Journal of Non-Crystalline Solids 481 (2018) 627–633

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

On the co-operative formation of local ground states and frustration fields in the structural glass As2Se3

C.B. Nelson

Department of Physics and Astronomy, St. Cloud State University, Minnesota, United States

ARTICLE INFO

Keywords:
Order parameter
Glass transition
Second order phase transition
Gauge freedom

ABSTRACT

A microscopic free energy model with an order parameter was introduced earlier that included a local frustration gauge field with U1 symmetry. Ad hoc values of this field were introduced to fit the NQR distribution of a powdered sample of As2Se3 glass and predict the glass and Kauzmann temperatures. Here we derive initial values of the local frustration force amplitudes from an associated molecular free energy. We show that these amplitudes as calculated solely as gradients of the free energy are too large, and that a force term derived from energy leaving the glass and entering the bath must be included to give the correct magnitude. The modification to the bath also acts as a U1 gauge transformation of the frustration field, and insures that the "freezing" process is irreversible, non-equilibrium, and approximately steady state.

1. Introduction

The microscopic nature of the structural glass transition in As–chalcogenide compounds has been a matter of discussion in the physics community for many years [1–4]. P.W. Anderson once stated that it is one of the last unsolved mysteries in condensed matter theory [5]. The different approaches include mode coupled theory [6], and replica theory [7]. All of these have some crucial features belonging to the glass transition but none of them can be viewed to be complete. Using a gauge field approach, we recently introduced [8] a free energy model in which a local fluctuation of an As—Se—As bond angle $\delta\beta_i$ (see Fig. 2) is identified as the square of an order parameter. The ground state values of $\delta\beta_{i0}$ were used to predict the correct glass transition temperature T_g [1], the Kauzmann temperature T_K [2], the Helmholtz free energy, the configurational entropy, and the observed NQR distribution (see Fig. 1) [9]. Here, we calculate the heat capacity and show that it has the signature "step" at the glass temperature [10]. The magnitude of the ground state of this local order parameter depends on a local frustration gauge field, which was included in the local free energy in an ad hoc manner, as was a term quadratic in the order parameter. This gauge field is shown to be the gradient of the free energy of another fluctuation field $\delta\theta_{ij}$. Here we introduce a model where the two local fields $\delta\beta_i$, $\delta\theta_{ij}$ are coupled to a single multimode temperature bath [11]. This is the simplest study of two coupled local free energies in turn coupled to a bath which in principle predicts the macroscopic behavior of the glass. Based on some work done earlier by Sethna cited in reference [8] we assumed that the order parameter is invariant with respect to variation of a scalar phase $\alpha_i(s_i)$, where s_i is an angular displacement. This gives the gauge field a U1 symmetry [12], defined as $\sqrt{\delta\beta_i} = O_{i0}e^{-i\alpha_i(s_i)}$. We attempt a crude model of the local time dependence of the freezing process where we assume that these fluctuations are short lived, and that we can write $\sqrt{\delta\beta_i} = (O_{i0}e^{-i\alpha_i(s_i)})e^{-\gamma_\beta t}$ [13]. Here γ_β is a type of inverse relaxation time for the fluctuation which presumably depends on temperature and the probability of the thermodynamic path connecting the bath with the glass [14]. We assume that both fields start out above the glass temperature in some type of distribution or superposition which does not allow for the definition of a local ground state $\delta\beta_{i0}$. We assume that as the glass cools the two fields couple first to each other, inducing the gauge frustration field f_i. The gauge field is a frustration force field which is calculated by taking the gradient of E_θ with respect to a distance parameter. This calculation predicts force magnitudes which are too large, and the terms required to define unique ground states (local minima in δE_β, δE_θ) $\delta\beta_{i0}$, $\delta\theta_{ij0}$ are not present in the free energies. Once the frustration field has formed, we assume the two fields $\delta\beta_i$, $\delta\theta_{ij}$ couple to the bath through a particular interaction Hamiltonian which is seen commonly in systems coupled to a bath [15]. We then solve Hamilton's equations for the fields $\delta\beta_i$, $\delta\theta_{ij}$. Assuming that the parameter $\gamma(T)$ has a temperature dependence such that $\lim_{T\to T_g}\gamma^2(T) \simeq 0$, then the Hamilton's equations can be integrated and the final fluctuation free energies contain all the terms necessary to define unique ground states $\delta\beta_{i0}$, $\delta\theta_{ij0}$. The minima of the derived fluctuations in the free energies can be shown to fit the experimental NQR measurements by predicting an amount of energy transferred to the bath which produces a quadratic distortion in a particular set of bath variables during the freezing

