on a PdSi alloy nano-pillars with diameter of 440 nm [16]. So far, an explanation has been based on a necessary critical volume for crack or shear band formation and propagation [16, 17]. With analogy to the Griffith criterion, the critical size is estimated from the balance between elastic energy stored under the applied stress σ and the crack or shear band energy, $\Delta \propto \Gamma E / \sigma^2$ where Γ is the energy per unit area of crack or shear band and E is the Young modulus. Origin and mechanism for the change in the deformation mode from brittle to ductile in glasses is still debating. In their work, Guo and collaborators [18] observed in situ at the microscopic scale, using transmission electron microscopy, the homogenous deformation of a metallic glass followed by instability leading to necking similar to deformation in crystals.

Evidence of shear band inhibition was interpreted through several angles. With the “Griffith criterion”, they proposed the interesting aspect of necessary distance for shear band to reach a mature stage. In addition, the authors emphasized the fact that the sample size is most likely below the range of shear band spacing. They suggest that the sample volume is less likely to contain “fertile” sites for the initiation of shear bands (those favorable to form shear transformation zones).

An alternative to the mechanical approach, necessarily based on stress localization and shear band properties, is to assume that the glass flows at a critical size as it does at the glass transition temperature. Hence, a “sample size—glass transition temperature” equivalence is envisaged similar to the “time-temperature” equivalence in thermally activated process. The glass transition is the temperature below which elementary species mobility is too low to observe relaxation at the time scale of experiment. In their statistical mechanics theory, Gibbs and DiMarzio, showed that the increase in relaxation time at the glass transition is related to a dramatic decrease towards very small value of the configurational entropy [19]. Later, using this idea Gibbs and Adam introduced the configurational entropy in the description of viscosity [13]. Based on this approach, an interpretation of the size dependence would be that an increase in specific configurational entropy happens with decreasing the sample size. Homogenous deformation should be then allowed when the value of the size dependent glass transition is reached at room temperature.

A change in entropy with size was first reported in [20]. Before, Stillinger suggested that minima in the PEL varies exponentially with size [21]. From the relation (1), rewriting $e^{-\lambda} = \lim_{n_c \rightarrow \infty} (1 - (\lambda/n_c))^{n_c}$ and identifying that $\lim_{n_c \rightarrow \infty} (1 - (\lambda/n_c))^{n_c} \approx \lim_{n \rightarrow \infty} (1 - (\lambda/n))^n$, n is the total number of ligaments, one obtains after Taylor series development, a size dependent specific entropy following:

$$s = k_b \ln \left(\frac{\lambda!}{\lambda^\lambda e^{-\lambda}} \right) + k_b \frac{\lambda^2}{2n}. \quad (2)$$

Reducing n means that the statistic is changing from Poisson to binomial, a well-known property for these distributions. In other words, the way events (serrations) are “drawn” (probed) changes with the reduction of the sample size. From this result and considering the Gibbs and Adam analysis [13], a “sample size—glass transition temperature” equivalence is defined writing that the entropy of an infinite sample at the glass transition temperature is equal to the entropy of the small size specimen at room temperature.

This simple equality needs however, some special care. It is emphasized that entropy of the small size sample is calculated with data obtained from the mechanical testing, then considering only the ligaments probed by the mechanical solicitation. Consequently, the entropy from room to glass temperature must be rescaled by the ligaments fraction probed in the mechanical testing. Heat capacity c_p is rescaled in number of ligaments (or mole of ligaments), that is by $\sim 3\lambda$, assuming cluster formed of about 3 atoms. Then the balance between the entropy of the small size specimen and the entropy of infinite specimen at the glass transition writes, with Ω the atomic volume and n_l/n the fraction of ligaments probed:

$$k_b \ln \left(\frac{\lambda!}{\lambda^\lambda e^{-\lambda}} \right) + k_b \frac{\lambda^2}{2n} = k_b \ln \left(\frac{\lambda!}{\lambda^\lambda e^{-\lambda}} \right) + \frac{n_l}{n} \int_{T_{RT}}^{T_g} c_p \frac{dT}{T}. \quad (3)$$

The volume of the specimen is $V = n3\lambda\Omega$ and the volume density of ligament is $\Psi = n_l/V = n_l/n3\lambda\Omega$.

