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EVIDENCE OF AGING IN GLASSY CHALCOGENIDES: NUMERICAL SIMULATIONS IN THE ELECTRON GLASS MODEL

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In this work we present a numerical study showing the presence of aging in glassy chalcogenides, based on an efficient Monte Carlo algorithm previously developed by some of us, employed for studying energy relaxation in Coulomb glasses. Some recent experiments have shown the relationship between glassy non-oxide chalcogenides and the Coulomb glass model, so we have employed our algorithm to numerically reproduce a typical aging experiment and determine an aging law in terms of the waiting time, t_w, and the relaxation time, t. The algorithm is specifically designed to study the relaxation of the total energy of the system and can reach greater simulation times than other previous methods. We have found a strong dependence of the relaxation energy on both t and t_w, which is indicative of aging in the system. Since our method reaches large times we can study in detail the influence of the waiting time on the aging phenomenon, a topic not discussed in much detail in numerical simulations so far. To complete the numerical study, we present the scalable dependence of the aging simulation in terms of t_w and t, for several values of the waiting time.

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1. Introduction

Historically, chalcogenides have been separated in two different families: oxide and non oxide materials, although nowadays only the latter maintain this specification. Almost over the last thirty years, the study of amorphous (also glassy or vitreous) oxide chalcogenides has been devoted to investigate the nature of its electronic properties [1-3], including slow relaxation [4] and non ergodicity [5], whereas the research on their glassy non-oxide counterparts was focused on the optical properties of the material, such as reversible photodarkening [6] and photoconductivity [7]. However, both families of amorphous materials possess semiconductor properties and present glassy behavior at very low temperatures [8-10]. In particular, they exhibit a set of features common to glassy systems, such as loss of ergodicity [11], slow relaxation to the quilibrium state [12], memory effects [13] and aging [14,15].

Generally, in amorphous semiconductors, the combined effect of disorder and interaction accentuates the frustration of the system: the inability of the physical system to minimize the energy of all interactions. The balance between thermal energy with characteristic energies of disorder and interaction will define the behavior of the material [16]. In particular, at sufficiently low temperatures, if disorder and interaction energies become comparable, as occurs in many chalcogenide materials (As_4Se_4, $Cd_{0.91}Mn_{0.09}Te$:In and amorphous indium oxides, for example), a

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gap appears in the electronic density of states, the so called *Coulomb gap*. Accordingly, at very low temperatures, the conductivity follows the Efros-Shklovskii law, inside the *variable-range hopping regime* [17]. In these context, glassy chalcogenide materials are well described theoretically by the electron (Coulomb) glass model [16,18]. Indium oxide is usually employed to experimentally study the conductivity at very low temperatures but, recently, El-Hakim and Morsy [19] have reported evidences of the Efros-Shklovskii law in the amorphous chalcogenide $As_4Se_4Te_2$, which confirms the validity of the electron glass model to describe amorphous non-oxide chalcogenides in which energies of interaction and disorder become comparable.

A very important kind of experiments that reveal the slow relaxation of Coulomb glasses to the state of thermodynamic equilibrium at very low temperatures, are those related to aging. This phenomenon is common to most glassy systems, and refers to the response of the material when it is subjected to the influence of two different imposed external conditions: the first one, extended over a macroscopic time, usually referred as t_w, immediately followed by another one of duration t. It is said that the system exhibits aging when the response depends on both t_w and t, in contrast to ergodic systems, where the response depends only on t. Besides, aging is related to the memory acquired by the system along its path through the configuration space, where electronic correlations play an essential role.

A typical experimental setup to observe the aging phenomenon is the *gate protocol* [14,20], in which samples with a mosfet structure are fabricated, as shown in Figure 1(d). Aging is observed in the relaxation of the excess of conductance, ΔG, when the value of the gate voltage, V_g, is changed from a value V_0 to V_1, and this last situation is maintained for a waiting time t_w. Finally, the gate voltage is reset to its initial value, V_0. The relaxation time t is measured from the end of this connection. In Figure 1(a), where we show data of Ovadyahu and Pollak [21], it is shown the operating regimes for a complete experiment concerning the measurement of the excess of conductance, $\Delta G = G - G_0$, as a function of time. G_0 is the conductance in the initial horizontal section. Similarly, the gate voltage applied to the sample as a function of time is shown in Fig. 1(c).

