



The race between relaxation and nucleation in supercooled liquid and glassy BaS – A molecular dynamics study

José Pedro Rino^{a,d,*}, Sandra Cristina C. Prado^b, Edgar D. Zanotto^{c,d}

^a Departamento de Física, Universidade Federal de São Carlos, Brazil

^b Faculdade de Tecnologia de Mococa, Ave. Dr. Américo Pereira Lima, s/n, 13736-260 Mococa, SP, Brazil

^c Departamento de Engenharia dos Materiais, Universidade Federal de São Carlos, Via Washington Luiz km 235, 13.565-905 São Carlos SP, Brazil

^d Center for Research, Technology and Education in Vitreous Materials, Universidade Federal de São Carlos, São Carlos SP, Brazil

ARTICLE INFO

Keywords:

Molecular dynamics
Supercooled liquid
Barium sulfide
BaS
Viscosity
Relaxation
Crystal nucleation

ABSTRACT

Details of the microscopic mechanisms and dynamics of most processes in supercooled liquids (SCL) and glasses remain blurred due to their complexity and the extraordinarily long or inaccessibly short timescales, depending on the supercooling degree. In this paper, we determined the structural relaxation times in an intermediate supercooling window ($0.67\text{--}0.78 T_m$, T_m = melting point) of barium sulfide liquid, used as a model material, through molecular dynamics (MD) simulations based on a reliable two-body interatomic potential. We also inferred these dynamics in the glassy state using extrapolated data and well-accepted models. The average structural α -relaxation times, $\langle \tau_\alpha \rangle$, were determined via the intermediate scattering function. Relaxation kinetics were also estimated by the Maxwell relation via the equilibrium shear viscosity and shear modulus, obtained by MD. We found that the viscosity derived (Maxwell) relaxation times are significantly shorter than the intrinsic α -relaxation times, corroborating two recent experimental studies of other substances. For the simulated system, with 36,000 particles and average volume of $1.4 \times 10^3 \text{ nm}^3$, the structural relaxation and nucleus birth time curves cross at the kinetic spinodal temperature, T_{KS} ($=0.33 T_m$), which is significantly below the glass transition temperature, T_g ($=0.44 T_m$). However, for larger sample sizes, the T_{KS} occurs at higher temperatures. As for temperatures above T_{KS} , crystal nucleation starts after structural relaxation, and vice-versa, to understand and describe crystal nucleation one must necessarily take the relaxation process into account, however, this is not included in nucleation theories. These discoveries shed light on some obscure aspects of supercooled liquids, i.e., they challenge a critical assumption of nucleation theories (that crystal nucleation always occurs in a fully relaxed SCL), and show that crystallization is BaS ultimate fate, corroborating studies with other substances.

1. Introduction

Semiconductors of the barium chalcogenide family (BaS, BaSe, BaTe) crystallize in a rock-salt structure. BaS, in particular, has a large band-gap and has been considered for several technological applications, such as laser diodes, light-emitting diodes, and magneto-optic devices. In a previous article, one of us developed and tested a two-body interatomic potential to describe several properties of BaS with great success [1]. This interatomic potential describes very well several thermodynamic quantities, the structural transformation under pressure to the cesium chloride structure [1], and the spontaneous homogeneous nucleation rate in a supercooled region [2].

In this study, we take advantage of this excellent potential and its

ability to describe nucleation kinetics to advance a further important step and compare the times required for the formation of the first critical nuclei with the structural relaxation times. Hence, we use BaS as *model material* to unveil the relationships between these two dynamic processes. This is an open relevant topic that has been scarcely explored. The key issue is to find out whether supercooled liquids (SCLs) *relax before crystal nucleation is triggered, or if the relaxation and nucleation time versus temperature curves crossover* at a (so-called) kinetic spinodal temperature, T_{KS} . This is a particularly relevant topic because it could shed light on the interplay of relaxation and nucleation. Also, if the existence of T_{KS} is confirmed, it would mean that crystallization is indeed the ultimate fate of supercooled liquids and glasses.

Another open question is whether *the structural relaxation times can be*

* Corresponding author at: Departamento de Física, Universidade Federal de São Carlos, Brazil.

E-mail address: djpr@df.ufscar.br (J.P. Rino).

described through the viscosity via the Maxwell relation. There is significant interest by the physics, chemistry, and materials science communities in these problems, especially in understanding whether the relaxation process is related to and can affect the birth of crystalline nuclei in SCLs. Although direct experimental observation of these quantities is quite difficult, computer simulations can yield valuable information regarding these dynamic processes.

To the best of our knowledge, only a few studies have been carried out on this particular problem. For instance, in pioneering work, Saika-Voivod et al. [3] performed molecular dynamics simulations of high-density liquid silica in a range of supercooling, in which both the crystallization and characteristic dynamics of the liquid were detectable. They found that the supercooled liquid could not be observed at temperatures smaller than T_{KS} , below which the crystal nuclei formed before relaxation to a metastable state.

Ingebritsen et al. [4] have unveiled a mechanism of crystallization in multicomponent systems. They found that the supercooled liquid of a toy model glass former (Kob-Andersen model) is inherently unstable to crystallization, i.e., nucleation is unavoidable on the structural relaxation timescale, for system sizes of 10,000 particles and larger. This is due to compositional fluctuations leading to regions composed of one species that are larger than the critical nucleus of that species, which rapidly crystallize. They have also shown that the same mechanism relates to the metallic glass former copper zirconium (CuZr). Their simulations of the KA model and CuZr supercooled liquid indicate that their flaw as a glass former, could be active in other mixtures. Local compositional fluctuations lead to regions populated only by one species, which can be larger than the critical crystal nucleus size of the one-component system under similar conditions. Nucleation in these regions is fast on the timescale of these deeply supercooled liquids, apparently requiring little rearrangement of the particles. The same behavior was reported for hard spheres at deep supercooling [5,6].