After rearrangement, a critical size for the transition in the specimen size effect on the mechanical behavior is obtained:

$$\Delta = \sqrt[3]{\frac{k_b \lambda}{6\Psi \int_{T_{RT}}^{T_g} c_p \frac{dT}{T}}}. \quad (4)$$

For the Mg based metallic glass used in our nano-indentation experiments, $\lambda = 5$ is determined from a robust statistical distribution. The ligaments density is estimated of 10^{-8} nm^{-3} , assuming a hemispheric zone, $\nu \approx 60h_{\text{max}}^3$, where h_{max} is the maximum indent depth. An entropy from room temperature to glass transition was numerically evaluated from [22] of about $10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Then the critical size for the transition from brittle to ductile is calculated of about 400 nm, consistent with observations by Lee and collaborators on pillars with diameter smaller than 1000 nm [23]. The approach was applied successfully for various metallic glasses tested on nanopillars reported in the literature [20]. In particular, the first observation by Volkert [16] reports on critical size of 440 nm, whilst the relation (4) predicts 500 nm.

4. Size dependence of the glass transition in glass polymer

In the previous section, the motivation was to evaluate the critical size for glass transition at room temperature. However, one notes that this relation is valid at any temperature below T_g and an apparent size dependent glass transition temperature can be naturally derived, substituting T_{RT} by $T_{g\Delta}$ in (4). Assuming that the c_p variation with temperature is little (c_p is from 25 to $50 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for metallic glass), a size dependent T_g is obtained from relation (4) following:

$$T_{g\Delta} \cong \frac{T_g}{\left[1 + \frac{k_b\lambda}{6\Psi C_p\Delta^3}\right]} = \frac{T_g}{\left[1 + \left(\frac{\Delta^*}{\Delta}\right)^3\right]} \quad (5)$$

$\Delta^* = \sqrt[3]{k_b\lambda/6\Psi C_p}$ is a characteristic length scale of the glass.

Substituting the exponent 3 by a free exponent δ , and verifying that $\Delta^* \ll \Delta$, a Taylor development of the relation (5) gives:

$$T_{g\Delta} = T_g \left[1 - \left(\frac{\Delta^*}{\Delta}\right)^\delta\right] \quad (6)$$

which is the empirical relation proposed by Keddie and collaborators to fit the experimental variation of T_g with polystyrene film thickness [24].

In their work, T_g is obtained by detecting the discontinuity in expansivity using ellipsometry as the films are heated. These authors found the fitting parameters of the relation (6) of $\delta = 1.8 \pm 0.7$, a bulk $T_g = 373.8 \pm 0.7 \text{ K}$ and $\Delta^* = 3.2 \pm 0.6 \text{ nm}$. Their data were fitted using the relation (5) with the exponent δ instead of 3, giving the fitting parameters: $\delta = 1.2 \pm 0.1$, a bulk $T_g = 375 \pm 1 \text{ K}$ and $\Delta^* = 1.4 \pm 0.4 \text{ nm}$. Figure 4 shows the fitting of Keddie's data with good agreement using the relation (5) derived from the entropic description.

