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Low temperature properties of glasses: a preliminary study of double well potentials microscopic structure

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Abstract

In this paper we report preliminary results concerning the microscopic structure of double well potentials observed in simulations of a two- dimensional model of glass. In spite of their diversity, it appears that the observed double well potentials share some general features.

1. Introduction

At low temperature (T below about 1 K), amorphous materials exhibit properties that are markedly different from their counterpart in crystalline systems. In addition, these properties are rather independent of the particular glassy material considered. For instance, the specific heat and the heat conductivity of insulating glasses have roughly linear and quadratic temperature dependencies respectively: $C \sim T^{1+\delta}$, $\delta \sim 0.1$–0.3, $\kappa \sim T^{2-\varepsilon}$, $\varepsilon \sim 0.1$–0.2. On the other hand, the specific heat of crystalline dielectrics has the characteristic cubic temperature dependence of the Debye law ($C \sim T^3$), and the heat conductivity shows the same dependence ($\kappa \sim T^3$) because at low temperature the phonon mean free path does not depend on T.

The present understanding of these differences is based on the assumption that amorphous material have intrinsic local microscopic arrangements formed by a small number of atoms or molecules that can switch between two potential minima. Because these double well potentials (DWPs) are related to the disordered nature of the material, it is believed that the asymmetry (the energy difference between the two wells) and the potential barrier of the DWPs are highly dispersed random quantities (i.e. they vary over a range much larger than the energy corresponding to a few kelvin). At low temperature, all the DWPs modes are frozen, except when by chance a DWP is nearly symmetric with a substantial potential barrier. When such a DWP is considered in the low temperature regime, transitions between the two potential minima occur only via tunneling and the system can be regarded as a two level system (TS) with a small excitation energy. The Hamiltonian for this system can be written as

$$H = \frac{1}{2}\begin{pmatrix} \Delta & \Delta_0 \\ \Delta_0 & -\Delta \end{pmatrix} \tag{1}$$

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where Δ and $\Delta_0 = \omega e^{\lambda}$ are the asymmetry and the tunneling matrix elements respectively; the excitation energy is given by $E = \sqrt{\Delta^2 + \Delta^2_0}$. As far as low temperature thermal properties are considered, the main effect of the TSs is to: (i) introduce new excitations that contribute to the specific heat, and (ii) make the phonon mean free path temperature dependent because now phonons undergo resonant scattering with two level systems.

A model based on those considerations, the standard tunneling model, has been proposed by Anderson, Halperin, Varma and Phillips [1, 2, 3] and constitute the usual theoretical framework in which the low temperature properties of glasses are understood. The main assumptions of this model are: (i) glasses have low energy excitations related to the presence of nearly symmetric DWPs (TSs), (ii) the TSs parameters Δ and λ are statistically independent and their distributions are flat (i.e. the density of probability is constant) over the relevant ranges, (iii) TSs are weakly coupled to the strain (or phonons) through deformation potentials. The standard tunneling model predicts quite successfully a wide range of low temperature properties of glasses: temperature dependence of specific heat and heat conductivity, acoustic saturation, phonon echo, temperature dependence of hole burning line width, etc. (see Refs. [3, 4]). In spite of this remarkable predictive capability, the standard tunneling model is a phenomenological approach whose basic hypotheses remain to be confirmed; indeed the good predictions of the model do not imply that all its assumptions are correct, it only shows that they are *consistent* with the experimental observations. Moreover the standard tunneling model does not explain universalities that are observed in the low temperature behavior of glasses. For instance, all glasses exhibit the same kind of deviation from the quadratic law $\kappa \sim T^2$ predicted by the standard tunneling model: κ is subquadratic in T with an exponent $2 - \varepsilon$, $\varepsilon \sim 0.1$–0.2, and this subquadratic behavior loses its validity around a few kelvin where the curve $\ln(C)$ versus $\ln(T)$ starts to show a plateau (this universal behavior, like others, can be made quantitative [5]).

