PHYSICAL REVIEW B **86**, 184105 (2012)

Structural interpretation of the Prigogine-Defay ratio at the glass transition

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(Received 29 March 2012; revised manuscript received 17 September 2012; published 9 November 2012)

On cooling through the glass transition, a many-particle system freezes into one of the many inherent structurally stable states which are freely accessible in the undercooled liquid. This implies a freezing of an additional heat capacity, an additional thermal expansion, and an additional compressibility. Analyzing the volume and energy distribution of the inherent states at the glass transition, one finds two kinds of slow density fluctuations, namely those which do require an energy change and those which do not. Their ratio determines the Prigogine-Defay ratio. If the second kind is absent, the Prigogine-Defay ratio is unity, enthalpy and volume fluctuations are strictly correlated, and the structural relaxation processes do not couple to an external compression. This case is not often found in real glasses, but seems to be realized to good approximation in Lennard-Jones systems, probably also in metallic glasses. In these two cases, the zero coupling is also reflected in the boson peak modes.

DOI: 10.1103/PhysRevB.86.184105 PACS number(s): 64.70.Q−, 77.22.Gm

I. INTRODUCTION

When an undercooled liquid freezes into a glass at the glass temperature T_g, the thermal expansion usually decreases by a factor of two to four.[1–5] Obviously, the possibility to jump from one possible structure to another leads to a strong thermal expansion. This possibility gets lost as the system enters the glass phase.

In the glass phase, the thermal volume expansion α_g has a textbook explanation[6] in terms of the Grüneisen relation for the vibrations

$$\alpha_g = \frac{\Gamma c_{Vg}}{B}, \tag{1}$$

where c_{Vg} is the heat capacity of the glass at constant volume per unit volume, B is the bulk modulus of the glass, and the Grüneisen parameter Γ describes the volume dependence $\overline{\omega} \propto 1/V^{\Gamma}$ of the average vibrational frequency $\overline{\omega}$.

The present paper intends the derivation of a similarly simple-minded relation for the additional thermal volume expansion $\Delta\alpha = \alpha_l - \alpha_g$ of the undercooled liquid. The additional expansion is ascribed to an increasing population of inherent states with a larger structural energy (and, consequently, a larger volume) with increasing temperature. As will be seen, this simple concept leads to a physical understanding of the Prigogine-Defay ratio at the glass transition,[4,5,7,8] which has at present several conflicting interpretations.[1,3,9–14]

On cooling through the glass transition at T_g, the structural rearrangements stop, while the vibrations persist. There is general agreement on that. It follows that the additional heat capacity, thermal expansion, and compressibility above T_g depend on the distribution function of the inherent states in volume and structural energy at T_g and zero pressure. This has never been realized before. The consequences are worked out in the present paper. They involve the recognition of two different kinds of density fluctuations in the undercooled liquid, of which one is responsible for the thermal expansion, while the other gives rise to the deviation of the Prigogine-Defay ratio from unity.

Section II provides the theoretical basis of the treatment and derives equations for the additional heat capacity, thermal expansion, and compressibility of the undercooled liquid. Section III discusses the connection to experimental and numerical work from the literature. Section IV summarizes the paper.

II. THEORETICAL BASIS

The theoretical description requires the concept of the inherent states of an undercooled liquid.[15] 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.

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 anharmonicity and decreases with increasing pressure due to its compressibility.

The Boltzmann factor for this inherent state contains not only the energy NE, but its vibrational entropy NS_{vib} as well. Denoting the average volume at the structural energy E with V_E, one has to reckon with a vibrational entropy which depends on V_E. It is reasonable to make a Grüneisen Ansatz for the volume dependence of the vibrational entropy S_{vib}

$$S_{\mathrm{vib}} = S_{\mathrm{vib},g} + k_B \Gamma_E \ln \frac{V_E}{V_g}, \tag{2}$$

where $S_{\mathrm{vib},g}$ is the vibrational entropy and V_g is the atomic volume at the glass transition. As will be seen in the comparison to experiment, Γ_E is not necessarily the same as the Grüneisen Γ of Eq. (1), because it reflects the behavior of the boson peak rather than the one of the entire spectrum.

