Residual entropy and structural disorder in glass: Fluctuation phenomena and time-dependent features as deduced from an Ising-type structural model

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A B S T R A C T

As part of our study of configurational entropy in non-equilibrium systems, we have determined the time-dependent fluctuations in a simple system that undergoes structural transformations similar to those of an Ising model. First, we demonstrate that the calorimetric entropy does approximate the statistical thermodynamic entropy, and that the former reflects the spatial arrangements dealt with by the latter. We then show that neither the assumption of ergodicity nor the use of a canonical ensemble is required to account for non-equilibrium states. We use instead the concept of 'spatial sampling' with which enthalpy, entropy and volume can be defined for each structure at any time. In this way fluctuations of all variables can be calculated without any inconsistency. Finally, we point out that introduction of the new concepts of magnitude and phase factor into configurational entropy can not only explain the existence of residual entropy at 0 K for disordered materials but also allows one to discuss spatially related randomness and kinetically induced fluctuations on an equal footing.

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1. Introduction

There is an ongoing controversy concerning the concept of configurational entropy in glasses down to 0 K that has fundamental consequences for the structure and properties of these materials. For convenience, we will term 'conventional view' the thesis that a definite residual entropy exists in glasses at 0 K, which depends both on composition and thermal history [e.g., 1–8]. On the other hand, we will term 'kinetic' [9–11] or 'entropy-loss' [12,13] the view according to which the configurational entropy of a liquid abruptly vanishes when the glass transition is crossed so that no residual entropy can exist at 0 K.

In a previous paper [14], we have summarized the pros and cons of each view and simulated a two-level system (TLS) to ascertain differences between entropies determined either in a calorimetric way or from statistical mechanical methods. New insights on configurational entropy were also obtained in terms of 'structural degeneracy', originating from microscopic structural disorder, and of macroscopic 'thermodynamic degeneracy' related to the number of microstates included in the most probable macrostate. In addition, we argued that, even for a microstate, entropy can be defined from a 'spatial sampling' without any need of an 'ensemble sampling'. This allowed us to show that ergodicity is not a prerequisite to derive meaningful configurational entropies so that residual entropies are well-defined properties in glasses and disordered crystals.

Because our TLS model dealt with only the most probable states of a system, time-dependent features such as fluctuation effects could not be addressed. These points are also relevant to the entropy controversy, however, because the 'conventional' view has been criticized for being unable to account for them and also for predicting that the configurational heat capacity would not vanish when the temperature tends to zero [15]. In this second installment we thus focus on time-dependent features through additional simulations performed with a structural model related to that of Ising [16–18]. As was pointed out by Landau [19], the residual entropy problem should in principle be discussed from a quantum statistics viewpoint. That this condition is actually not necessary, however, is indicated by our results since these have been obtained within the framework of classical statistical mechanics.

Our system is made up of two different substrates whose distributions are calculated. In a real disordered material, these substrates are the analogs of the two energy levels of the system we discussed in our previous study [14], or of the α- and β-structures defined in our structural model of silica [20–22]. This model is well suited for our purpose because both energy and structural fluctuations can be most simply investigated and their contribution to entropy evaluated from either a thermal or a statistical standpoint. In short, our main objective is the same as in our previous study. The difference is that residual entropies are now calculated from simulations of interacting systems

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