E-mail address: cbnelson@stcloudstate.edu.

https://doi.org/10.1016/j.jnoncrysol.2017.12.014
Received 5 October 2017; Received in revised form 22 November 2017; Accepted 4 December 2017
Available online 08 December 2017
0022-3093/

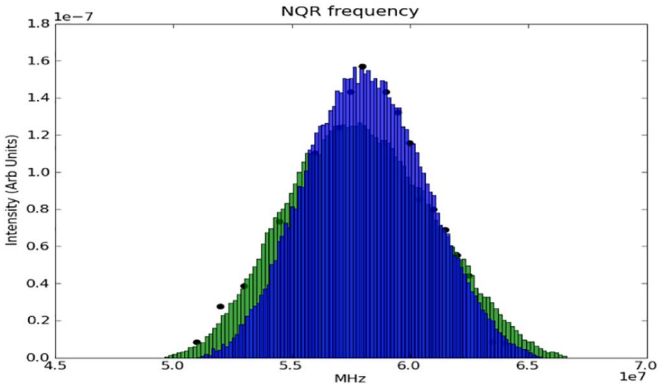

Fig. 1. NQR distribution as predicted in reference [8].

process. We show that this transfer is equivalent to choosing a particular choice of gauge for the frustration field. This procedure is known to be necessary to obtain physical results for many gauge theories [12]. It should be noted that this particular choice of gauge is interesting because it simultaneously allows us to define unique ground states $\delta\beta_{i0}$, $\delta\theta_{ij0}$, while ensuring that the entropy exchange between the glass and bath fields [16] during this process is irreversible, non-equilibrium, and steady state at a microscopic level.

2. Model of the local frustration gauge fields and associated ground states

The valence electronic energy in the ith bond of a pyramidal unit of the glass is dominated by the associated hybrid angle β_i [8]. Here it is assumed that $\delta\beta_i$ fluctuates around the preferred β_i above the glass temperature, finally freezing at $T \approx T_g$. This makes $\delta\beta_i$ a good choice for the square of the order parameter. In addition, all the relevant energies in the partition function can be written in terms of $\delta\beta_i$. The fluctuation on the free energy associated with a particular bond is both linear and quadratic in the quantity $\delta\beta_i$, which is the amount of distortion in the hybrid angle of the ith bond away from the local preferred structure as seen in Fig. 2.

Each pyramidal unit has three such angles, so each pyramidal unit has three separate connected partition functions. Here we define

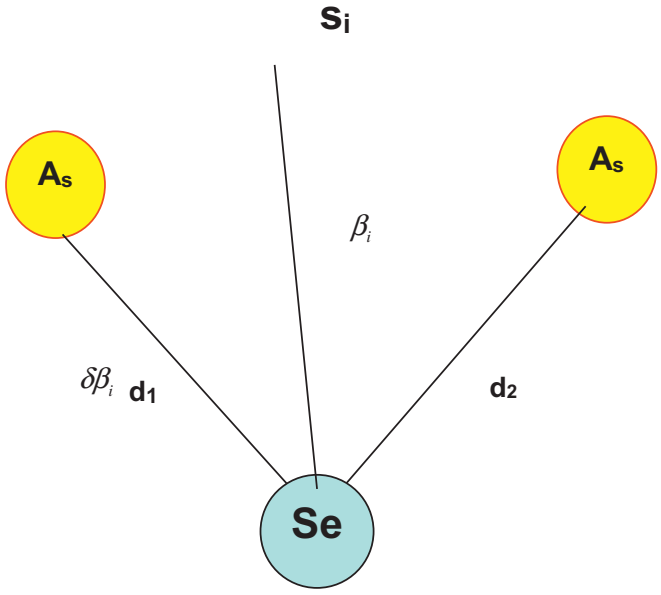

Fig. 2. The arc length parameter s_i of the ith bond defined with respect to a central Se atom.

