Review

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

Akira Takada a,b,* Reinhard Conradt c, Pascal Richet d,e

a Research Center, Asahi Glass Co. Ltd., 1150 Hanaaro-cho, Yokohama 221-8755, Japan
b University College London, Gower Street, London WC1E 6BT, UK
c RWTH Aachen University, 52064 Aachen, Germany
d, e Institut de Physique du Globe de Paris, 1 rue Jussieu, 75005 Paris, France

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A B S T R A C T

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 as the rapid slow down 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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* Corresponding author at: Research Center, Asahi Glass Co. Ltd., 1150 Hanaaro-cho, Yokohama 221-8755, Japan.
E-mail addresses: akira-takada@acp.com (A. Takada).

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