The conductance G, the typical magnitude measured in these experiments, is generally a function of t and t_w, and often depends exclusively on the ratio t/t_w. When this dependence only involves the first power of t/t_w this regime is referred in the literature as *full (simple) aging* [14,22,23]. For an optimal measurement of the relaxation process, time t must be at least of the order of magnitude of the waiting time, t_w. As seen in Figure 1(b), the characteristic relaxation is logarithmic and it is valid for times of the order of t_w. As the relaxation time tends to t_w, the value of $\Delta G/G$ deviates from the logarithmic behavior. This situation occurs because the relaxation times are much larger than the simulation ones as the system approaches the equilibrium.

However, the conductivity is not the only physical magnitude susceptible of presenting aging. Any variable that shows slow relaxation should usually offer a response in terms of t_w and t. This is the case of total energy per particle, which shows a non-exponential relaxation towards equilibrium, as can be depicted from previous numerical simulations by some of us [24]. Computationally, this variable is easier to monitor, and its related aging effects have not been studied in detail so far.

Generally, numerical simulations do not verify the aging phenomenon [25]. In cases in which aging is observed, it is not possible to present the magnitudes as an exclusive function of t/t_w, and obtain a good linear behavior such as in Figure 1(b). This fact is one of the main discrepancies with the experimental data. One of the reasons for this disagreement is the short simulation time employed in the standard numerical procedures, usually orders of magnitude far from the macroscopic regime.