The value of δ (non integer) from these measurements is rather intriguing; thickness variation would have made more intuitive to find 1. However, from our analysis it is pointed out that the exponent 3 is not related to the 3 dimensions of the sample, but to volume (or spacial) distribution of ligaments which should be still valid for films. As a result, the reduction of one dimension or more, should affect the ligament based entropy in the same way and the $T_{g\Delta}$ variation with thickness should be intuitively expected to follow the relation (5) with thickness exponent of 3. Forrest and collaborators, proposed another model to explain the thickness effect on T_g [25]. It is not discussed in the present paper, but is emphasized by these authors that the polystyrene thin film studied by Keddie and collaborators were supported on a (111) oriented silica wafer most likely affecting the size dependence. In their work, Forrest and collaborators measured the variations of $T_{g\Delta}$ with the thickness of free standing polystyrene films, with molecular weight ranging from 116 K to 347 K. Their data were replotted and fitted with the relation (5) with still exponent δ instead of 3 (Figure 5). The fitting parameters are obtained as $\delta = 3.2 \pm 0.5$, a bulk $T_g = 366 \pm 3 \text{ K}$ and $\Delta^* = 13 \pm 1 \text{ nm}$. The exponent δ close to 3 confirms the entropic description well. The bulk value of T_g is corresponding to polystyrene with average

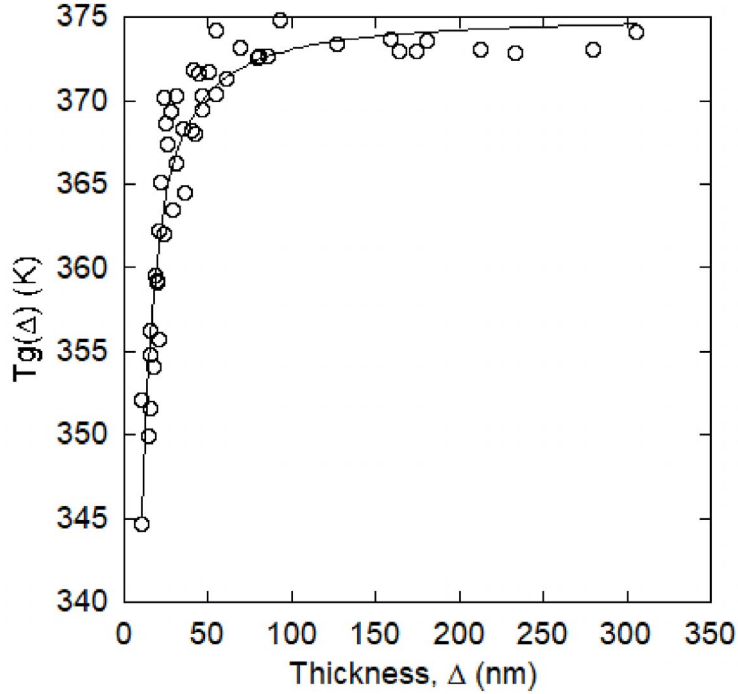


Figure 4. Replot of the data from Keddie *et al.* [24], $T_{g\Delta}$ as a function of the polystyrene film thickness Δ fitted with the relation (6) with exponent δ instead of 3.

molecular weight of 120 K, consistent with the values reported by Forrest *et al.* [25]. As pointed out by these authors influence of the substrate in the work of Keddie is understood from the relation (5) as a “bulk” glass transition dependence with the film thickness related to a gradient of material properties induced by the substrate.

5. Concluding remarks

An analysis based on a statistical physics evaluation of entropy also from mechanical testing with a strong hypothesis that serrations are related to the PEL, leads to identification of two main structural parameters: the average number of successive “clusters” λ corresponds to easy displacement domain (favorable energy domain for rearrangement or “fertile” sites for the initiation of shear bands) and the volume density Ψ is the number of these domain per unit volume. The cluster size which is the unit domain in the statistical analysis is seemingly corresponding to the activation volume, v_a controlling deformation in the glass, then this value has to be associated to the two others. If our original objective was to identify structural parameters, it must be emphasized that λ , v_a and Ψ are derived from mechanical testing, which means that other properties may reveals other parameters. A second aspect is that Ψ is a hidden parameter in the entropy definition and is revealed by the size effect on the mechanical behavior of the glass at the glass transition temperature. Eventually the analysis is based on the investigation of a metallic glass for which serrations are visible with the spatial resolution of the nano-indentation technique. Most positively, is that derivation from the size effect on the glass transition, leads to a unique characteristic length scale which gathers all the structural parameters and which writes with inserting the activation volume, $\Delta^* = \sqrt[3]{k_b \lambda / 3 v_a \Psi C_p}$. This

