



Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

Thermodynamic cooperativity in glass-forming liquids: Indications and consequences

Lianwen Wang

School of Physical Science and Technology, Lanzhou University, Tianshui South Road 222, Lanzhou 730000, People's Republic of China

ARTICLE INFO

Article history:

Received 7 November 2012

Received in revised form 28 January 2013

Available online xxxxx

Keywords:

Glass transition;

Cooperativity;

Structural relaxation

ABSTRACT

From our recent studies on crystal melting, a small-liquid-nucleus scenario is concluded. On this basis, a thermodynamic cooperativity is proposed to be the number of atoms in a liquid nucleus, which may serve as an upper limit for the kinetic cooperativity. Preliminary applications of the concept of a thermodynamic cooperativity in elucidating several significant features of glass-forming liquids are promising. In this work, efforts are devoted for a detailed examination of the existence of the suggested thermodynamic cooperativity by exploring a variety of research results on crystal melting, gas condensation, and liquids, specifically, in a logical chain of reasoning, (i) whether vacancies may dominate the high-temperature properties of crystals, (ii) whether liquid nucleation may be initiated from vacancies, and (iii) whether the liquid nucleus may be very small. In addition, successful applications of the concept of a thermodynamic cooperativity are briefly reviewed, lending further supports to its existence.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In view of atomic arrangements, solids are either crystalline or amorphous, see Fig. 1(a). For crystalline solids, the past century has witnessed the growing-up of Materials Science in which ultramolecular structures [1] e.g. dislocations, grain boundaries, surfaces and interfaces are known well to dominate material properties. In comparison, present knowledge to the ultramolecular structures of non-crystalline solids is limited to the kinetic cooperativity [2] and the dynamic heterogeneity [3,4]. Even with regard to the kinetic cooperativity and the dynamic heterogeneity, available knowledge is too qualitative and incomplete: for the dynamic heterogeneity, we only roughly know its length and time scales [3,4]; for the kinetic cooperativity, large discrepancies [5] exist for the size of the cooperatively rearranging region (CRR) [2]; the above information can not be quantitatively related with material properties [6].

Behind the unclearness of amorphous solids, is the unclearness of their mother phases, liquids, see Fig. 1(a). In contrast to the gaseous state (characterized by random, translational motions of constituting molecules and relatively little molecular interactions) and the solid state (in which the main characteristics are fixed sites for individual atoms or molecules and very little translational movements), the liquid state does not have a simple model that could be developed into a quantitative theory [7–9]. Studies on liquids can be traced back to the work by J. D. van der Waals [10] in the 1870 s. It was about sixty years later, in the late 1930s, that various attempts began to appear on the structure and properties of liquids e.g. those by J. D. Bernal [11,12], H. Eyring [13,14], J. Frenkel [15,16], N. F. Mott [17–19], J. E. Lennard-Jones [20],

M. Born and H. S. Green [21–23]. Shortly thereafter, since the 1950s, intensive efforts have been devoted to the understanding of glass-forming liquids e.g. those by D. Turnbull and M. H. Cohen [24,25], G. Adam and J. H. Gibbs [2], M. Goldstein [26], and so on [27–30]. Despite these efforts on glass-forming liquids, a consensus understanding of glass transition has not been reached as yet [31,32], which, in my opinion, may be attributed to the regrettable failure in the understanding of normal liquids.

Then, what should be responsible for the unclearness of liquids? For this, again, we turn to the mother phases of liquids, from which a liquid is nucleated, i.e. a crystal near the melting point, T_m , or a dense gas near the condensation temperature. Since the dense gas is also poorly understood [33–35] and, in comparison, a crystal near T_m is relatively easier to study, the mystery hidden in liquids is, to a certain extent, to be uncovered by studying liquid nucleation at the instance of crystal melting, see Fig. 1(a).

However, the issue of crystal melting itself also has been under disputing for over a century. Following the early qualitative studies by M. Faraday [36] and J. J. Thomson [37], quantitative analyses were given on crystal melting by e.g. F. A. Lindemann [38] and several scientists who also contributed in liquid theories including J. Frenkel [15,16], J. E. Lennard-Jones [39,40], M. Born [41], N. F. Mott [42], and so on [43–46]. In the present stage, microscopic details of crystal melting still remain quite elusive, with the exact atomic details in the nucleation of liquids from crystalline solids unresolved.

Our approach to the ultramolecular structure of non-crystalline solids was initiated from the studies of liquid nucleation at melting. In the past decade, we have studied the role that atomic migrations may play in crystal melting [47,48], from which we developed a kinetic model for liquids and concluded the existence of a thermodynamic cooperativity in liquids [49,50]. Following this, the concept of thermodynamic cooperativity was

E-mail address: lwang@lzu.edu.cn.