The lack of microscopic basis for the standard tunneling model has motivated numerical works where glasses are simulated at the microscopic level; in this way DWPs can be accessed directly and their properties compared to those assumed by that model. In our early work [6, 7] , we have studied a model for a glass, by freezing a liquid of 150 atoms in a system with periodic boundary conditions. We examined over 200 glass configurations for DWPs and found over 300 which we analyzed statistically. From the statistical analysis, we constructed distribution functions of the parameters describing the DWPs. It was shown by this approach that, at least for this specific model, the major assumptions of the standard tunneling model are qualitatively correct [6] ; however, there are small deviations in the distribution function of tunneling parameters that are consistent with the $T^{1+\delta}$ law for the specific heat and the $T^{2-\varepsilon}$ law for the thermal conductivity. The simulations have also confirmed the weak-coupling assumption [7]. The reader is referred to Refs. [6, 7] for details. It should be stressed that, in spite of this agreement, we do not yet understand the microscopic reasons for the validity of the standard tunneling model and we do not have any insight about the mechanisms by which universalities arise.

One way to tackle the problem is to gather information about the microscopic structure of DWPs; something that was not addressed in previous simulations of amorphous materials and which remains almost unknown even about a quarter of century after the standard tunneling model was proposed. In this paper we report preliminary results concerning the microscopic structure of numerically observed DWPs and we discuss briefly how the geometric structure of a DWP could be linked to some of its low temperature relevant parameters.

2. Model and simulations

To facilitate the visualization of DWPs microscopic structure we consider a 2D model of glass, a strategy which has proven to be useful in early works performed to understand the dynamics of defects in crystals [8], and in more recent experiments, devised to identify microscopic events responsible for plastic deformation or indentation-adhesion processes in amorphous systems [9, 10].

We consider a system composed of two types of atoms X_1 and X_2 interacting through pair potentials

$$V_{ij}(r) = \begin{cases} A[(\alpha_{ij}r)^{-12} - 1]\exp[(\alpha_{ij}r - a)^{-1}], & 0 < \alpha_{ij}r \leqslant a, \\ 0, & \alpha_{ij}r \geqslant a, \end{cases} \quad (2)$$

where r is the interatomic distance and where the indices $\{i,j = 1,2\}$ refer to the kind of atom considered in the interaction. With appropriate values for the parameters α_{ij}, A, and a, the potentials (2) can be used to model atomic interactions in a Ni–P 3D system [11]. Molecular dynamics simulations based on these potentials were performed to generate glassy configurations in which DWPs were detected [6]. In this paper, atoms are restricted to a 2D plane but the values of the parameters α_{ij}, A, and a are chosen with the same order of magnitude as in the 3D Ni–P model: $A = 8200$ K, $a = 1.652$, $\alpha_{11} = 1.000\,\sigma^{-1}$, $\alpha_{22} = 1.400\,\sigma^{-1}$, $\alpha_{12} = 1.166\,\sigma^{-1}$; the energy is expressed in kelvin and $\sigma = 2.2$ Å is the unit length.

Simulations of the model were performed with 100 atoms (50 of each species) confined into a $L \times L$ square box with periodic boundary conditions; all the results presented here are with $L = 9.1142\,\sigma$. The simulation modus operandi is the same as the one used in Ref. [6] where details can be found: first a glass configuration is constructed by quenching an equilibrium liquid state to a local minimum of the potential energy. In a second step it is checked whether another local energy minimum exists which is close to the original one. This is performed by trying to rearrange the configuration of one central atom and its $n = 16$ nearest neighbors while keeping the rest of the glass configuration frozen; only configurations that are close to the initial one are considered in this search. When another stable configuration is found for the cluster, the whole glass is relaxed to check whether a true DWP has indeed been found. A simulated annealing method is used in this step which is repeated around each atom of the system. Each detected DWP is characterized by different parameters among which are the asymmetry Δ, the potential barrier V measured from the upper well (this requires numerically finding a reaction path connecting the two wells [11]), the distance d between the two wells, and the participation number p [6].

It should be stressed that most of the DWPs so produced have an asymmetry Δ much larger than a few kelvin so that they do not contribute to the low temperature properties (they are not TS's). However, observation of DWPs that are not TS's may allow important conclusions concerning the TSs to be drawn because some general features concerning the DWPs extend naturally to the nearly symmetric ones that are infrequently observed. This approach was used for the Ni–P model, and the distribution of TS parameters inferred from the DWPs was shown to be in agreement with the form assumed by the standard tunneling model; as noted above, small deviations were however observed above 10^{-2}–10^{-1} K and up to a few kelvin where the standard tunneling model becomes inappropriate [6]. An important point for our concern is that the distribution of TS parameters was obtained exclusively from the distribution $p(\Delta, V, d)$ observed in the population of DWPs.