The inherent state ensemble is described by its density in structural energy and volume at T_g and zero pressure (see Fig. 1). Without loss of generality, one can split any distribution $g_{EV}(E,V)$ into a product

$$g_{EV}(E,V) = g_E(E) g_V(E, V - V_E), \tag{3}$$

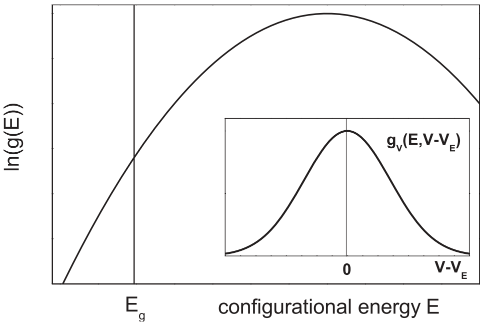

FIG. 1. The distribution $g(E)$ of inherent states in energy at zero pressure. The inset shows the volume distribution of the states at E around the average value V_E. The curves shown here are both Gaussians, but they need not be Gaussians in the general case.

with a normalized volume density at constant structural energy $g_V(E,V-V_E)$:

$$\int_0^\infty g_V(E,V-V_E)dV = 1, \qquad (4)$$

an average volume V_E at the structural energy E:

$$\int_0^\infty V g_V(E,V-V_E)dV = V_E, \qquad (5)$$

and a volume fluctuation contribution:

$$\int_0^\infty (V-V_E)^2 g_V(E,V-V_E)dV = v_E^2. \qquad (6)$$

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 $\exp(-\beta N E)$ alone, one defines the generalized distribution function

$$g(E) = g_E(E)\left(\frac{V_E}{V_g}\right)^{\Gamma_E}. \qquad (7)$$

The average particle volume V_E tends to increase with increasing structural energy E due to the anharmonicity of the interatomic potential. As will be seen, this effect is responsible for the additional thermal expansion of the undercooled liquid. Let us assume a linear relation

$$V_E = V_g + a(E-E_g), \qquad (8)$$

where E_g is the average structural energy at T_g and $V_g = V_E(E_g)$. 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

$$Z = \int_{-\infty}^\infty g(E)\exp(-\beta N E)dE, \qquad (9)$$

which contains the vibrational entropy contribution via Eq. (7) for the generalized distribution function $g(E)$ (note that the equation contains an implicit assumption, namely an equal S_{vib} for different volumes at equal structural energy 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:

$$\overline{E} = \frac{1}{Z}\int_{-\infty}^\infty E g(E)\exp(-\beta N E)dE \qquad (10)$$

and

$$\overline{E^2} = \frac{1}{Z}\int_{-\infty}^\infty E^2 g(E)\exp(-\beta N E)dE. \qquad (11)$$

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

$$\Delta c_p = \frac{1}{V}\frac{\partial\overline{E}}{\partial T} = \frac{1}{VkT^2}(\overline{E^2}-\overline{E}^2). \qquad (12)$$

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

$$\overline{V} = \frac{1}{Z}\int_{\infty}^\infty\int_0^\infty V g(E) g_V \exp(-\beta N E)dEdV. \qquad (13)$$

Because of Eq. (5), one can again integrate the volume out and gets $\overline{V} = \overline{V_E}$, a single integral over E. Inserting Eq. (8) for V_E, one gets

$$\overline{V} = V_g + a(\overline{E}-E_g). \qquad (14)$$

The same procedure can be followed for the expectation value $\overline{V^2}$, this time using Eq. (6) to evaluate the volume integral. Again replacing V_E with Eq. (8), one finds finally

$$\overline{V^2}-\overline{V}^2 = a^2(\overline{E^2}-\overline{E}^2)+\overline{v_E^2}, \qquad (15)$$