At least two other MD simulations of metallic systems have been reported on this particular problem. Zhang et al. [7], using an embedded atom model for Ni, showed that in a supercooling range of 160 K, crystallization of the liquid only occurs *after* relaxation. In the second study, Pang et al. [8] worked with supercooled liquid Cu. They also concluded that, in a window of 150 K in the supercooled region, structural rearrangements were a leading factor before incipient nucleation. Hence, both studies obtained similar results showing that, in the supercooling regime accessible to their MD simulations (above T_g), these systems relax before the beginning of crystallization.

Regarding experimental studies, in two related projects, Zanotto and Cassar [9] and Gupta et al. [10] using a large thermodynamic and kinetic dataset, together with a well-established theoretical model, calculated the kinetic spinodal temperature and the Kauzmann temperature, T_K (where the entropy of the SCL would be equal to the crystal entropy) for the oxide glass-forming systems $Li_2O.2B_2O_3$ and $Li_2O.2SiO_2$. They showed that T_{KS} exist for these systems and are significantly *higher* than the predicted T_K . Hence, the temperature of entropy catastrophe cannot be reached by these supercooled liquids; they would crystallize first. Their finding corroborated the simulations results for silica of Saika-Voivod et al. [3].

Hence, this relevant topic in glass science has not been extensively studied and calls for further research to extend, generalize or not the findings of the above reported articles.

To understand and describe the structural relaxation process, it is necessary to analyze a massive number of atomic configurations of the system as a function of time. An appropriate way to perform this task is by evaluating the “intermediate self-scattering function”, which characterizes the density fluctuations of all particles at different times. This function can be obtained experimentally, using time-of-flight neutron scattering, or by computer simulations. An alternative way to obtain details of the relaxation process is through viscosity. The shear viscosity, η , and instantaneous shear modulus, G_{00} , which can also be obtained experimentally or by simulations, are connected by the average

relaxation time through the classical Maxwell relation ($\tau_\eta = \eta / G_{00}$).

In this article, we use a successful pair potential to describe barium sulfide for determining the intermediate scattering function and the shear viscosity as a function of temperature. We aim at evaluating the structural relaxation times for this system, used as a model material due to its reliable interatomic potential. Then, we compare the average relaxation times with the average times needed to form the first critical nucleus (determined in our previous publication [2], using the same potential) in the same supercooling range. Finally, we extrapolate these times to test whether they cross at any temperature range defining a T_{KS} .

2. Molecular dynamics details

The present work is partly dedicated to studying the temperature dependence of the Self Intermediate Scattering Function. We use molecular dynamics simulations based on a two-body interaction potential, which has been previously proposed by Rino [1]. The model was validated by successfully comparing some simulated properties with experimental values: crystal lattice constant, cohesive energy, bulk modulus, and the C_{11} elastic constant. A more robust validation was provided by the experimental agreement of the melting temperature, vibrational density of states, and the adequate description of a phase transformation induced by hydrostatic pressure: rock-salt to cesium chloride structure. Hence, the used potential seems to be quite solid.

Initially, our BaS was organized as a rock-salt (B1) structure containing 36,000 particles at the experimental density. Periodic boundary conditions were applied in all directions. The velocity Verlet algorithm was used to integrate the motion equations with a time step of 1.5 fs. The initial RS structure at low temperature (50 K) was heated up to 3400 K with a heating rate of 20 K/ps. The system was cooled down to 50 K using two cooling rates, 20 K/ps and 50 K/ps, from a well-thermalized liquid. At each temperature, the system was allowed to thermalize for 50,000-time steps before computing the average values of the physical quantities of interest over additional 50,000-time steps. All simulations were done using the LAMMPS package [11] in a NPT ensemble. The self-diffusion coefficient, viscosity, and the intermediate scattering function were computed for two system sizes, 36,000 and 64,000 particles, and no effects were detected for these two box sizes.

The specific methods and theoretical models used to obtain the properties of interest to this research, melting point and relaxation times (T_m , τ_α , τ_η), are described in the next section jointly with the results.

3. Results and discussion

3.1. Melting point

The melting temperature knowledge is a necessary step to determine the supercooled region and calculate crystal nucleation rates. Fig. 1 shows the volume fraction (V_0 is the volume of the system at 0 K) for both heating and cooling procedures. Depending on the cooling rate, we obtained a recrystallized or a vitreous sample. The melting temperature was obtained through the two-phase coexistence method, resulting in $T_m = 2450 \pm 20$ K [1].

4. Relaxation

The incoherent intermediate self-scattering function is defined as

$$F_s(q, t) = N_\alpha^{-1} \sum_{j=1}^{N_\alpha} \langle \exp(i\vec{q} \cdot [\vec{r}_j^\alpha(t) - \vec{r}_j^\alpha(0)]) \rangle \quad (1)$$

where N_α is the total number of particles (Ba and S) and $\vec{r}_j^\alpha(t)$, the atomic position of all j particles of species α . The MD trajectories give the $\vec{r}_j^\alpha(t)$ for all particles in the supercooled region at several temperatures.