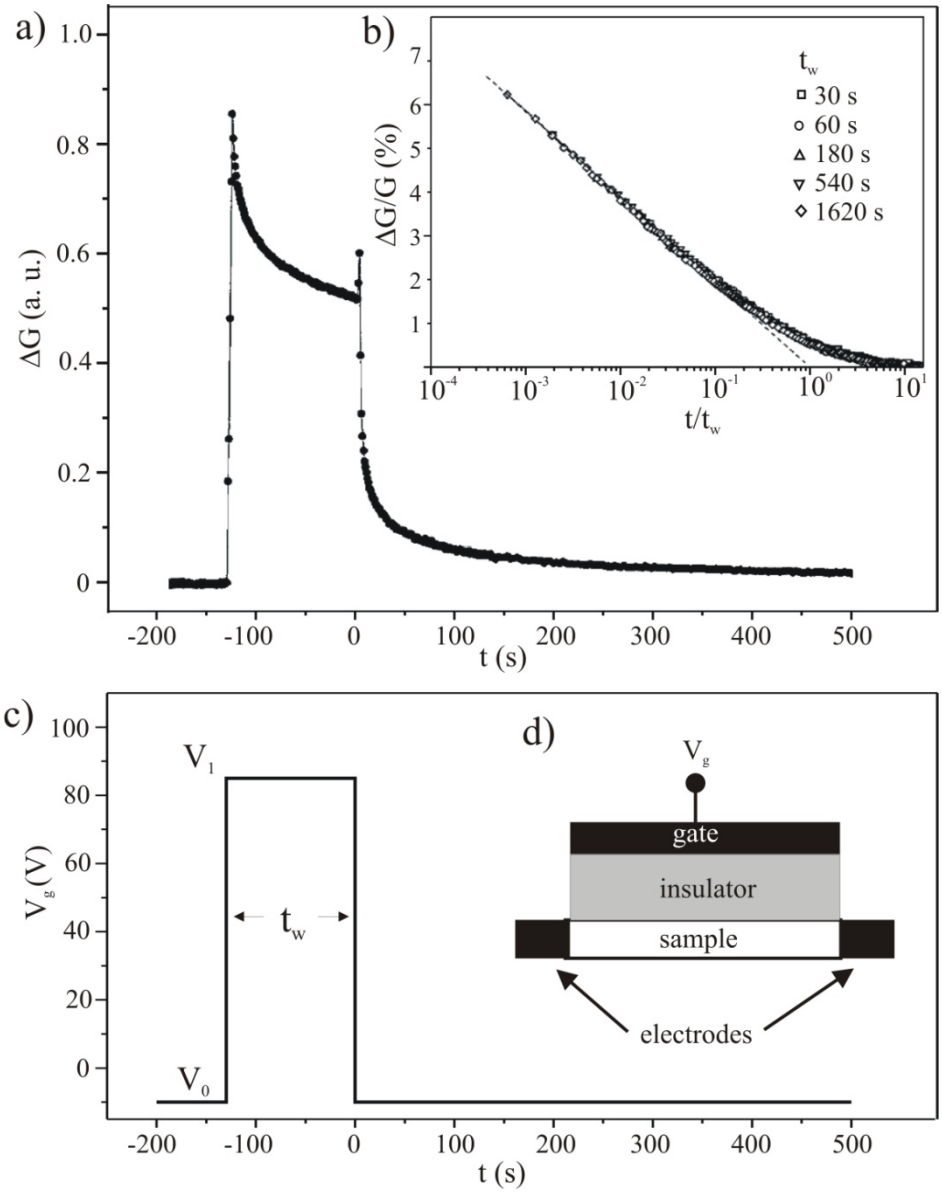

Fig. 1. (a) Excess of conductance as a function of time in a typical aging experiment. (data extracted from Pollak and Ovadyahu, 2006 [21]). (b)Relative variation of the conductance, $\Delta G/G$, as a function of t/t_w in logarithmic scale, for an applied gate voltage of 100 V. Data from different waiting times collapse in the same curve (Ovadyahu and Pollak, 2003 [4]). (c) Corresponding applied gate voltage as a function of time in the aging experiment. (d) Experimental setup for a sample with mosfet structure.

Grempel [26] performed a preliminary numerical study in electron glasses that did not reproduce a complete experiment, but the results offered signs of aging in the system. He calculated the total response function, called $\langle \Delta X(t, t_{\mathrm{w}}) \rangle$, to a disturbance caused by the application of a small external field, for various small values of t_{w}. From these data, he found evidence that the dependence of this function over time was

$$\langle \Delta X(t, t_{\mathrm{w}}) \rangle \approx \ln t\,, \qquad t \gg t_{\mathrm{w}}$$

In these data, the long time response depends on the value of t_{w}, which is indicative of the existence of aging in the system, although this study employed very small sizes and very short simulation times.

In the present work we numerically study the presence of aging in the total energy of the system in Coulomb glasses, a model which remains valid for characterizing amorphous

chalcogenides with balanced energies of interaction and disorder, respectively, at very low temperatures [19,27]. We employ an effective Monte Carlo method previously developed by some of us, the *cluster algorithm*, which works so well at very low temperatures. It is specifically designed to reach large simulation times, even macroscopic when we simulate a pure relaxation process [24]. This fact allows us to employ high different values of t_w, a fundamental requirement to properly observe the aging phenomenon.

2. Mathematical model and numerical details

At very low temperatures, the behavior of amorphous chalcogenides with comparable characteristic energies of disorder and interaction is well described by the Coulomb glass Hamiltonian [16,18]:

$$H = \sum_i \phi_i n_i + \sum_{i<j} \frac{(n_i - K)(n_j - K)}{r_{ij}},$$

where n_i is the occupancy number of site i, which can either be 0 or 1, and r_{ij} is the distance between sites i and j. Variable ϕ_i is the so-called *random site potential* [28], which represents the structural disorder of the sample, and K is the compensation, which ensures the electrical neutrality of the system. Generally we consider a value of K=0.5. It is usual to set the value of the electron charge and the dielectric constant of the medium equal to one. In this model, the electron is considered to be exactly in the position of the center of the impurity, which reflects the assumption that the localization length is small [17].

Square 2D samples of lateral dimension L are studied, with randomly placed sites in them. Half of the sites is occupied by localized electrons. The units employed in all the simulations are the following: $l_0 = L/\sqrt{N}$ is the unit of length and $1/l_0$ the unit of energy and temperature, because the electron charge, e, and Boltzmann's constant , k_B, have been taken as the unit. We consider systems in the range of 2000-4000 sites, with a minimum distance between them of 0.2. In all the simulations, the range of disorder is W=2 ($\phi_i \in [-W/2, W/2]$) and the localization length ξ is equal to 1. The characteristic time of the electron-phonon interaction, τ_0, is taken as the time unit. We impose periodic boundary conditions and consider that each particle interacts only with its nearest image and, therefore, we do not perform Ewald summation.

In our Monte Carlo simulations we have further investigated the existence of aging in glassy chalcogenides through the application of the Coulomb glass model, and we have employed sizes and times larger than those of Grempel's simulation [26]. The study reproduces the experimental situation and clearly defines all operating regimes. We will focus on the excess of energy E with respect to the ground state, E_0, E-E_0. The objective is to obtain a plot of the full experiment similar to Figure 1(a). After this, we will show the relaxation of the last stretch (after t_w) for several values of the waiting time, and try to obtain a good linear behavior that reveals the dependence of the energy excess on the variables t_w and t.

To avoid finite size effects, we have chosen samples in which the typical hopping length is small when compared with the dimensions of the system. It is worth pointing out that the algorithm lose effectiveness as we increase temperature.

