



Review

Residual entropy and structural disorder in glass: A review of history and an attempt to resolve two apparently conflicting views

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ABSTRACT

With the aim of discussing recent conflicting views of configurational entropy in frozen-in systems, we begin this paper with a brief review of the history of the entropy concept. Whereas the 'conventional' view of entropy had been elaborated after long and heated debates, a recently proposed 'kinetic' view has denied the existence of residual entropy in amorphous systems. We thus examine the validity of the 'conventional' view and then propose a more complete picture of the glassy state from the complementary roles of two conflicting views. Above all, we analyze the consistency of the 'spatial sampling' method and the difference from the other two methods by using three simple models and thought experiments. Our first conclusion is that, as defined for non-equilibrium systems within the framework of thermodynamics, entropy remains an objective state variable for which an observation time needs not to be specified. The second is that, owing to its extensive nature, entropy is in fact strongly linked to the distribution in configuration and momentum space rather than to temporal integration. As an obvious consequence, the degree of structural disorder remains an essential issue in glass thermodynamics. The third is that the new concepts of magnitude and phase factor of entropy indicate that the 'conventional' view, according to which configurational entropy does not vanish in irreversibly frozen-in systems, is not only consistent with thermodynamic theory and available data, but also accounts for kinetic effects such as fluctuation phenomena. With the concept of phase factor of entropy, the number of phase factors visited during the observation time in the 'conventional' view turns to be almost equivalent to the entropy value defined by the 'kinetic' view. Finally, non-zero values of residual entropies measured by calorimetry based on the 'conventional' view are real and useful features that have a fundamental bearing on the physics and chemistry of real crystals and glasses. The 'kinetic' view is also a useful tool as well to understand the kinetic effects, such the rapid slowdown from liquids to glass and the glass transition. It is strongly hoped that a complete picture of the glassy state will be advanced further.

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1. Introduction

Two definitions of "glass" prevail even though the term has various meanings and can be defined in different ways depending on the scientist's perspective. If emphasis is put on microscopic features, glass is characterized as a solid material with a non-crystalline structure. Ever since Zachariasen proposed his landmark "random network model" [1], this structural aspect has been one of the central topics of glass research. As proposed by Greaves [2], however, more detailed analyses have led to the "modified random network model" whereby interest is focused on structural ordering around network formers and modifiers. Because the structure then is considered to be microscopically non-uniform, it has become important to quantify the pattern and degree of medium-range order/disorder up to a scale of about 3–20 Å in order to understand and design glass properties [3,4]. In view of the general relationship posited between entropy and disorder, this is one of the reasons why configurational entropy of melts and glasses is important in glass science and technology.

If emphasis is put instead on mechanical, thermal, or transport properties, one alternatively defines glass as a material usually obtained from cooling of a melt at rates high enough that crystallization does not take place and viscosity increases until the material becomes a solid [5,6]. This transformation of a melt into a glass is accompanied by abrupt changes in second-order thermodynamic properties (heat capacity, thermal expansion coefficient, compressibility) whereas first-order properties (enthalpy, volume) vary continuously. Glass can thus be defined as a solid material either obtained through such a *glass transition* or, conversely, exhibiting this transition when heated up to the liquid state. The glass transition range then is the interval where marked variations of second-order properties are observed. As characterized by the glass transition temperature (T_g), it increases with faster heating or cooling rates and is empirically found close to the temperature at which viscosity is 10^{12} Pa s for typical rates of 10 ~ 100 K/min. As a result, the glass transition is a non-equilibrium transformation and the structure and properties of a given glass depend not only on instantaneous pressure and temperature but also on thermal and pressure history.

It has long been considered that the configurational entropy of a melt is frozen in at the glass transition and then remains approximately constant down to 0 K where it manifests itself as residual entropy [7], notwithstanding the subsequent relaxation phenomena called 'physical aging' possibly observed below the glass transition [e.g., 8]. Lately, however, this 'conventional' view has been challenged by the proponents of the 'kinetic' view according to whom the irreversible nature of the liquid-glass transition results in an abrupt loss of configurational entropy of the material. The question is then to know what sense can be made of the experimental determinations of residual entropy made since the 1920s for a variety of disordered systems, beginning with ice or carbon monoxide, which has been accounted for quantitatively by simple statistical mechanical models of atomic disorder [e.g. 33,37–39]. And the availability of a growing body of residual entropy data for silicate glasses [e.g. 50,56] has rendered the problem still more serious.

The dispute between the 'conventional' and 'kinetic' views is in fact closely related to the different ways in which entropy can be defined for a non-equilibrium system. The aim of the present contribution is to clarify this issue. First, we review the various ways in which entropy may be defined and their resulting differences for configurational entropy in frozen-in systems. Second, we deal with the ongoing controversy that

affects residual entropy as related to the third law of thermodynamics. Third, we critically review the 'kinetic view' in terms of the extensive nature of entropy. Fourth, we state that the 'conventional' view not only matches the thermodynamic and statistical thermodynamics entropies but can also provide important information on the topology of glass networks and on the nature of the "structural disorder" that is specific to glass as compared with crystal phases. Finally, this discussion allows us to arrive at a new interpretation of configurational entropy with a bifocal view. The new features that have been invoked to support the 'kinetic' view appear to be consistent with the 'conventional' view, in harmony with the conclusions of our previous papers [9,10]. In this way it is hoped that the apparent conflict between these two views is resolved.

2. Entropy: from heat to information

Entropy can be defined in at least four different ways. The term was originally coined in 1865 by Clausius [11] in relation to the celebrated equation.

$$S = \sum Q/T, \quad (1)$$

where S , Q and T are the entropy (originally denoted by the symbol N by Clausius), heat exchanged and temperature, respectively, for the transformation of interest. For a reversible, cyclic process, Clausius then pointed out that

$$\oint dQ/T = 0, \quad (2)$$

and that N is necessarily positive in a real, irreversible cyclic process, in which case it represents the effect of "uncompensated heat". While stating in this manner the second law of thermodynamics, Clausius was in fact imagining internal entropy generation in irreversibly evolving systems and its connection with the probability of molecular movements (see Appendix A). Much later Prigogine [12] and other scientists developed non-equilibrium thermodynamics by extending the original Clausius equation into the following formula:

$$dS = dS^{ext} + dS^{int}, \quad (3)$$

where dS^{ext} is the entropy change due to the exchange of energy or substance, and dS^{int} that due to internal energy dissipation. In the absence of friction between the system of interest and its environment, the first right-hand side term is given by Eq. (1) whereas the second is zero for reversible transformations and larger than zero for irreversible ones. This formula is a rigorous definition of "thermodynamic entropy" under either equilibrium or non-equilibrium conditions. In general the dS^{ext} term can be easily determined from calorimetric experiments but estimating precisely the other dS^{int} term remains a theoretical challenge.

Of particular importance is the concept of "demon" also introduced by Maxwell [13] and the fact that, as he stated himself [14], "the second law has only a statistical certainty" as "it is valid only as long as we consider very large numbers of molecules which we cannot deal with individually". Stimulated by Maxwell's publications, Boltzmann went on to establish the kinetic theory of gases and, in particular, to deduce the second law of thermodynamics from the mechanical principle of least

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