Fig. 2(a) and 2(b) show the time dependence of the intermediate-scattering function for Ba and S, respectively, for several

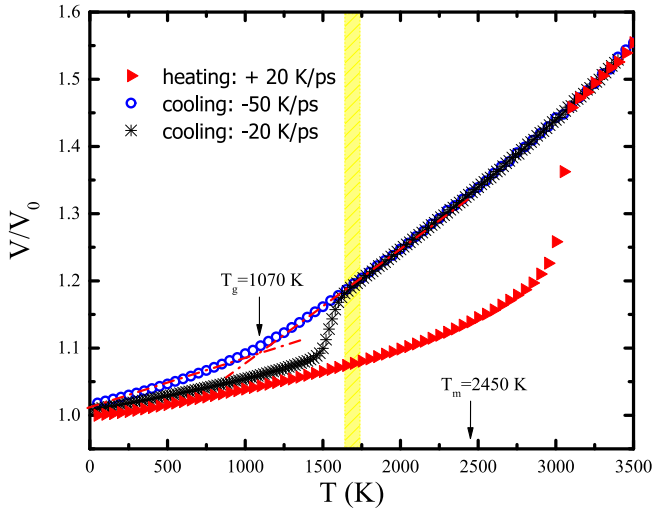


Fig. 1. Normalized volume as a function of temperature for the heating and cooling procedures. This figure shows an overall map of the temperature ranges where relaxation and nucleation processes were focused in this research. On cooling at 20 K/ps the system crystallizes, whereas at 50 K/ps it vitrifies at $T_g \sim 1070$ K ($0.44 T_m$). The yellow stripe ($0.67\text{--}0.78 T_m$) shows the region where spontaneous nucleation was observed in our isothermal simulations after fast quenching. Relaxation kinetics were measured in this same temperature interval.

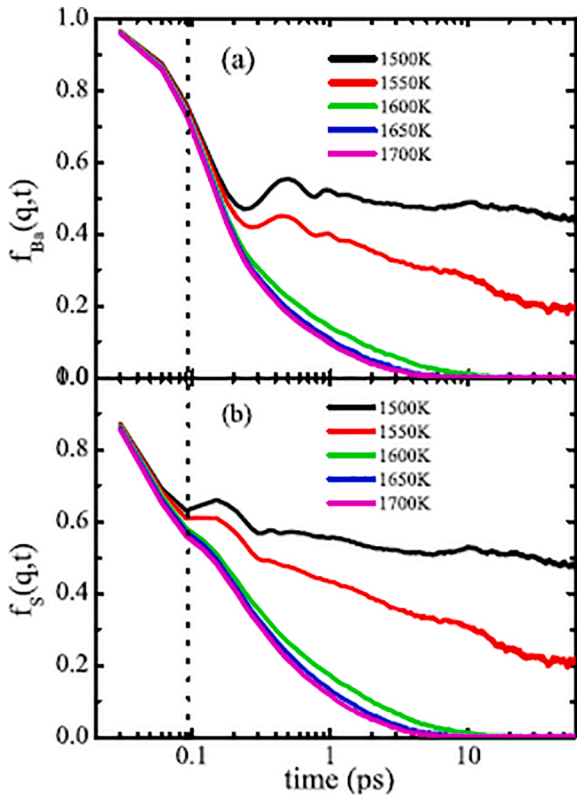


Fig. 2. Time dependence of the incoherent intermediate-scattering function at five temperatures in the supercooled liquid region for (a) Ba, and (b) S.

temperatures. The wave-vector q corresponds to the first sharp diffraction peak position in the static structure factor, in our case, 3 \AA^{-1} . For the barium atoms at temperatures above 1650 K, all intermediate-scattering functions decay exponentially. However, for sulfur correlations (Fig. 3), this function shows different behavior. Even at 1700 K, a

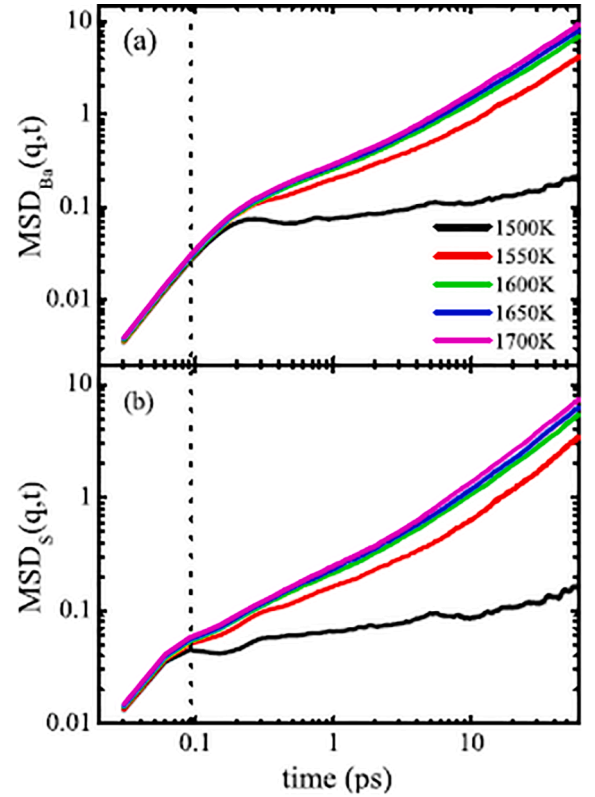


Fig. 3. Mean squared displacements as a function of time for (a) Ba and (b) S. Around 0.1 ps, the sulfur atoms display a plateau for low temperature and a change in the curve slope for higher temperatures. This behavior was also observed for Ba atoms for longer times.

plateau appears around 0.1 ps. As discussed in other publications [12,13], this plateau is related to the “cage effect”, that is, in that time scale, the S atoms are trapped by their neighbors. Hence, the sulfur atoms become ensnared somewhat earlier than the barium atoms. This conclusion could be observed more explicitly through the mean squared displacement in a log–log scale [14], as shown in Fig. 4.