$d_i = \frac{(d_1+d_2)}{2}$ as an average ith bond length connecting each As atom with a central Se atom. This single index is not to be confused with the double index (ij) used later to define the distance d_{ij} between two Se atoms connected to a single As atom (see Fig. 4). $\delta\beta_i$ is the fluctuation associated with the hybrid angle β_i required to minimize the fluctuation in the free energy. We define the order parameter $O_{\beta i}$ field [8] in terms of the fluctuation $\delta\beta_i$ as,

$$O^*_{\beta i} O_{\beta i} = \delta\beta_i. \tag{1}$$

We define the contributions to the free energy at the superposition level as a function of the fluctuations are defined as $\frac{\partial EValence}{\partial\beta_i} O^2_{\beta i}$, a Taylor series term of the local valence electronic energy expanded around $\delta\beta_i$, plus the kinetic term $E_{Kinetic} = \frac{1}{2\mu_\beta}(\partial_{S_i} O_{\beta i})^* \cdot (\partial_{S_i} O_{\beta i})$, associated with the change in the order parameter with respect to the variable s_i as defined in Fig. 2 above. Here μ_β is the reduced mass of the As−Se−As bond. A fluctuation in the free energy is defined as,

$$\delta F_{0i} = \left[\left(\frac{\partial E_0(O^2_{\beta_i})}{\partial\beta_i} + \frac{\partial E_i(O^2_{\beta_i})}{\partial\beta_i}\right) O^2_{\beta_i} + \frac{1}{2\mu_\beta}\left(\frac{\partial O_{\beta i}}{\partial s_i}\right)^*\left(\frac{\partial O_{\beta i}}{\partial s_i}\right)\right]. \tag{2}$$

It is a well-known fact that frustration forces act in structural glasses [8]. Following reference [12] we assert that the variation in the free energy in Eq. (2) should be invariant with respect to fluctuations in the order parameter,

$$O'_{\beta i}(t=0) = O_{\beta i 0} e^{-i\alpha_i(s_i)}. \tag{3}$$

Here $\alpha_i(s_i)$ is a single valued function of the arc length parameter s_i as defined in Fig. 2. Since $\alpha_i(s_i)$ is a phase parameter that is a function of one variable, it is obvious [12] that α_i has U1 gauge symmetry and we assume it is evaluated at some time t and position s_i. A derivative of the order parameter with respect to s_i now becomes,

$$\frac{\partial O_{\beta i}{}'}{\partial s_i} = \left(\frac{\partial O_{\beta i}}{\partial s_i}\right) e^{-i\alpha_i(s)} - O_{\beta i}(s)\left(i\frac{\partial\alpha_i(s)}{\partial s_i}\right). \tag{4}$$

As per the gauge field approach the presence of the term $\alpha_i(s_i)$ makes the free energy dependent on the value of s_i. This requires [12] that the dynamic term involve a gauge covariant derivative which includes a frustration gauge field Φ_i which couples to the order parameter $O_{\beta i}$,

$$D_s = \frac{\partial}{\partial s_i} + i\sqrt{d_i}\Phi_i(t). \tag{5}$$

Here it is obvious that the frustration gauge field $\Phi_i(T,t)$ is a function of temperature as well as time, however here we consider only the amplitude for $T \approx T_g$. We define the gauge field Φ_i in terms of the frustration forces as shown in Fig. 3.

$$\Phi_i = \left(\sqrt{|\vec{f_i}|} + i\sqrt{\hat{f_i}\cdot\sum_{j\neq i}\vec{f_j}}\right). \tag{6}$$

This definition is consistent with the fact that the frustration forces

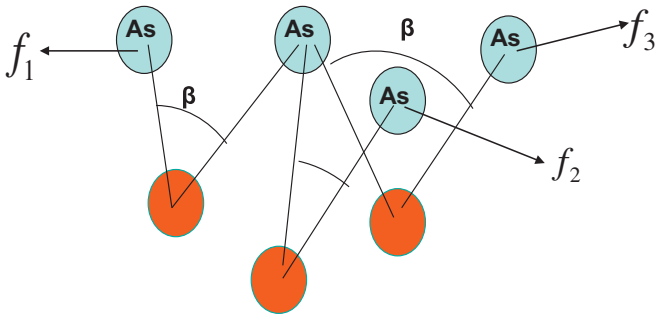

Fig. 3. The frustration forces acting to expand the pyramidal unit. As atoms are blue, Se atoms red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)