As a preliminary investigation, we generated 70 two-dimensional glass configurations in which about 150 DWP's systems were found and analyzed. Each DWP was characterized by a triplet (Δ, V, d) and the observed distribution $p(\Delta, V, d)$ was compared with the corresponding distribution obtained in the 3D Ni-P simulations. A good quantitative[1] agreement was observed, showing that the distribution from which the TS's statistics are inferred is only weakly affected by the reduction of dimensionality. For that reason, it is likely that the microscopic features responsible for the low temperature properties in the 3D Ni–P model are well captured by our 2D system. This justifies our consideration of the 2D model before we turn our attention to the more complex 3D case.

3. Microscopic structure of DWP's in 2D

Before we comment on the microscopic structures represented in Figs. 1–4, we mention how these configurations were chosen as typical examples of DWP's.

[1] It should be emphasized that the 2D and 3D potentials are quantitatively comparable: the form is the same, and the energy and length scales have the same order of magnitude.

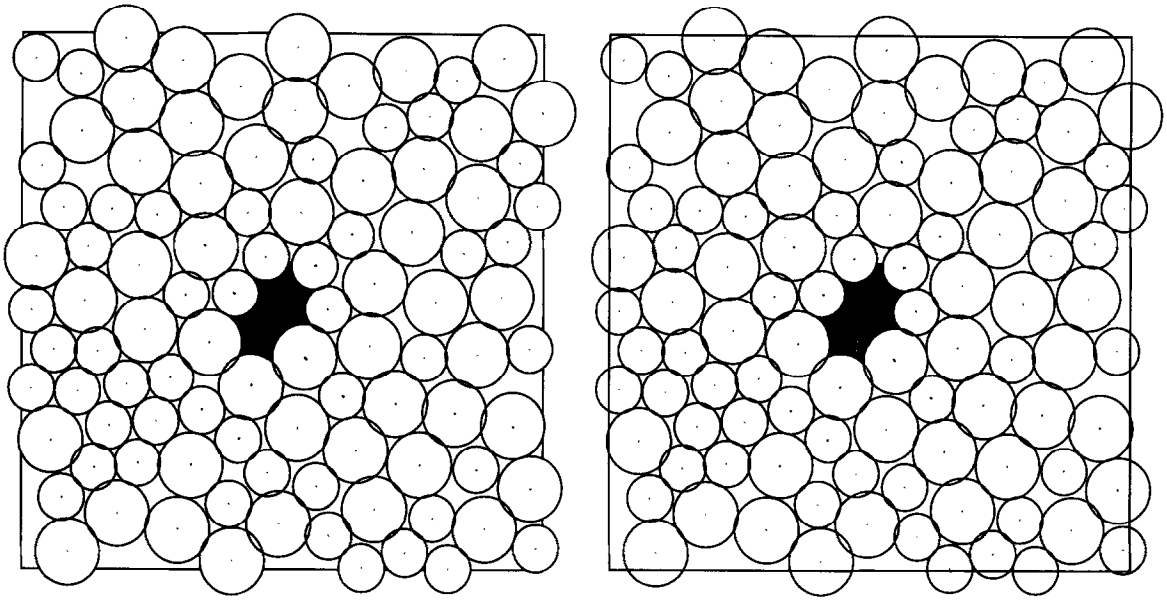

Fig. 1. A single-atom DWP: the participating atom is shaded; the excess free volume related to the DWP is indicated in black. DWP parameters: $\Delta = 624$ K, $V = 967$ K (these values are not typical, see text). Other DWP's exist in the configuration and are not shown.