At 1550 K, sulfur correlations display a minimum at around 0.1 ps, a little earlier than for Ba. For the other two temperatures, 1550 and 1500 K, the intermediate-scattering functions do not reach zero due to the short time scale considered, and the system starts to crystallize.

The incoherent intermediate-scattering function allows us to determine the characteristic structural relaxation time, τ_α^{KWW} through a stretched exponential equation, known as the Kohlrausch–Willian–Watts (KWW) function, which provides a good fit to the long-term behavior [15].

Thus, the KWW function allows us to obtain the α -relaxation time, and the factor β is defined by [15]

$$F_s(q, t) = F_s(q, t_0) \exp\left[-\left(\frac{t - t_0}{\tau_\alpha^{KWW}}\right)^\beta\right] \quad (2)$$

The instant of reference, t_0 , was chosen to be 0.54 ps when F_s reached the value of 0.2 for the highest temperature; hence β could be determined unambiguously [15]. Table 1 summarizes the values of α -relaxation time, τ_α^{KWW} , and the stretched-exponential factor, β , as a function of temperature for each species.

In the whole SCL interval studied, the sulfur atoms always relax later than barium. This was an expected result knowing that the sulfur atoms become trapped for some time, Fig. 2.b.

The α -relaxation times and the non-exponential factors, β , are shown in Fig. 4 as a function of temperature. As the temperature increases, the system relaxes faster, as expected. Even at 1900 K, the system does not

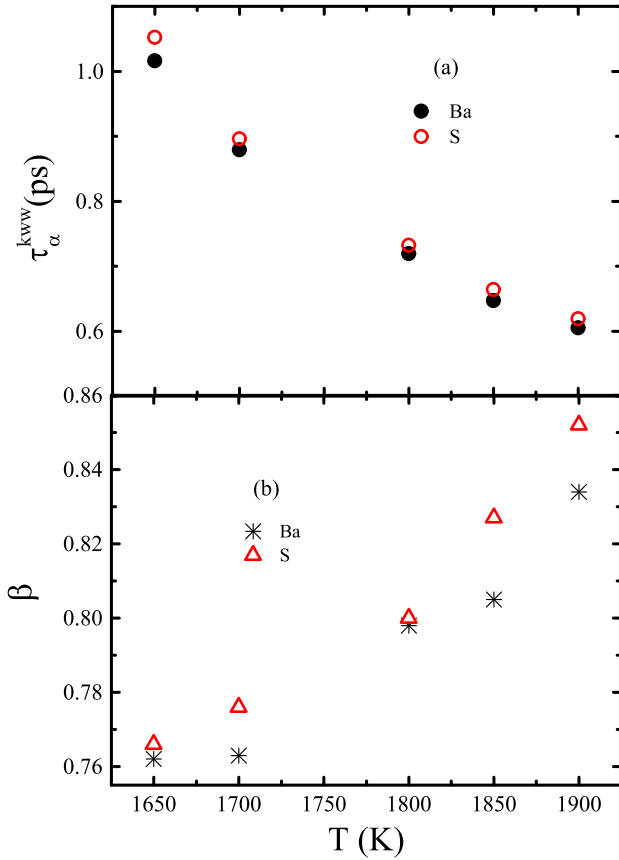


Fig. 4. Structural relaxation time and the stretched-exponential factor, β , as a function of temperature in the SCL region.

Table 1

Average structural relaxation times, τ_{α}^{kww} — and the stretched-exponential factors, β , calculated from the KWW fitting for each atomic species.

T (K)	τ_{α}^{kww} — Ba (ps)	β — Ba	R^2	χ^2
1650	1.059 ± 0.005	0.761 ± 0.003	0.998	0.001
1700	0.878 ± 0.004	0.763 ± 0.002	0.998	0.001
1800	0.718 ± 0.004	0.798 ± 0.004	0.997	0.001
1850	0.647 ± 0.005	0.805 ± 0.005	0.996	0.001
1900	0.605 ± 0.005	0.833 ± 0.006	0.996	0.001
T (K)	τ_{α}^{kww} — S (ps)	β — S	R^2	χ^2
1650	1.052 ± 0.004	0.766 ± 0.002	0.999	0.001
1700	0.895 ± 0.004	0.773 ± 0.002	0.998	0.001
1800	0.732 ± 0.003	0.800 ± 0.003	0.998	0.001
1850	0.664 ± 0.004	0.827 ± 0.005	0.997	0.001
1900	0.618 ± 0.004	0.852 ± 0.005	0.997	0.001

show a real exponential decay, the stretched-exponential factor is still below 1.00, i.e., $\beta = 0.84$.

Knowing the α -relaxation time and the non-exponential factor computed from the KWW equation, we can evaluate the average relaxation time, $\langle \tau_{\alpha} \rangle$, through the equation $\langle \tau_{\alpha} \rangle = \frac{\tau_{\alpha}^{kww}}{\beta} \Gamma\left(\frac{1}{\beta}\right)$ [16–18], where Γ is the Gamma function. These average relaxation times are summarized in Table 2. τ_{α}^{kww} is the average obtained over seven simulated samples, hence the minimum and maximum relaxation times were also determined.