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

This is the central result of the present paper. It shows that one has two kinds of density fluctuations in the undercooled liquid. Those in the first term of the right side of Eq. (15) 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, as will be seen in the next section, there are indeed substances where the second term is practically zero, which implies a strong correlation between energy and density fluctuations, a correlation which is actively debated in the community.[5,7,8,16,17]

Returning to the additional thermal expansion at T_g, one finds from Eq. (14)

$$\Delta\alpha = a\frac{1}{V}\frac{\partial\overline{E}}{\partial T} = a\Delta c_p. \qquad (16)$$

From the volume fluctuations, one calculates the additional compressibility $\Delta\kappa$ as in Eq. (12):

$$\Delta\kappa = \frac{\overline{V^2}-\overline{V}^2}{Vk_BT}. \qquad (17)$$

The two terms in Eq. (15) give rise to two terms in $\Delta\kappa$:

$$\Delta\kappa = \Delta\kappa_{PD} + \Delta\kappa_0. \qquad (18)$$

The first is the compressibility contribution from the possibility to change the average structural energy:

$$\Delta\kappa_{PD} = a\frac{1}{V}\frac{\partial\overline{E}}{\partial p} = \frac{a^2}{VkT}(\overline{E^2}-\overline{E}^2). \qquad (19)$$

This part of the compressibility has the index PD, because it satisfies the Prigogine-Defay relation for a second-order phase transition:[9]

$$\frac{\Delta c_p \Delta\kappa_{PD}}{(\Delta\alpha)^2 T} = \frac{\overline{\Delta E^2}\ \overline{\Delta V^2}}{(\overline{\Delta E \Delta V})^2} = 1. \qquad (20)$$

Here ΔE and ΔV are the additional energy (enthalpy) and volume fluctuations from the structural energy changes, respectively. For completely correlated enthalpy and volume fluctuations (an implicit property of the first term), the Prigogine-Defay ratio is one.

But there is also the second term

$$\Delta\kappa_0 = \frac{\overline{v_E^2}}{V k_B T}, \qquad (21)$$

which stems from the density fluctuations at constant structural energy. At zero pressure, these additional density fluctuations occur at constant energy and contribute neither to the heat capacity nor to the thermal expansion. As a consequence, one finds the Prigogine-Defay ratio

$$\Pi = \frac{\Delta\kappa_0 + \Delta\kappa_{PD}}{\Delta\kappa_{PD}} = \frac{\Delta\kappa}{\Delta\kappa_{PD}}, \qquad (22)$$

where $\Delta\kappa$ is the measured value. Π is larger than one if $\Delta\kappa_0$ is larger than zero. This provides a new explanation of the much-debated[1,3,9–14] Prigogine-Defay ratio of the glass transition.

This new explanation confirms the traditional view[1,3,9,13,14] of more than a single order parameter freezing in at the glass transition. The equilibration of the distribution function $g_V(E,V-V_E)$ is clearly distinct from the equilibration of $g(E)$ and must be even expected to occur with different relaxation times.[18] One therefore needs two different order parameters to describe the actual deviation of the system from equilibrium. The present paper identifies the corresponding two different kinds of density fluctuations and expresses the Prigogine-Defay ratio quantitatively in terms of their properties.

One must bear in mind, however, that one has an important class of glass formers, the strongly correlated ones, in which $g_V(E,V)$ is close to a δ-function, its equilibration plays no role, and the Prigogine-Defay ratio is close to 1. They occur more often on the computer, but they are also found in reality.[5] They show strikingly simple properties, both in dynamics[19] and thermodynamics.[7,8]

An alternative explanation of the deviation of the Prigogine-Defay ratio from unity has been given in terms of nonequilibrium thermodynamics,[10–12,14] beginning with work by Nieuwenhuizen,[10] who identifies the freezing of the configurational entropy as a reason for a violation of the second Ehrenfest relation, thus leading to a deviation of the Prigogine-Defay ratio from unity. However, as he himself and, later, Speedy[11] pointed out, this influence tends to lead to a Prigogine-Defay ratio smaller than 1, opposite to the experimental findings.