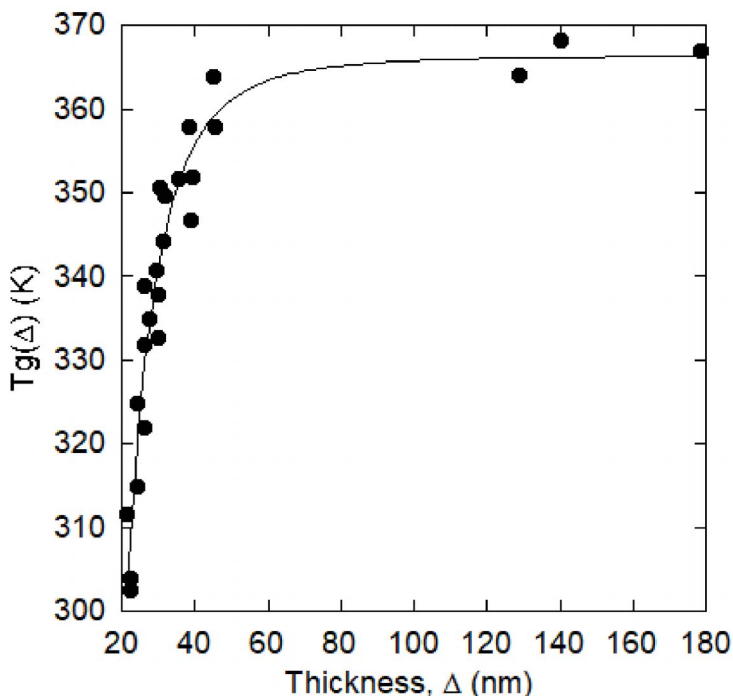


Figure 5. Replot of the data from Forrest *et al.* [25], $T_{g\Delta}$ as a function of the polystyrene film thickness Δ fitted with the relation (6) with exponent δ instead of 3.

value gives a first insight on the understanding difference in the size effect on the mechanical properties, in particular the fact that oxide glass shows the largest size, in the range of micron, compare to metallic glasses, in the range of 50 to 500 nm, and polystyrene in the range of 20 nm. The characteristic length scale shows the dominant role of Ψ , which can be assumed to be the lowest in silica glass characterized by strong atomic bonds and local well defined polyhedra, compared to softer bonds and larger disorder in metallic glass and polymers.

Conflicts of interest

The author has no conflict of interest to declare.

References

- [1] F. H. Stillinger, T. A. Weber, "Packing structures and transitions in liquids and solids", *Science* **225** (1984), p. 983-989.
- [2] P. K. Gupta, W. Kob, "Basis glass states: New insights from the potential energy landscape", *J. Non-Cryst. Solids X* **3** (2019), article no. 100031.
- [3] D. L. Malandro, D. J. Lacks, "Relationships of shear-induced changes in the potential energy landscape to the mechanical properties of ductile glasses", *J. Chem. Phys.* **110** (1999), p. 4593-4601.
- [4] C. E. Shannon, "A mathematical theory of communication", *Bell Syst. Tech. J.* **27** (1948), p. 379-423.
- [5] J. P. K. Doye, C. P. Massen, "Characterizing the network topology of the energy landscapes of atomic clusters", *J. Chem. Phys.* **122** (2005), p. 1-13.
- [6] P. H. Cao, M. P. Short, S. Yip, "Potential energy landscape activations governing plastic flows in glass rheology", *Proc. Natl. Acad. Sci. USA* **116** (2019), p. 18790-18797.
- [7] R. Limbach, K. Kosiba, S. Pauly, U. Kuhn, L. Wondraczek, "Serrated flow of CuZr-based bulk metallic glasses probed by nanoindentation: Role of the activation barrier, size and distribution of shear transformation zones", *J. Non-Cryst. Solids* **459** (2017), p. 130-141.