5. Crystal nucleation

In a previous work [2], we computed the *birth times*, τ_1 , i.e., the

Table 2

Average birth times and average relaxation times for BaS estimated in two different ways—from Maxwell relation (τ_{η}), and from the intermediate scattering function (τ_{α}^{kww}). The time for the system to relax 99.9% is also displayed.

T(K)	Average birth time τ_1 (ps)	α -relaxation time τ_{α}^{kww} (ps)	Average relaxation time $\langle \tau_{\alpha} \rangle$ (ps)	From Maxwell relation τ_{η} (ps)	Time to relax 99.9% T99.9% (ps)
1650	120 ± 50	1.03 ± 0.02	1.21 ± 0.02	–	7.9
1680	170 ± 60	0.95 ± 0.02	1.11 ± 0.02	0.36 ± 0.02	–
1700	270 ± 70	0.89 ± 0.02	1.04 ± 0.02	0.34 ± 0.02	5.6
1800	–	0.73 ± 0.01	0.82 ± 0.01	0.30 ± 0.02	4.1

average time needed for the first critical crystal nucleus to appear in the supercooled liquid at any given supercooling. These birth times were computed based on the detection and crystal growth process observed in atomic configurations in snapshots, using the standard neighbor analysis implemented in the OVITO software [19]. The number of face-centered cubic structures forming as a function of time was identified, and the birth time was then determined. This procedure was carried out for 8 to 15 samples, and the reported birth time refers to the average over all samples [2].

6. Viscosity

The shear viscosity of a liquid can be calculated using the Green–Kubo relation:

$$\eta = \frac{\beta V}{N} \int_0^{\infty} \langle P_{\alpha\gamma}(0)P_{\alpha\gamma}(t) \rangle dt \quad (3)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, V and N are the volume and the number of particles in the system, respectively, and $P_{\alpha\gamma}$ are the off-diagonal, P_{xy} , P_{xz} or P_{yz} , of the stress tensor. The shear viscosity is an average over all three off-diagonal terms $\eta = \frac{1}{3} (P_{xy} + P_{xz} + P_{yz})$, and averaged over six samples.

The rationale behind these calculations is that average structural relaxation times can also be estimated by the shear viscosity, which relies on cooperative atomic rearrangements in the liquid. Recalling that the Maxwell relation states that the average relaxation time is proportional to the shear viscosity, $\tau_{\eta} = \eta / G_{00}$. The shear modulus for BaS glass is unavailable, so using MD trajectories, we computed the elastic constants for the crystalline phase [1] and the corresponding elastic moduli, resulting in approximately 58 GPa for the shear modulus. As, the infinite frequency shear modulus of the isochemical glass is typically similar to the crystal, the magnitude of the average structural relaxation times can be estimated using the crystal value. This part of this work is also vital because many experimental studies rely on the shear viscosity to describe structural and stress relaxation times, however, this topic is currently still under debate.

Defining the atomic relaxation time as the arithmetic average between Ba and S atoms' relaxation times, we compare all these relaxation times and nucleus birth times in Table 2. Once we have all the fitted parameter for Eq. (2), we computed the time, $\tau_{99.9\%}$, needed for the system to relax 99.9%. Table 2 also display this time, $\tau_{99.9\%}$.

Fig. 5 shows the average relaxation times computed from the intermediate scattering function, $\langle \tau_{\alpha} \rangle$ and from Maxwell relation, τ_{η} . In the supercooled region studied, τ_{η} are approximately 5 to 6 times *smaller* than $\langle \tau_{\alpha} \rangle$, and this difference *increases* with decreasing temperature. Such difference is clearly shown in Fig. 5.

These two types of relaxation times were fitted with the Waterton [20] / Mauro–Yue–Ellison–Gupta–Allan (MYEGA) [21] equation:

$$\log_{10}(\eta) = \log_{10}(\eta_{\infty}) + \frac{E}{T} \exp(A/T) \quad (4)$$

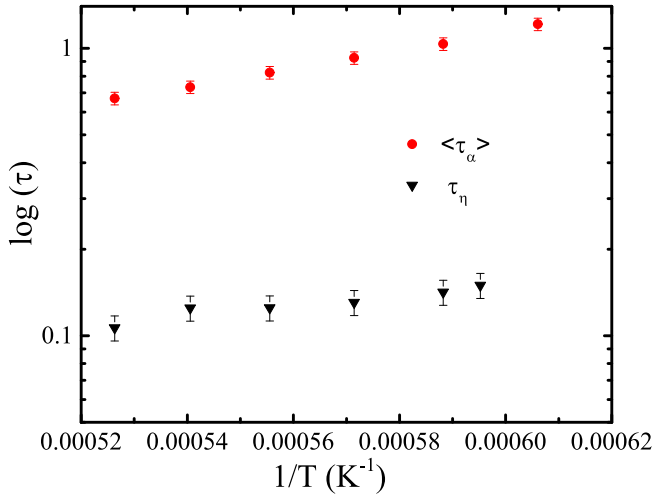


Fig. 5. Comparison of the average relaxation times calculated from the intermediate scattering function via the KWW expression, and obtained from the shear viscosity and shear modulus via the Maxwell relation.

where E , A , and η_{∞} are adjustable parameters obtained from the regressions with equilibrium viscosity data. The MYEGA equation is likely to give a better estimate at deep supercooling than other viscosity models [16].