One of the fundamental tasks in our simulations is to model the gate voltage switch from V_0 to V_1. In experiments, this change produces a distortion in the electronic configuration of the material, resulting in a variation of the chemical potential, μ. Thus, the initial equilibrium state becomes an excited state after the variation. Following experimental studies of Hughes *et al.* [29], it can be assumed that the change in the number of electrons due to the new applied voltage produces a quasi-random variation of site potentials ϕ_i. The study of these authors focused on the analysis of fluctuations of the conductance when a change of voltage was performed in the sample. In our simulations we model the effect of the gate voltage by a random variation of the potential site. We start placing the system in its ground state and, since we chose a very low temperature, it is a good approximation to consider that it is in equilibrium before starting the calculations. We

randomly vary the site potentials ϕ_i from the initial time. The standard procedure is similar to that we previously employed in the study of the fluctuation-dissipation theorem [30], which performs a change in the Hamiltonian of the system, ΔH, which can be written as:

$$\Delta H = \sum_i f n_i \phi'_i,$$

where ϕ'_i are random potentials completely uncorrelated with respect to the set ϕ_i and f is the amplitude of the random variation of the original potential ϕ_i. This variable plays the role of an external field. This new regime is dominated by the presence of V_1 in the experiments. We apply this change and keep the new situation for several values of the waiting time t_w. If we call t' the total simulation time, at $t'=t_w$ we will remove the effect of the external field by setting $f=0$, and measure the relaxation time $t=t'-t_w$.

3. Results and discussion

Fig. 2 shows the results of the complete simulation of aging for a system of size $N=2000$ and $T=0.001$. We selected $f=0.1$ and $t_w=7\cdot10^6$. The relaxation time t reaches a maximum value $t_{max} \approx 3t_w$. The total simulation time is $t' \approx 4t_w$. The vertical axis represents the averaged total energy per particle with respect to the fundamental level, $\langle (E-E_0)/N \rangle$, in logarithmic scale. The horizontal axis is divided into two parts. The first one, which goes from time $t'=0$ to $t'=t_w$, represents $\log t'$. The second one, for times $t'>t_w$, refers to $\log t_w + \log t$, from $t=0$. Thus, we can appreciate in more detail the last stretch of the relaxation due to the restart of the logarithmic scale. The error of the data was calculated as the standard deviation of the energy per particle of the samples. The main difference with respect to Figure 1(a) lies in the fact that, in the latter graph, the scales of the axes are both linear. In our case, this picture does not lead to an adequate viewing of the data, as long as the relaxation of the energy does not follow a pure logarithmic law, as determined in previous works [16].

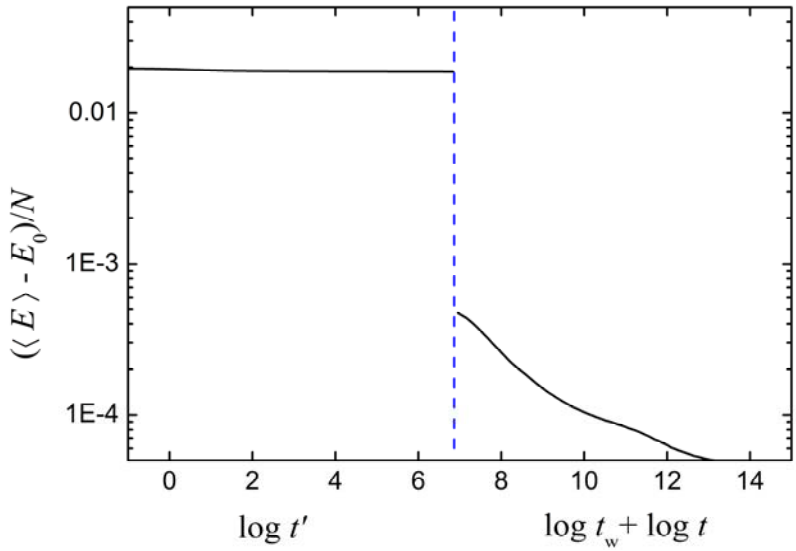

Fig. 2. Excess of energy per particle, in logarithmic scale, versus logarithm of time for a system of 2000 sites. The new relaxation process starts from time t_w, so we have restarted the logarithmic scale in the representation.

In fact, if we set the linear scale in both axis of Figure 2 we observe a sudden drop in energy and a rapid saturation of that magnitude. The low value of T imposed by the effectiveness of the cluster algorithm is another important factor which affects this phenomenon. Figure 3

represents the data concerning the first stretch of Figure 2, from t'=0 to $t'=t_w$, where we have selected linear scale on the vertical axis.