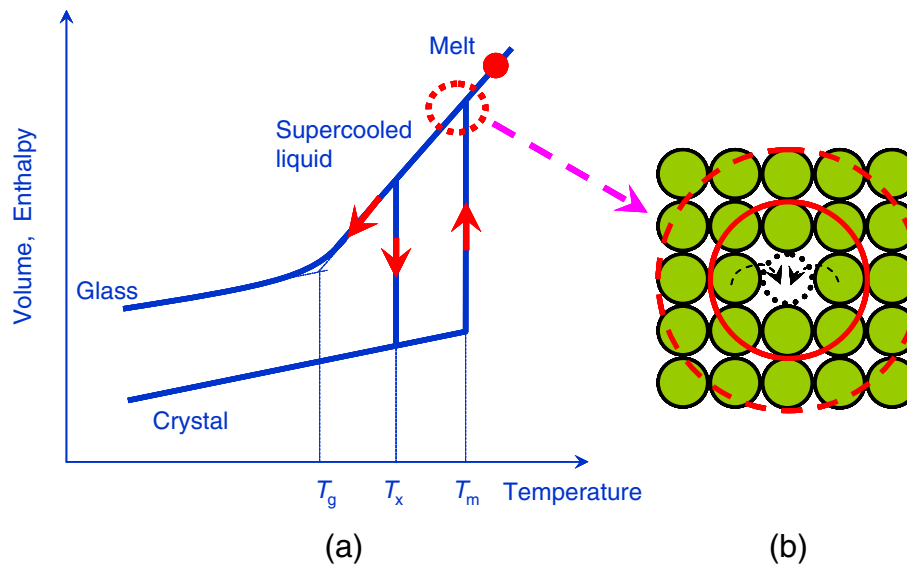


Fig. 1. Liquid nucleation at the instant of crystal melting, in relating with some fundamental problems that are of the central interests of modern technologies and natural sciences and are hotly debated, as are shown in (a), namely, crystal melting (at T_m), crystallization of liquids (at T_x), glass transition (at T_g), each indicated by a solid arrow, and the structure and thermal physical properties of liquids, indicated by the filled circle. The as-important gas–liquid transition, not shown in the figure, is also noticed. While resolving any of these problems requires a clear understanding of liquids, the nucleation of liquids at crystal melting, i.e. liquids at the birth, indicated by the dotted circle, is critically important for the understanding of liquids. Dashed arrow indicates our approach to liquid nucleation at melting. (b) Two-dimensional sketchy illustration of atomic migration processes (dashed arrows) near a vacancy (dotted circle) in a crystal. With temperature increasing, when there are two (or more) atoms neighboring each vacancy that are migratable, a vacancy will be squashed and lattice instability will be locally triggered [47]. By the squashing of a vacancy, the energy stored in the system is exactly enough to bring the vacancy and the nearest neighboring atoms (inside the unfilled solid circle) into the liquid state [48]. Additional atoms (e.g. the second nearest neighboring atoms included in the unfilled dashed circle) are not needed.

preliminarily applied to elucidate several significant features of glass-forming liquids [50–52]. Over the years, the coming and definition of a thermodynamic cooperativity and its indications were intermittently and briefly given in the above several scattered papers [47–52]. In this work, efforts will be devoted to present a comprehensive view of the thermodynamic cooperativity in connecting crystal melting, liquids, and glass transition, to summarize its successful applications to date, and especially, to fully examine available indications of its existence. On this basis, arguments will be made about the strategies in understanding liquids and non-crystalline solids.

2. The coming and definition of a thermodynamic cooperativity

To gain insight into the microscopic details of crystal melting, we have focused on atomic migrations towards thermal vacancies in elemental metals [47], see Fig. 1(b). At temperatures near T_m , the concentration of thermal vacancies, C_v , in metals is in the range of 10^{-4} to 10^{-3} [53]. In comparison, the concentration of migration atoms, C_m , increases exponentially with temperature ascending to exceed around 20% at temperatures near T_m [47]. We proposed that when two (or more) atoms neighboring each vacancy are migratable, the vacancy will be squashed and lattice instability will be triggered locally [47].

Further, we found that, when a vacancy was squashed by neighboring migration atoms, the energy stored in the system was exactly enough to bring the vacancy and its nearest neighboring atoms into the liquid state [48]. Additional atoms, e.g. the second nearest neighboring atoms, were not actually needed, see Fig. 1(b). That is to say, the liquid nucleus may be very small, containing only a vacancy and its nearest neighboring atoms.

Because a liquid nucleus is a liquid already, we proposed that the kinetic cooperativity should be limited within the atoms in a liquid nucleus. In other words, the kinetic cooperativity may not become infinite in the vicinity of glass transition as was suggested e.g. in [2]. We called the number of atoms within a liquid nucleus the thermodynamic cooperativity, which was an upper limit to the kinetic cooperativity

[50]. To avoid possible confusions in understanding the proposed thermodynamic cooperativity, additional discussions on the term defined here in comparison with several relating ones in literature will be given in Section 5.3.

3. Indications for the existence of a thermodynamic cooperativity

Although preliminary applications of the concept of a thermodynamic cooperativity in elucidating several significant features of glass-forming liquids are promising [50–52], before the concept is further developed, a critical examination is nevertheless needed concerning whether the supposed thermodynamic cooperativity may really exist: specifically, in a logical chain of reasoning, (i) whether vacancies may dominate the high-temperature properties of crystals, (ii) whether liquid nucleation may be initiated from vacancies, and (iii) whether the liquid nucleus may be very small.

3.1. Factors that dominate high-temperature properties of crystals: vacancies, interstitials, or anharmonicity?

Since, in our model, the liquid phase was nucleated at the instance of melting among a vacancy and its nearest neighboring atoms, for the purpose of supporting the concept of the thermodynamic cooperativity, it is of critical interests to know whether vacancies are the dominating factor for high-temperature properties of crystals.

At temperatures near T_m , vacancies [53], interstitials [54–57], and anharmonicity [58] all are argued to significantly affect the properties of crystals e.g. thermal expansion, specific heat, and diffusion. It is a long-standing debate to determine which of the above factors is dominant. It seems only recently that an explicit and unarbitrary conclusion can be drawn on this issue on the basis of detailed computer simulation results [58,59].

In [58], Grabowski et al. concluded, on the basis of ab initio computer simulations on a prototypical example aluminum, that “in contrast to common belief, the explicit anharmonicity gives rise to a negative

Download English Version:

<https://daneshyari.com/en/article/7902658>

Download Persian Version:

<https://daneshyari.com/article/7902658>

[Daneshyari.com](https://daneshyari.com)