The birth times can be readily extrapolated to lower temperatures because in ref. [2] we have already determined the temperature dependence of the homogeneous nucleation rates, $J_{ss} = 1/\tau_1 V$ [2]. The nucleation rates were fitted with the Classical Nucleation Theory (CNT) expression:

$$\frac{J_{ss}\sqrt{T}}{D} = A\hat{A}\exp\left(-B^*\frac{1}{T\Delta G^2}\right) \quad (5)$$

where \hat{A} and B are fitting parameters, which are related to the pre-factor, the nucleus shape and the interfacial free energy, respectively [2], and D is the diffusion coefficient.

Previous MD simulations [2] also yielded the diffusion coefficient as a function of temperature, hence the $J_{ss}(T)$ curve could be obtained (Fig. A1). Therefore, by inverting $J_{ss}(T)$, the birth times [$\tau_1 = 1/(VJ_{ss}(T))$; $V = \text{box volume}$], could be extrapolated to lower temperatures. The parameters in the MYEGA expressions were determined using

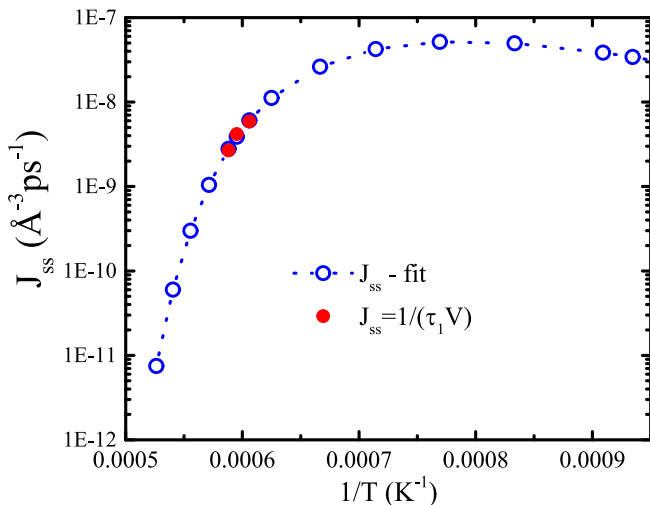


Fig. A1. Homogeneous nucleation rates, J_{ss} , obtained from MD simulations (red circles) and extrapolation using a CNT fit (open blue circles) to shallow and deep supercoolings.

all MD values calculated for the equilibrium shear viscosity from 2100 K to 1680 K.

Fig. 6 summarizes the main results of this article. It displays the average nucleus birth times for different system sizes, the two relaxation times ($\langle \tau_{\alpha} \rangle$, τ_{η}) and their corresponding extrapolated curves down to a very deep supercooling, using the MYEGA approach.

We provide detailed information on all the fitting parameters in the Appendix.

The τ_{η} relaxation times obtained from the Maxwell relation were also fitted with the MYEGA equation, however, the extrapolated τ_{η} never crosses the τ_1 curve. On the other hand, using the same equation, the average α -relaxation times, $\langle \tau_{\alpha} \rangle$, crossed the extrapolated birth time curve at $T_{KS} = 810$ K, corresponding to $0.33 T_m$. In this case, a very small simulation box, $V = 1.28 \times 10^3 \text{ nm}^3$ at 1000 K (36,000 particles), was used. The equation $\tau_1 = (J_{ss}V)^{-1}$ indicates that for any larger simulation box, τ_1 would be even smaller, i.e., the two curves would cross at an even higher T_{KS} , even surpassing T_g .

It is important to mention that, in the intermediate supercooling range above T_g directly probed by MD, the shear viscosity (Maxwell) relaxation times are 5–6 times *shorter* than the intrinsic structural relaxation times, and this difference *increases* with decreasing temperature. This finding corroborates two detailed, recent *experimental* studies on the relaxation kinetics of Jade glass [16] and lead metasilicate glass [17]. In other words, the use of shear viscosity and the Maxwell equation *underestimates* the actual structural relaxation times.

However, due to the above-mentioned problem, even if we leave the viscosity relaxation aside, due to the long extrapolations of $\langle \tau_{\alpha} \rangle$ and τ_1 , and the volume dependence of τ_1 , the exact location of T_{KS} is uncertain. However, our results indeed indicate that the average structural α -relaxation times eventually *cross* the nucleation birth time curve. Therefore, only for $T < T_{KS}$, crystal nucleation would take place *before* structural relaxation. At higher temperatures, relaxation takes place simultaneously or before the birth of the first critical nucleus. Fig. 6 further shows that, in the supercooling range (0.67–0.70 T_m) probed by MD, the times necessary for the birth of the first crystal nucleus are over two orders of magnitude *longer* than the average relaxation times. We also calculated the times necessary for 99.9% relaxation; they are only