- [8] C. A. Schuh, T. G. Nieh, "A nanoindentation study of serrated flow in bulk metallic glasses", *Acta Mater.* **51** (2003), p. 87-99.
- [9] C. Q. Chen, Y. T. Pei, O. Kuzmin, Z. F. Zhang, E. Ma, J. T. M. De Hosson, "Intrinsic size effects in the mechanical response of taper-free nanopillars of metallic glass", *Phys. Rev. B* **83** (2011), p. 1-4.
- [10] N. Thurieau, L. Perriere, M. Laurent-Brocq, Y. Champion, "Activation volume in heterogeneous deformation of $Mg_{65}Cu_{12.5}Ni_{12.5}(Ce_{75}La_{25})_{10}$ metallic glass", *J. Appl. Phys.* **118** (2015), p. 1-5.
- [11] P. Schall, D. A. Weitz, F. Spaepen, "Structural rearrangements that govern flow in colloidal glasses", *Science* **318** (2007), p. 1895-1899.
- [12] J. D. Ju, D. Jang, A. Nwankpa, M. Atzmon, "An atomically quantized hierarchy of shear transformation zones in a metallic glass", *J. Appl. Phys.* **109** (2011), p. 1-8.
- [13] G. Adam, J. H. Gibbs, "On the temperature dependence of cooperative relaxation properties in glass-forming liquids", *J. Chem. Phys.* **43** (1965), p. 139-146.
- [14] E. W. Taylor, "Plastic deformation of optical glass", *Nature* **63** (1949), p. 323.
- [15] G. Kermouche, G. Guillonneau, J. Michler, J. Teisseire, E. Barthel, "Perfectly plastic flow in silica glass", *Acta Mater.* **114** (2016), p. 146-153.
- [16] C. A. Volkert, A. Donohue, F. Spaepen, "Effect of sample size on deformation in amorphous metals", *J. Appl. Phys.* **103** (2008), p. 1-6.
- [17] Y. F. Shi, "Size-dependent mechanical responses of metallic glasses", *Int. Mater. Rev.* **64** (2019), p. 163-180.
- [18] H. Guo, P. F. Yan, Y. B. Wang, J. Tan, Z. F. Zhang, M. L. Sui, E. Ma, "Tensile ductility and necking of metallic glass", *Nat. Mater.* **6** (2007), p. 735-739.
- [19] J. H. Gibbs, E. A. DiMarzio, "Nature of the glass transition and the glassy state", *J. Chem. Phys.* **28** (1958), p. 373-383.
- [20] Y. Champion, N. Thurieau, "The sample size effect in metallic glass deformation", *Sci. Rep.* **10** (2020), p. 1-7.
- [21] F. H. Stillinger, "Exponential multiplicity of inherent structures", *Phys. Rev. E* **59** (1999), p. 48-51.
- [22] R. Busch, W. Liu, W. L. Johnson, "Thermodynamics and kinetics of the $Mg_{65}Cu_{25}Y_{10}$ bulk metallic glass forming liquid", *J. Appl. Phys.* **83** (1998), p. 4134-4141.
- [23] C. J. Lee, J. C. Huang, T. G. Nieh, "Sample size effect and microcompression of $Mg_{65}Cu_{25}Gd_{10}$ metallic glass", *Appl. Phys. Lett.* **91** (2007), p. 1-3.
- [24] J. L. Keddie, R. A. L. Jones, R. A. Cory, "Size-dependent depression of the glass-transition temperature in polymer-films", *Europhys. Lett.* **27** (1994), p. 59-64.
- [25] J. A. Forrest, J. Mattsson, "Reductions of the glass transition temperature in thin polymer films: Probing the length scale of cooperative dynamics", *Phys. Rev. E* **61** (2000), p. R53-R56.