Schmelzer and Gutzow[12] have developed a quantitative treatment of the glass transition in terms of nonequilibrium thermodynamics. This treatment explains the difference between cooling and heating experiments. It turns out that one has to expect different Prigogine-Defay ratios for heating and cooling experiments and, generally, a Prigogine-Defay ratio which depends on the cooling rates. Schmelzer and Gutzow claim that these effects are also able to explain the experimentally measured Prigogine-Defay ratios in terms of the diffusiveness of the glass transition. However, this special conclusion is debated by others.[14]

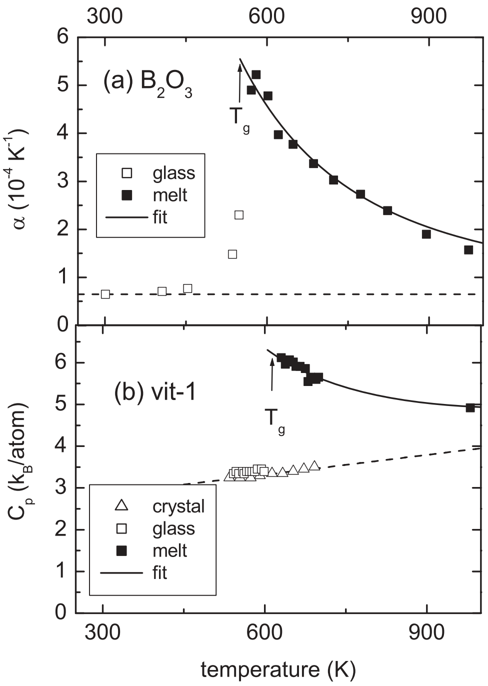

FIG. 2. (a) The temperature dependence of the thermal volume expansion[24] in B_2O_3 compared to the sum (continuous line) of a constant Grüneisen term (dashed line) and the structural expansion of Eq. (25). (b) The temperature dependence of the heat capacity of the metallic glass vitralloy-1 at ambient pressure[25] compared to the sum (continuous line) of the vibrational heat capacity of the glass (dashed line) and the inherent structure contribution of Eq. (24).

From the point of view of the present paper, one does not need the Schmelzer-Gutzow explanation, because the existence of two kinds of density fluctuations explains the deviation of the Prigogine-Defay ratio from unity in a natural way. Of course, the present approach contains the idealization of a sudden stop of all configurational changes at T_g, which is not true. In many glass formers, one has pronounced secondary relaxations which persist deep into the glass phase.[20,21] This influence is clearly visible in the thermal expansion of B_2O_3 in Fig. 2(a) of the next section, where the glass transition is at 550 K, but the final glass value is only reached around room temperature.

Experimentally, one can get rid of the nonequilibrium effects in the glass by extrapolating the glass properties from low enough temperatures, because the influence of the relaxational states on the heat capacity, the compressibility, and the thermal expansion becomes rapidly very small as one cools down from T_g. In many glasses, these three quantities are then close to the ones of the corresponding crystals, because they are exclusively determined by the vibrations [see, for example, the heat capacity of metallic glass and crystal in Fig. 2(b)]. If one extrapolates the glass values from low enough temperature like in Fig. 2(a) (that is what Gupta and Moynihan[3] did to arrive at their value 4.7 for the Prigogine-Defay ratio of B_2O_3), one gets the idealized Prigogine-Defay ratio as defined in the present paper.

Finally, let us discuss the further assumptions needed to arrive at the derived equations. With respect to the distribution function $g_{EV}(E,V)$ there are no specific assumptions. Also, it is not necessary to assume the same compressibility and the same vibrational anharmonicity for all inherent states. The fact that their frozen occupation probability just below T_g equals the equilibrium occupation probability just above T_g ensures the continuity of their contributions to the heat capacity, the thermal expansion, and the compressibility. The temperature slope of these quantities must be expected to be different above and below T_g, but a correct extrapolation from both sides should provide discontinuities Δc_p, $\Delta\alpha$, and $\Delta\kappa$ which depend only on the distribution functions $g(E)$ and $g_V(E,V-V_E)$.