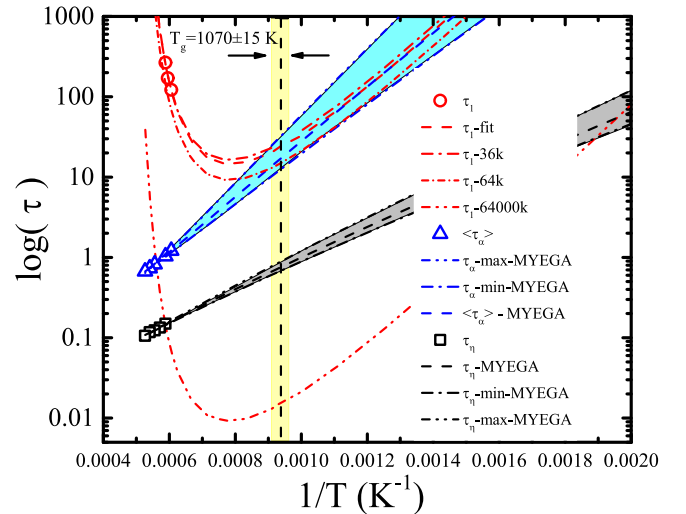


Fig. 6. Logarithm of the average nucleation birth times, τ_1 , fitted with the CNT (see Appendix), and relaxation times estimated via the intermediate scattering function, $\langle \tau_{\alpha} \rangle$, and via viscosity, τ_{η} , and the respective fittings with the MYEGA equation. The vertical band depicts the glass transition range (T_g) for the cooling rate used, 0.83 K/ps. The T_{KS} , where the birth times and the structural relaxation times cross, vary with the system volume. It covers a wide range from above to below T_g . Here τ_1 -64 k and τ_1 -64000 k mean the birth time for a system with 64,000 and 64,000,000 particles, respectively. For a system of 64,000 particles ($V \sim 2.4 \times 10^6 \text{ nm}^3$) and above, $T_{KS} > T_g$.

5.0–6.5 times longer than the average relaxation times and still much shorter than the times to form the first nucleus.

This means that the structural relaxation process does not play a significant role on the nucleation kinetics of the SCL in *this temperature range*, which supports the nucleation theories. Most models assume that nucleation takes place in a fully relaxed SCL. However, depending on the system size, for understanding and describing crystal nucleation at deeper supercoolings, we must necessarily take the relaxation process into account. And this is exactly what was shown in two recent studies [22,23]. Finally, the findings of this work demonstrate that the fate of this metastable supercooled liquid and its derived (unstable) glass, before or after relaxation, is to crystallize in a finite time [24,25], becoming a thermodynamically stable material. In other words, after the first crystal nucleus overcomes the thermodynamic barrier and forms, crystal growth takes place spontaneously leading to full crystallization after some time. For crystal growth there is no longer a thermodynamic barrier, only the kinetic barrier remains.

This interplay between relaxation and crystal nucleation is an essential feature of the glassy state and warrants further studies with other systems and other approaches to generalize them.

7. Conclusions

We demonstrated that the relaxation times calculated from the shear viscosity are *shorter* than the structural (α -relaxation) times, confirming two recent experimental studies with different materials. Therefore, the use of shear viscosity to infer structural relaxation times, as is frequently done in experimental studies, only gives a lower bound.

Another relevant finding is that the structural relaxation time and nucleus birth time curves indeed *cross* at a T_{KS} , which can be above or below the glass transition temperature, depending on the system size. For experiments at temperatures below T_{KS} , crystal nucleation starts before relaxation, whereas above it, the system relaxes (the metastable SCL state is reached) *before* the nucleation process is triggered. Therefore, depending on the supercooling probed, structural relaxation can

Appendix

The relaxation times calculated from the KWW function and viscosity using the Maxwell relation, were obtained at four temperatures. These relaxation times were fitted with the MYEGA equation, Eq. (4). Table A1 below summarizes the values of all fitted parameters for this equation.

The extrapolation of the birth times, τ_1 , to deep supercoolings, was done as follows:

Molecular dynamics simulation provided the melting temperature, nucleus birth times, τ_1 (T), enthalpy, self-diffusion coefficient, viscosity as a function of temperature. Knowing

τ_1 (T), we computed the homogenous nucleation rates, J_{ss} . Assuming that the homogenous nucleation rate can be described by the Classical Nucleation Theory (CNT), and assuming that the driving force is given by $\Delta G = \frac{\Delta H}{V} \left(\frac{T_m - T}{T_m} \right)$, $\frac{J_{ss}\sqrt{T}}{D}$ was plotted as a function of $\frac{1}{T\Delta G^2}$. This curve was fitted by the CNT expression $\frac{J_{ss}\sqrt{T}}{D} = A \exp(-B^* \frac{1}{T\Delta G^2})$. The fitted parameters A and B are $A = 0.12805$ and $B = -0.10577$, with a coefficient of determination $R^2 = 0.992$.

From the fitted equation and the diffusion coefficient as a function of temperature, it was straightforward to obtain the homogeneous nucleation rate for all temperatures, as shown below. As $J_{ss} = 1/(\tau_1 V)$, inverting it we obtained τ_1 for a whole supercooling range, Fig. 6. In this particular case, for a system with 36,000 particles, the box volume, due to thermal expansion, is in the range of $1.28 \times 10^3 \text{ nm}^3 \leq V \leq 1.45 \times 10^3 \text{ nm}^3$ for temperatures ranging from 1000 K to 1900 K.

Data Statement

Any data can be provided upon request.

References

- [1] J.P. Rino, An interaction potential for barium sulfide: A molecular dynamics study, *Comput. Mater. Sci.* 92 (2014) 334–342.
- [2] S.C.C. Prado, J.P. Rino, E.D. Zanotto, Successful test of the classical nucleation theory by molecular dynamic simulations of BaS, *Comput. Mater. Sci.* 161 (2019) 99–106.
- [3] I. Saika-Voivod, R.K. Bowles, P.H. Poole, Crystal Nucleation in a Supercooled Liquid with Glassy Dynamics, *Phys. Rev. Lett.* 103(22) (2009) 225701-1.

Table A1

Fitting parameters of the curves of Fig. 6.