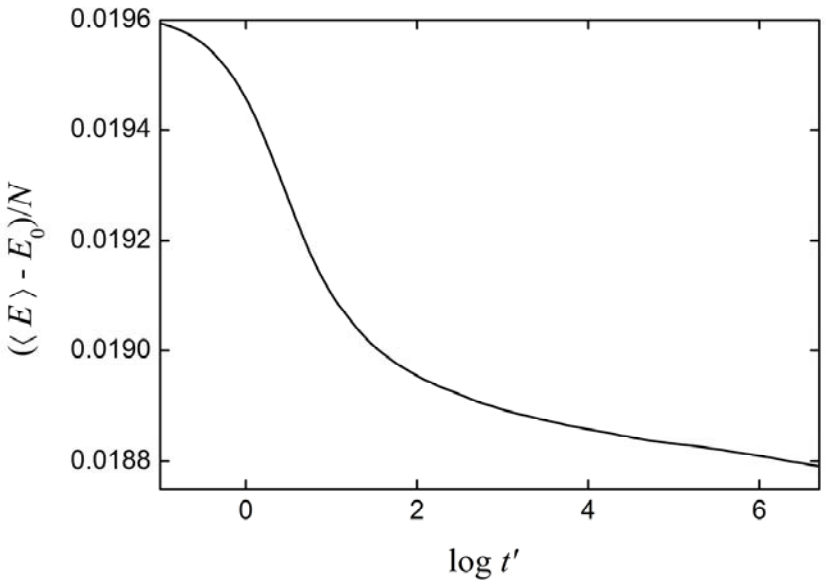

Fig. 3. Detail of the first relaxation time (before t_w) of Figure 2, where we have selected linear scale on the vertical axis.

The choice of parameters f and t_w should be carried out carefully. In the aging experiment, it is mandatory that the applied field is large enough to cause some decorrelation of the initial state, and small enough to not completely decorrelate the system in the new situation. In order to set an appropriate operating range for the variable f we have considered that 20% of the electrons change its status once the electric field is connected, which corresponds to a numerical value of f=0.1. In addition, the waiting time should be sufficiently large to achieve the slow relaxation regime while maintaining a certain memory in the system. To fulfill this condition it seems reasonable to assume the hypothesis proposed by Pollak and Ovadyahu [21]. According to their theoretical argument, in an aging experiment, the energy that the system relaxes during the time t_w must be roughly the same as the difference of energy with respect to the ground level once the last relaxation process is initiated. This hypothesis is fulfilled reasonably well with t_w ranging from 10^6 to 10^7, for all our simulations.

Finally, we discuss the behavior of the system once we disable the electric field and return to the original situation, in terms of t_w and t. Initially, we plotted the energy per particle as a function of t_w and t, but we found no evidence to obey a law of the type $\log(t/t_w)$. Within this frame, the curves corresponding to different t_w are not scalable, do not present linear behavior and do not extrapolate to the value 1 observed in the experiments (see Figure 4). This fact may be due to different factors. Among them, we can argue that the dependence of the energy on time does not follow a pure logarithmic law, and that the sizes considered in the simulations can still be small. Greater control over the selection of the parameters f and t_w is another determining factor. Finally, the presence of multi-electron processes can be crucial, especially for longer relaxation times. With all this in mind, we can assume that our simulations do not verify the phenomenon of full aging.

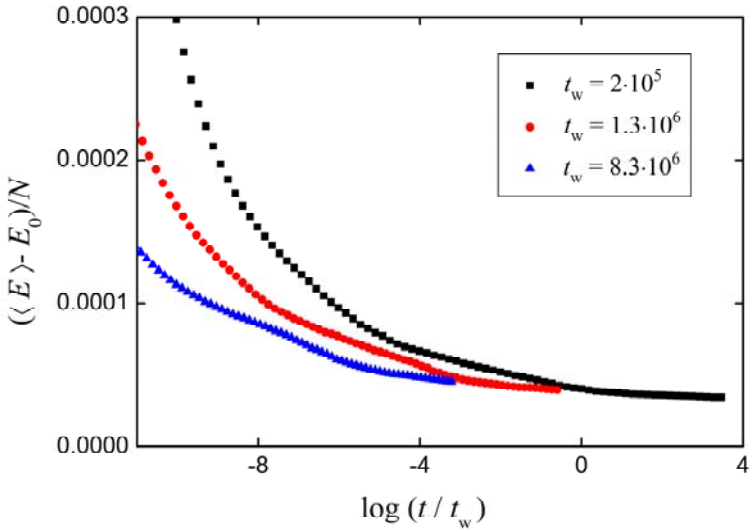

Fig. 4. Excess of energy per particle as a function of $\log t - \log t_w$ *for a system of 2000 sites and waiting times 2· 10^5 (squares), 1.3·10^6 (circles) and 8.3·10^6 (triangles).*

