Journal of Non-Crystalline Solids 407 (2015) 179–183

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Thermodynamics and dynamics of the inherent states at the glass transition

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ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 9 August 2014
Available online 30 August 2014

Keywords:
Glass transition;
Isomorphism;
Prigogine–Defay ratio

ABSTRACT

It has been recently shown that one can understand the Prigogine–Defay ratio at the glass transition in terms of freezing into one of the many inherent states of the undercooled liquid. In the present paper, the treatment is extended to the dynamics at the glass transition to show the connection to isomorphism and density scaling. In addition, the energy limits for stable inherent states are discussed.

1. Introduction

When an undercooled liquid freezes into a glass at the glass temperature T_g, the sample stays in one of the many inherent states between which it could choose freely in the liquid [1–5]. Obviously, the possibility to jump from one possible stable structure to another gets lost as the system freezes into a glass, leaving only the vibrational degrees of freedom to contribute to dynamics and to thermodynamics.

Though this freezing process is in principle continuous, the explosive increase of the structural relaxation times with decreasing temperature at the glass temperature concentrates the freezing process into a relatively small temperature interval [6]. The present paper is focused on the equilibrium liquid just above this temperature, in particular on the contributions of the possibility to jump from state to state to its thermodynamic and dynamic properties.

The concept of an inherent state stems from molecular dynamics simulations of undercooled liquids [2], where one can remove the whole kinetic energy at a given moment in time and look for the nearest structural energy minimum of the atomic ensemble. The dynamic and thermodynamic consequences of the concept have been mainly studied in connection with numerical work [3–5], providing deep insights into the microscopic basis of the glass transition phenomenology. Instead of a single inherent state, it was found necessary to introduce the concept of a basin, an ensemble of inherent states with small barriers between them, in which the system stays a long time before jumping into the next basin.

Naturally, the concept is even better adapted to the glass transition in real systems, where the separation between vibrational and relaxational degrees of freedom is much more pronounced than in numerical simulations and the basin begins to resemble a single inherent state. Close to the glass transition, the system can then be considered to spend a long time vibrating in a single inherent state before it jumps into another one.

This picture has been recently applied [7] to the Prigogine–Defay ratio [8], providing an explanation for values larger than one in terms of the properties of the inherent states. In the present paper, this treatment is extended to include predictions on the dynamics of the undercooled liquid. In addition, a consideration on the possible energy range of the stable inherent states in terms of melting and boiling points is given.

The paper gives a short summary of the theoretical basis and of the results of the preceding paper [7] in the next section following this introduction. The extension to dynamics follows in Section 3. Section 4 summarizes and concludes the paper.

2. Properties of inherent states

The inherent state is a structurally stable minimum of the potential energy for a sample of N particles. N should be large enough to get rid of finite size effects. A thermodynamic description of the undercooled liquid in terms of inherent states is reasonable in the temperature region where the structural relaxation is slow on the picosecond vibrational time scale, enabling one to distinguish between structural and vibrational entropy contributions.

An inherent state is characterized by its energy Ne and its volume Nv at the glass temperature T_g and zero pressure, where e is the average structural energy per particle and v is the average particle volume. One has to specify temperature and pressure, because the volume of a given inherent state increases with temperature due to the vibrational

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.08.025

anharmonicity and decreases with increasing pressure due to its compressibility.

With these definitions, it is clear that one of these inherent states has the lowest energy of the whole ensemble. That is the Kauzmann state. Its free energy must be higher than the one of the crystal; otherwise the liquid could never crystallize. However, from all the evidence at our disposal [9], it seems clear that the free energy of this Kauzmann state is rather close to the crystalline one. The difference is probably negligible at the temperatures where one is able to study the undercooled liquid.

The Boltzmann factor for the inherent states contains not only the energy Ne, but also its vibrational entropy Ns_{vib} as well. One has to reckon with a vibrational entropy which depends on e. Denoting the average volume at the structural energy e with v_e, it is reasonable to make a Grüneisen Ansatz for the volume dependence of the vibrational entropy s_{vib}

$$s_{vib} = s_{vib,K} + k_B \Gamma_e \ln \frac{v_e}{v_K}, \tag{1}$$

where $s_{vib,K}$ is the vibrational entropy of the Kauzmann state and v_K is its atomic volume at T_g. As shown in the previous paper [7], Γ_e can be much larger than the usual [10] Grüneisen Γ, because it reflects the behavior of the boson peak rather than the one of the entire spectrum.