It is necessary to assume the same vibrational entropy for the states at constant structural energy, but with different volumes. If this does not hold, the equations get more complicated. However, a linear volume dependence of the vibrational entropy at constant structural energy could be compensated by an external pressure, so one would get the same situation at a nonzero pressure. In any case, the existence or nonexistence of inherent states with different volume at constant structural energy remains the central point for the analysis.

The separation of the partition function into a vibrational and a configurational part works as long as the time scale of the configuration changes is well separated from the vibrational time scale. This implies a validity of the scheme between the glass temperature and the critical temperature T_c of the mode coupling theory,[22] a bit more than half of the interval between glass temperature and melting temperature.

In this interval, the total volume change is only a few percent. This justifies the assumption of a completely linear volume-energy relation in Eq. (8).

A more severe limitation is the restriction to the pressure zero (but note that in the glass transition case the atmospheric pressure is still practically equal to zero). The restriction is necessary to keep the equations simple. Therefore the task of treating the pressure dependence of the glass transition must be left to future work.

If one talks about two kinds of density fluctuations, one must keep in mind that a given density fluctuation will usually be a mixture of both. But for a Prigogine-Defay ratio of unity one only has one kind, namely a density fluctuation which is due to a fluctuation of the structural energy. This has important implications,[5,16] in particular the property of isomorphicity.[7,8] Some other important implications will be discussed in the next section.

III. COMPARISON TO EXPERIMENT AND SIMULATION

A. Heat capacity and thermal expansion

According to numerical simulation results[23] the density $g(E)$ of the inherent states tends to be a Gaussian in the configurational energy E, with the maximum E_0 of the Gaussian at a value higher than kT_g (see Fig. 1):

$$g(E) = g_0 \exp\left[\frac{-(E-E_0)^2}{2\overline{w^2}}\right], \tag{23}$$

where $\overline{w^2}$ is the mean squared deviation of E from E_0. In this simple case

$$\Delta c_p = \frac{\overline{w^2}}{Vk_BT^2}, \tag{24}$$

and the thermal expansion at zero pressure

$$\Delta\alpha = \frac{a\overline{w^2}}{Vk_BT^2}. \tag{25}$$

While one cannot expect every glass former to have a single Gaussian density of inherent states, it turns out to be easy to find substances which have the $1/T^2$ dependence. Figure 2 shows two examples,[24,25] B_2O_3 and the metallic glass vitralloy-1. There are more such cases,[2] but there are also cases like glycerol[26] and selenium,[27] where the additional heat capacity decreases more slowly. The equations derived here suggest that the function $g(E)$ is not a Gaussian in these two cases.

The case of selenium allows us to compare the two Grüneisen constants Γ and Γ_E describing the volume dependence of the average vibrational frequency in the glass and in the undercooled liquid, respectively. From Eq. (2), one has in the undercooled liquid a vibrational component $\Delta c_{p,\mathrm{vib}}$ of Δc_P

$$\Delta c_{p,\mathrm{vib}} = T\left.\frac{\partial S_{\mathrm{vib}}}{\partial T}\right|_{T_g} = \Gamma_E k_B \Delta\alpha T_g. \tag{26}$$

Inserting the data[28] for selenium at T_g, the product $\Delta\alpha T_g$ is 0.076. There is an inelastic neutron scattering measurement[29] of $\Delta c_{p,\mathrm{vib}}$, which places it at about one third the total Δc_p of 1.72 k_B per atom. With this value, one calculates $\Gamma_E = 15$. On the other hand, Eq. (1) with the values from Ref. 28 provides $\Gamma = 0.5$, a much smaller value.