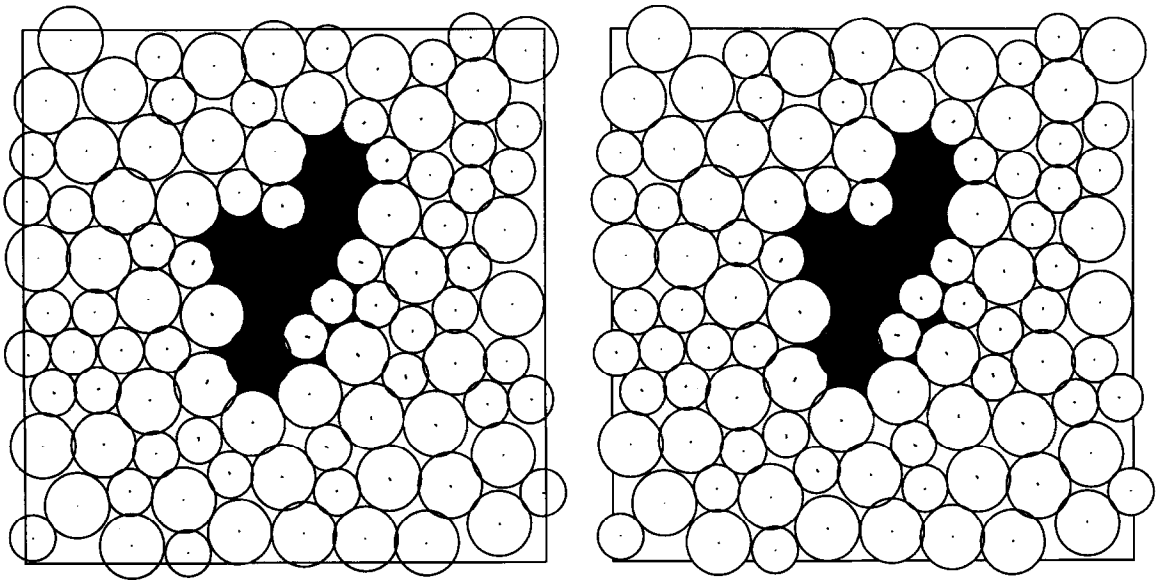

Fig. 2. A DWP where the excess free volume (black area) is distributed at different places. DWP parameters: $\Delta = 191$ K, $V = 59$ K. An other DWP exist in the configuration and is not shown.

The importance of the distribution $p(\Delta, V, d)$ and its role in our motivation to consider a 2D model explain why all our examples have typical values of Δ, V and d; the only exception to that rule is the DWP represented in Fig. 1 which will be commented on. DWP's with typical values of (Δ, V, d)

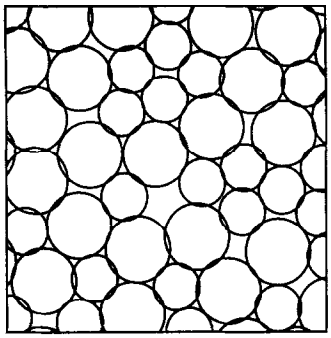

Fig. 3. Detail of a glass configuration where excess free volume exists with no DWP.

were examined to identify any recurrent pattern. Two general features were observed and a selection of examples was performed upon a procedure based on visual inspection. When possible, this subjective procedure was combined with objective criteria based on quantitative indicators like the participation number [6]. This method has been preferred to a purely quantitative approach because, at this stage of the work, it is more important to identify relevant characteristics of DWPs rather than to try to quantify the problem. Of course, a precise quantification will be required in the future to confirm the judgments based on visual examination. It is worth mentioning that this can be a difficult task even for simple features that appear readily to the eyes.

The first general feature that was identified is a link between DWPs and excess free volume (in 2D excess free area): most of the time an excess free volume is found in the immediate surroundings of a DWP. This could be related to the observation that the two-particle radial distribution function $g(r)$ measured around soft mode systems in glasses is significantly different from the whole averaged $g(r)$ function [12]. It should be stressed that excess free volumes without any DWP in the surroundings are commonly observed, it is only the contrary that is infrequent.