Here it is assumed that s_{vib} depends *only* on the structural energy e and not on the volume v. The assumption is necessary to keep the equations simple. It is supported by the finding that a vacancy in a crystal does practically not soften the vibrational spectrum [11]. One could argue that in two inherent states of equal energy, but different volume, the interatomic potential must be sampled at the same places, leading to a very similar vibrational spectrum. But it is an assumption which must not necessarily hold in every system.

The inherent state ensemble is described by its density in structural energy and volume at T_g and zero pressure. Without loss of generality, one can split any distribution $g_{ev}(e, v)$ into a product

$$g_{ev}(e, v) = g_e(e) g_v(e, v - v_e), \tag{2}$$

with a normalized volume density at constant structural energy $g_v(e, v - v_e)$

$$\int_0^\infty g_v(e, v - v_e) dv = 1, \tag{3}$$

an average volume v_e at the structural energy e

$$\int_0^\infty v g_v(e, v - v_e) dv = v_e, \tag{4}$$

and a volume fluctuation contribution

$$\int_0^\infty (v - v_e)^2 g_v(e, v - v_e) dv = v_e^2. \tag{5}$$

In the thermodynamic limit of large N, $g_e(e)$ and $g_v(e, v - v_e)$ are N-independent. In order to be able to work with the Boltzmann factor $\exp(-\beta Ne)$ alone, one defines the generalized distribution function

$$g(e) = g_e(e) \left(\frac{v_e}{v_K} \right)^{\Gamma_e}. \tag{6}$$

The average particle volume v_e tends to increase with increasing structural energy e due to the anharmonicity of the interatomic potential. This effect is responsible for the additional thermal expansion of the undercooled liquid. One assumes a linear relation

$$v_e = v_K + a(e - e_K) \tag{7}$$

where e_K is the structural energy of the Kauzmann state and v_K is its volume at the glass temperature T_g. The coefficient a, an inverse pressure, is a measure for the anharmonicity of the interatomic potential.

To get the partition function Z, one has to integrate the density $g_{ev}(e, v)$ of the inherent states per atom over the configurational energy e and over the volume v. At zero pressure, the volume integrates out and one has

$$Z = \int_{-\infty}^{\infty} g(e) \exp(-\beta Ne) de, \tag{8}$$

which contains the vibrational entropy contribution via Eq. (6) for the generalized distribution function $g(e)$.

One can calculate the average structural energy $\overline{e}$ per atom and the average squared structural energy $\overline{e^2}$ per atom at zero pressure

$$\overline{e} = \frac{1}{Z} \int_{-\infty}^{\infty} e g(e) \exp(-\beta Ne) de \tag{9}$$

and

$$\overline{e^2} = \frac{1}{Z} \int_{-\infty}^{\infty} e^2 g(e) \exp(-\beta Ne) de. \tag{10}$$

The configurational part Δc_p of the heat capacity at zero pressure per unit volume is given as

$$\Delta c_p = \frac{1}{v} \frac{\partial \overline{e}}{\partial T} = \frac{1}{vkT^2} \left(\overline{e^2} - \overline{e}^2 \right). \tag{11}$$

The average volume $\overline{v}$ is given by the double integral

$$\overline{v} = \frac{1}{Z} \int_{\infty}^{\infty} \int_0^{\infty} v g(e) g_v \exp(-\beta Ne) dedv. \tag{12}$$

Because of Eq. (4), one can again integrate the volume out and gets $\overline{v} = \overline{v_e}$, a single integral over e. Inserting Eq. (7) for v_e, one gets

$$\overline{v} = v_K + a(\overline{e} - e_K). \tag{13}$$

The same procedure can be followed for the expectation value $\overline{v^2}$, this time using Eq. (5) to evaluate the volume integral. Again replacing v_e with Eq. (7), one finds finally

$$\overline{v^2} - \overline{v}^2 = a^2 \left(\overline{e^2} - \overline{e}^2 \right) + \overline{v_e^2}, \tag{14}$$

where $\overline{v_e^2}$ is the thermal average over the values v_e^2 at the different structural energies.

This central result [7] shows that one has two kinds of density fluctuations in the undercooled liquid. Those in the first term of the right side of Eq. (14) stem from a change of the structural energy, those in the second term occur at constant structural energy. Of course, in a given transition from one inherent state to another one will usually find a mixture of both. But there are indeed substances where the second term is practically zero, which implies a strong correlation between energy and density fluctuations, the property of isomorphism which is actively debated in the community [12–14,16,17].

Returning to the additional thermal expansion at T_g, one finds from Eq. (13)

$$\Delta \alpha = a \frac{1}{v} \frac{\partial \overline{e}}{\partial T} = a \Delta c_p. \tag{15}$$