The large difference becomes understandable if one looks at the neutron scattering data.[29] In fact, the large increase of the vibrational entropy above T_g is only due to changes at the low frequency end of the vibrational spectrum, at and around the boson peak. Thus one does not see an effect of the entire vibrational spectrum, but merely the one of a small minority of soft modes close to a structural instability.[30] They are still tractable in terms of the quasiharmonic approximation, but it is no wonder that their Grüneisen parameter under structural changes should be much larger than the average one of the entire spectrum in a fixed configuration.

B. Coupling to longitudinal and transverse sound waves

Measurements of the Prigogine-Defay ratio at the glass transition[3] in B_2O_3 show a value of 4.7, much larger than unity. This shows that the constant-energy component of the density fluctuations is a factor of 3.7 larger than the rest. But there are also substances with a Prigogine-Defay ratio close to unity,[5] for which the volume distribution function $g_V(E,V-V_E)$ of Eq. (3) is essentially a δ function at V_E, with practically no contribution to the density fluctuations.

This possibility of a practically complete absence of a volume variation at constant structural energy is surprising if one considers the volume variation as just a special case of a distortion. One knows that there must be infinitely many shear distorted inherent states at constant structural energy, because otherwise one cannot understand the viscous flow. If one applies a small shear strain to a given inherent state, the sample ends up after the equilibration in another sheared inherent state with the same structural energy. If the Prigogine-Defay ratio is unity, this sheared inherent state has the same volume as the initial one. The consideration shows that a Prigogine-Defay ratio of unity implies a zero coupling of the structural shear relaxation processes to an external compression.

One can get an independent experimental access to this aspect of the problem by comparing the acoustic absorption of longitudinal and transverse sound waves at low temperatures in the glass phase.[28] The low temperature absorption is due to tunneling states,[31–33] which can be viewed as two inherent states separated by a very small energy barrier. If these two states differ only in the shear strain, the ratio of the square of the coupling constants γ_l for longitudinal waves and γ_s for transverse waves is $\gamma_l^2/\gamma_t^2 = 4/3$, because the longitudinal modulus $M = B + 4/3G$ (B bulk modulus and G shear modulus). If the ratio exceeds 4/3, one has evidence for a volume difference of the two inherent states. One can quantify this influence in terms of the definition of a bulk-shear coupling ratio

$$\frac{\delta B}{\delta G} = \frac{\gamma_b^2}{\gamma_s^2} = \frac{\gamma_l^2}{\gamma_s^2} - \frac{4}{3}, \tag{27}$$

where γ_b is the coupling constant of the tunneling state to an external compression. In most glasses,[31–33] this ratio lies between 1 and 2, showing that there is indeed a strong coupling to an external compression.

It is not straightforward to define a comparable ratio $\delta B/\delta G$ at the glass transition. The proper way would be to define the ratio in terms of compliances. But the shear compliance diverges, while the bulk compliance (the compressibility) stays finite.

One can make a crude compromise[28] by saying that the processes which reduce the shear modulus G to zero reduce the bulk modulus by ΔB, and that this defines the average coupling ratio $\delta B/\delta G$. Then

$$\Delta B = \frac{\delta B}{\delta G} G. \tag{28}$$

One calculates ΔB from the difference

$$\Delta B = B_{PD} - B_0, \tag{29}$$

where B_{PD} is the zero frequency modulus one would have for a Prigogine-Defay ratio of unity (the low frequency modulus for zero compression coupling)

$$B_{PD} = \frac{1}{1/B + \Delta\kappa/\Pi} \tag{30}$$

and B_0 is the actual measured zero frequency modulus of the undercooled liquid

$$B_0 = \frac{1}{1/B + \Delta\kappa}. \tag{31}$$

This recipe allows us to determine the average coupling ratio $\delta B/\delta G$ from the measurements at T_g via

$$\frac{\delta B}{\delta G} = \frac{B\Delta\kappa(\Pi - 1)}{1 + B\Delta\kappa(\Pi - 1)} \frac{B}{G}. \tag{32}$$

It turns out that this approximation works rather well for a large number of substances. One gets essentially the same dependence on the Poisson ratio for both glass transition data and tunneling states. Also, substances measured both at T_g and at low temperature show the same ratio within experimental error.[28] The substances with zero bulk coupling (a Prigogine-Defay ratio of unity) occur at the high Poisson ratio end, at a value of about 0.4.