However, we are able to collapse the corresponding curves that belong to different values of the waiting time and obtain a good linear dependence in order to establish an aging law related to the energy. In previous numerical simulations [24] we found that the energy relaxation followed a time dependence of the type $1/\log t^{\alpha}$, with α=3, so it is reasonable to assume that the aging relaxation will exhibit a nearly similar behavior in terms of t. For the aging simulations we have found in all cases that, at sufficiently long times, the excess of energy per particle verifies

$$\frac{\langle E\rangle - E_0}{N} \propto \frac{1}{\log t}$$

Therefore, it seems natural to infer that the scaling of the energy for different values of t_w can be obtained by employing the variable $1/\log t - 1/\log t_w$ on the horizontal axis. This new frame is shown in Figure 5, which represents the excess of energy per particle as a function of $1/\log t - 1/\log t_w$, measured from t_w, for a system of size N=2000 and waiting times t_w=2· 10^5 (squares), 1.3·10^6 (circles) and 8.3·10^6 (triangles). As can be seen, the overlap of the data is quite good throughout the range considered.

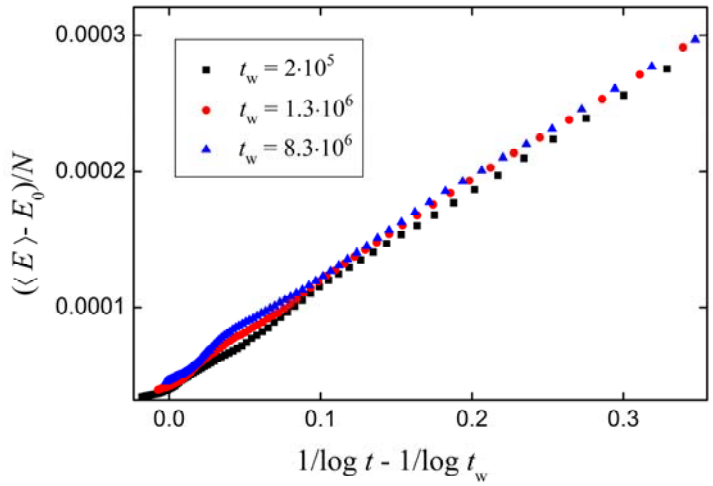

Fig. 5. Excess of energy per particle as a function of $1/\log t - 1/\log t_w$ *for a system of 2000 sites and waiting times 2· 10^5 (squares), 1.3·10^6 (circles) and 8.3·10^6 (triangles).*

4. Conclusions

We have employed an effective Monte Carlo procedure, the cluster algorithm, to numerically simulate the aging effect in glassy non-oxide chalcogenides. The method works so well at very low temperatures (when the aging phenomenon is accentuated) and allows us to reach large times of simulation, which is the main deficiency of previous numerical algorithms. This fact enable us to analyze the behavior of the system for several large values of the waiting time.

We found that we can model aging phenomenon by means of the energy relaxation in electron glasses. The results are clear and reproduce the aging experiment, and can help to explain the behavior of glassy chalcogenides at very low temperatures, when energies of disorder and interaction are comparable. The key of the presented results is the dependence of the excess energy per particle on both the waiting time and the relaxation time. To characterize the final relaxation process we have proposed a model that collapses the curves for different values of the waiting time, and so defines an aging law, although we do not observe full aging. A nearby target is to extend the study of this phenomenon. Future work is focused towards: (a) trying larger sizes and temperatures, (b) performing three-dimensional and pseudo two-dimensional simulations and (c) optimizing the algorithm for the study of conductivity. All this in order to accurately reproduce the experimental situation. Since we use the cluster algorithm previously developed by some of us, we cannot reach temperatures much higher than 0.001, because the numerical method becomes inefficient. However, the times reached by the algorithm allow us to study in detail the influence of t_w, which is the main lack of numerical simulations in aging, because we can get larger relaxation times with respect to previous numerical methods.

Acknowledgments

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