The importance of excess free volume appears clearly in single-atom DWP's: a particular type of DWP's where one atom undergoes an important displacement in a vacancy while the rest of the configuration is weakly affected. DWP's of that

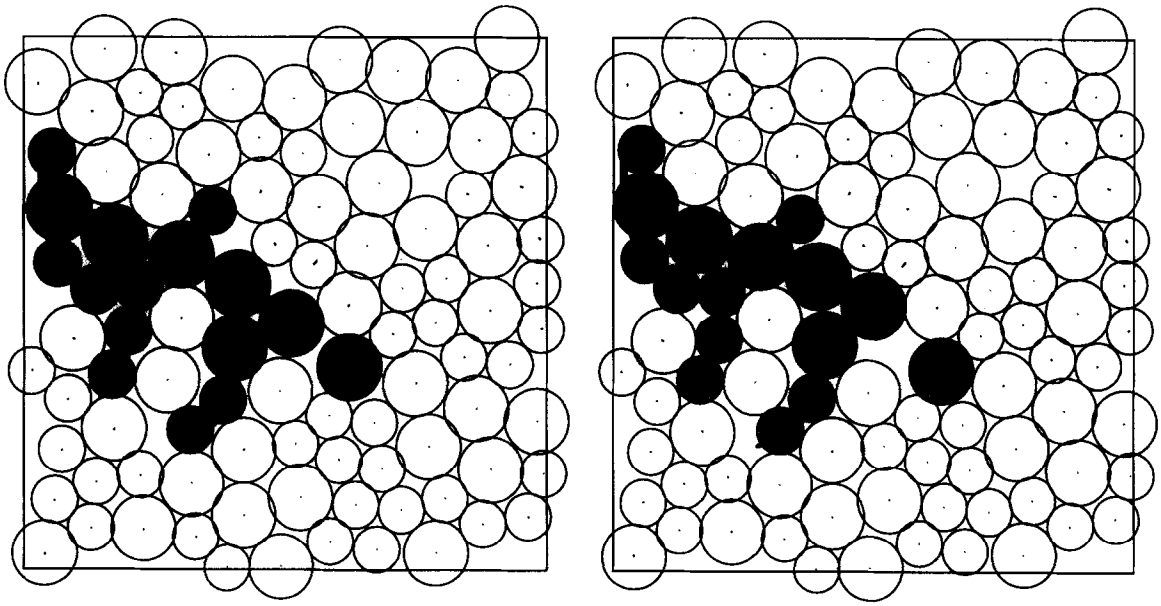

Fig. 4. A many-atom DWP with three "snake-like" motions (see lines). DWP parameters: $\Delta = 190$ K, $V = 191$ K. Other DWP's exist in the configuration and are not shown.

type are observed in about 10% of the cases and have a marked tendency to have large potential barriers. For that reason, the triplets (Δ, V, d) of single-atom DWP's do not give a correct view of the distribution $p(\Delta, V, d)$ observed in the entire population of DWP's. The "Right" and "Left" configurations of a single-atom DWP are represented in Fig. 1. In this figure, each atom is represented by a disk with a diameter corresponding to the equilibrium distance of a two-body interaction X_1–X_1 or X_2–X_2 depending of the species of the considered atom. To facilitate the visualization of the differences between the two configurations, a line is drawn from the center of each atom to the position of the same center in the other configuration. The atom involved in the DWP is lightly shaded.

Most of the DWPs are not single-atom DWP's: they involve more than one atom and the associate excess free volume is distributed at different places around the DWP; an example is given in Fig. 2. It should be mentioned that it is quite frequent to have different DWP's using a same excess free volume. In this situation the different DWP's constitute indeed a multi-well potential system. As noted above, it is frequent to have excess free volume with no DWP in the surroundings; an example is given in Fig. 3.

The second general feature that was observed concerns the DWPs where several atoms are involved (typically 4 or more; about 40% of the observed DWP's have a participation ratio above 4). In these DWP's, the displacements performed by the participating atoms are often very correlated: the atoms move one behind the other in a "snake-like" motion. Different 'snakes' are usually present and their extremities correspond generally to excess free volume zones, but this is not always the case: a "snake" can also end in a zone with no identifiable free volume. It is also observed that many atoms DWP's are less likely than the others to have a very high potential barrier. A many-atom DWP with a "snake-like" motion is represented in Fig. 4.

4. Conclusion

Results reported in this paper are preliminary and must be confirmed by further analyses which are in progress. However, it appears already that general features concerning the DWP's are observed in spite of their diversity. Most promising is the fact that some morphological characteristics could be statistically linked to the values of the parameters that are relevant for the low temperature properties.

Further development of this work will concentrate both on 2D and 3D glasses.

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