C. Comparison to simulation

The question is: Why do some glass formers like B_2O_3 have a large Prigogine-Defay ratio (a strong coupling of the structural relaxation processes to an external compression), while others have a Prigogine-Defay ratio close to unity,[5] i.e., structural relaxations which do not couple to an external compression? Part of the answer to this question has been given in numerical studies[16,17] of different interatomic potentials. These studies have a relaxation time range of nanoseconds, in the best case microseconds. Therefore they do not discriminate between vibrations and structural relaxation, but calculate the total enthalpy-volume correlation. They find a strong correlation in the Lennard-Jones potential, a slightly weaker but still strong correlation in the MGCU-potential applicable to metallic glasses, but a rather weak correlation for hydrogen bonded substances.

Taking the heavily studied[34] Lennard-Jones example, the strong enthalpy-volume correlation (equivalent to a Prigogine-Defay ratio close to unity) at zero pressure is the same as the one for a steep inverse power law potential with an applied external pressure.[16,17] The inverse power law is $1/r^{18.9}$ (r interatomic distance). This shows that the Lennard-Jones potential is rather close to the hard-sphere case. The applied external pressure needed to hold the atoms together in the equivalent inverse power potential can be estimated from the linear potential term of 2.4 r in Lennard-Jones units at the first coordination shell;[16,17] it is not small.

The effect of an external pressure on the structural states of the inset of Fig. 1, the ones responsible for the compressibility $\Delta\kappa_0$, is to change their energies. Thus they are no longer at equal energy and begin to contribute to the heat capacity and to the thermal expansion. As a consequence, the Prigogine-Defay ratio diminishes. Its deviation from its zero pressure value should become notable at the critical pressure

$$p_{\text{crit}} = \frac{1}{a} = \frac{\Delta c_p}{\Delta\alpha}, \tag{33}$$

because then the structural states of the inset of Fig. 1 have half the energy-volume coefficient of the other ones.

The strong enthalpy-volume correlation of the Lennard-Jones system extends down to low temperatures in the glass and even in the crystal,[16] showing that in this case the vibrations reflect the properties of the structural relaxation. This is consistent with the finding $\delta B/\delta G = 0$ in a Lennard-Jones glass at zero temperature.[35,36] The instantaneous affine shear deformation modulus G_∞ is a factor of two higher than the final G, but $B_\infty = B$. Since B_∞ and G_∞ have the central-force Poisson ratio $\nu = 1/3$, this pushes[36] the final ν up to 0.4. The effect is due to a nonaffine motion of the atoms which lowers the shear energy, but does not couple to the compression. The nonaffine motion is intimately related to the boson peak and to the tunneling states which dominate the glass behavior at very low temperatures[30,37] as well as to the plastic modes responsible for the shear thinning in non-Newtonian flow.[38]

One can define a (numerically accessible) vibrational coupling ratio in the low-temperature glass

$$\frac{\delta B}{\delta G} = \frac{B_\infty - B}{G_\infty - G}, \tag{34}$$

which in the Lennard-Jones case is zero, as well as the one defined in Eq. (32). There seem to be several examples for an equality even if the ratio is nonzero.[28] This supports numerical evidence[39] for an intimate relation between the soft modes and the structural rearrangements of the undercooled liquid, a property which glass forming liquids seem to share with colloids and granular matter.[40]

D. Metallic glasses and the Ioffe-Regel limit

There are some indications that one has a low $\delta B/\delta G$ in metallic glasses as well, though their anharmonic thermal expansion[41] $\alpha_l T_g = 0.035$ is a factor of ten smaller than the Lennard-Jones one.[16] Tunneling state measurements[33] show a coupling constant ratio of 4/3, consistent with the complete absence of a coupling to the compression. This implies a Prigogine-Defay ratio of unity.