Waterton / MYEGA equation: $\log(\tau) = A + \frac{B}{T} \exp(C/T)$				
	A	B	C	R ²
$\langle \tau_\alpha \rangle$	0.125	26.324	6952.4	0.999
τ_1	0.042	48.634	4008.9	0.990

significantly affect the crystal nucleation process. Hence, T_{KS} ' existence challenges a fundamental assumption of nucleation theories—that crystal nucleation always takes place in a fully relaxed SCL—and shows that, in general, relaxation should be considered in theoretical models for an accurate description of nucleation kinetics.

This work sheds light on some relevant and still obscure aspects of supercooled liquid and glass dynamics. They show that structural relaxation and crystal nucleation can interplay in a wide temperature range and indicate that BaS glass's ultimate fate is crystallizing, corroborating results for other substances.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We would like to thank the São Paulo Research Foundation, FAPESP (contract CEPID) Grant No. #2013/07793-6 and the Brazilian National Research Council, CNPq, Grant No. #301126/2015-1 for the financial support of this research. We are also thankful to Leila Separdar, Ricardo F. Lancelotti and Helena R. Acosta for their constructive critique of the manuscript. An anonymous reviewer also made relevant suggestions.

- [7] Y.N. Zhang, L. Wang, W.M. Wang, Thermodynamic, dynamic and structural relaxation in supercooled liquid and glassy Ni below the critical temperature, *J. Phys.-Condens. Matter* 19 (19) (2007), 196106.
- [8] H. Pang, Z.H. Jin, K. Lu, Relaxation, nucleation, and glass transition in supercooled liquid Cu, *Phys. Rev. B* 67 (9) (2003), 094113.
- [9] E.D. Zanutto, D.R. Cassar, The race within supercooled liquids-Relaxation versus crystallization, *J. Chem. Phys.* 149 (2) (2018), 024503.
- [10] P.K. Gupta, D.R. Cassar, E.D. Zanutto, Role of dynamic heterogeneities in crystal nucleation kinetics in an oxide supercooled liquid, *J. Chem. Phys.* 145 (21) (2016), 211920.
- [11] S. Plinton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *J. Computat. Phys.* 117 (1995) 1–19.
- [12] J. Horbach, W. Kob, The structural relaxation of molten sodium disilicate, *J. Phys.-Condens. Matter* 14 (40) (2002) 9237–9253.
- [13] W. Kob, Computer simulations of supercooled liquids and glasses, *J. Phys.-Condens. Matter* 11 (10) (1999) R85–R115.
- [14] W. Kob, H.C. Andersen, Testing Mode-Coupling Theory for a Supercooled Binary Lennard-Jones Mixture - the Van Hove Correlation-Function, *Phys. Rev. E* 51 (5) (1995) 4626–4641.
- [15] S. Sastry, P.G. Debenedetti, F.H. Stillinger, Signatures of distinct dynamical regimes in the energy landscape of a glass-forming liquid, *Nature* 393 (6685) (1998) 554–557.
- [16] K. Doss, C.J. Wilkinson, Y.J. Yang, K.H. Lee, L.P. Huang, J.C. Mauro, Maxwell relaxation time for nonexponential alpha-relaxation phenomena in glassy systems, *J. Am. Ceram. Soc.* 103 (6) (2020) 3590–3599.
- [17] R.F. Lancelotti, O. Peitl, D.R. Cassar, M. Nalin, E.D. Zanutto, Is the structural relaxation of glasses controlled by equilibrium shear viscosity?, *J. Am. Ceram. Society*, accepted. (2021).
- [18] C.T. Moynihan, P.B. Macedo, C.J. Montrose, P.K. Gupta, M.A. DeBolt, J.F. Dill, B. E. Dom, P.W. Drake, A.J. Easteal, P.B. Elterman, R.P. Moeller, H. Sasabe, J. A. Wilder, Structural Relaxation in Vitreous Materials, *Ann. N. Y. Acad. Sci.* 279 (Oct15) (1976) 15–35.
- [19] A. Stukowski, Visualization and analysis of atomistic simulation data with OVITO-the open visualization tool, *Model. Simul. Mater. Sci. Eng.* 18 (2010), 015012.
- [20] S.C. Waterton, The viscosity-temperature relationship and some inferences on the nature of molten and of plastic glass, *J. Soc. Glass Technol.* 16 (1932) 244–247.
- [21] J.C. Mauro, Y.Z. Yue, A.J. Ellison, P.K. Gupta, D.C. Allan, Viscosity of glass-forming liquids, *P. Natl. Acad. Sci. U.S.A.* 106 (47) (2009) 19780–19784.
- [22] V.M. Fokin, A.S. Abyzov, N.S. Yuritsyn, J.W.P. Schmelzer, E.D. Zanutto, Effect of structural relaxation on crystal nucleation in glasses, *Acta Mater.* 203 (2021), 116472.
- [23] J.W.P. Schmelzer, T.V. Tropin, V.M. Fokin, A.S. Abyzov, E.D. Zanutto, Effects of Glass Transition and Structural Relaxation on Crystal Nucleation: Theoretical Description and Model Analysis, *Entropy* 22 (10) (2020) 1098.
- [24] E.D. Zanutto, J.C. Mauro, Response to comment on “The glassy state of matter: Its definition and ultimate fate”, *J. Non-Cryst. Solids* 502 (2018) 251–252.
- [25] E.D. Zanutto, J.C. Mauro, The glassy state of matter: Its definition and ultimate fate, *J. Non-Cryst. Solids* 471 (2017) 490–495.