In the Lennard-Jones glass, both vibrational and relaxational modes have a zero coupling to an external compression, i.e., a coupling constant ratio of 4/3 to longitudinal and transverse sound waves, respectively. Assuming the same for metallic glasses resolves a controversy of long standing[42,43] on the scattering of sound waves at the boson peak. The existence of a plateau in the thermal conductivity of glasses[44,45] at about 5 K shows that one reaches the Ioffe-Regel limit of strong damping (mean free path equal to wavelength) more or less in the boson peak region. While it is not yet possible to measure the damping of transverse waves at the boson peak, one can measure the damping of longitudinal waves with the x-ray Brillouin technique. On the basis of such measurements, it was concluded that the Ioffe-Regel limit is reached at the boson peak.[43] But there is one notable exception: in the x-ray Brillouin scattering of a metallic glass[42] at the boson peak, the damping is decidedly smaller than the Ioffe-Regel limit.

The controversy is resolved if one assumes a Prigogine-Defay-ratio of one in the measured metallic glass. If one has zero coupling to an external compression, the ratio γ_l^2/γ_t^2 is only 4/3. The damping is proportional[45] to γ^2/v^3, where v is the sound velocity. In the metallic glasses, the ratio of the sound velocities is approximately a factor of 2, so the damping of the longitudinal waves at the boson peak should be about a factor of six weaker than the one of the transverse waves.

Independent support of this interpretation of the x-ray Brillouin data is supplied by a soft-sphere simulation,[46] which only shows the Ioffe-Regel limit for the transverse waves. The findings indicate that one has $\delta B/\delta G$ close to zero in the rather harmonic metallic glasses as well as in the anharmonic Lennard-Jones case, in agreement with the numerical finding[16] for the MGCU potential. This is another example where the absence of a coupling to an external compression seems to be shared by all three groups of glassy excitations, namely relaxations, tunneling states, and boson peak modes.

Both Lennard-Jones systems and metallic glasses belong to the close packed systems. There are two possible reasons for a weak compression-relaxation coupling in close packing: (i) the attractive part of the potential acts as a critical pressure in both Lennard-Jones systems and metallic glasses, (ii) the elementary structural relaxation processes in close packing couple only very weakly to the compression. The second possibility is supported by two atomic models for the structural relaxation in close packing, the interstitial[47,48] and the gliding triangle,[49] both of which couple only to the shear.

IV. SUMMARY

To conclude, the paper presents a thermodynamic description of the undercooled liquid at zero pressure which allows us to calculate the additional thermal expansion, the additional heat capacity, and the additional compressibility above T_g from the properties of the inherent states. The description provides a physical explanation for the large measured Prigogine-Defay ratios at the glass transition. According to this explanation, one has to distinguish two kinds of slow density fluctuations in the undercooled liquid (in agreement with the traditional view of more than one order parameter freezing in at the glass transition). The first kind is always present and is due to a change to an inherent state with a different structural energy and, consequently, a different volume. This first kind is responsible for the thermal expansion. The second kind is due to the existence of inherent states with different volumes at the same structural energy. If this second kind is absent, enthalpy and volume fluctuations are strongly correlated and the Prigogine-Defay ratio is one.

A Prigogine-Defay ratio of unity is equivalent to a zero coupling of the structural relaxation processes (flow processes) to an external compression. In glass forming systems, this case is the exception rather than the rule. The most important example is the heavily studied Lennard-Jones system. In this case, the zero coupling is found both for the relaxations and for the boson peak vibrations. The relatively weak coupling of the longitudinal sound waves to tunneling states and boson peak modes indicates a Prigogine-Defay ratio close to unity in metallic glasses as well. In spite of intense numerical studies, the reason for the zero coupling is not yet fully clear.

ACKNOWLEDGMENTS

Helpful discussions with Michael Ohl and Herbert Schober are gratefully acknowledged.

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