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Constant-volume heat capacity at glass transition

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ABSTRACT

We analyze the jump of heat capacity at glass transition, and calculate the constant-volume heat capacity change ΔC_v at glass transition in the common glass formers. The experimental heat capacity jump ΔC_p includes both dynamic and dilation's contributions. The ΔC_v removes the dilation's contribution, and only refers to the dynamic contribution. We find that the ratio $\Delta C_v/\Delta C_p$ does not change with the liquid fragility, and almost keeps a constant: 0.85. The results might have implications for a fundamental understanding to the nature of glass transition.

1. Introduction

The glass or the amorphous solid can be achieved by quenching a liquid sufficiently rapidly below its glass transition temperature T_g [1]. The liquid forms a similarly disordered solid glass without a traditional phase transition, yet heat capacity changes with a jump at T_g. And the nature of the jump or the glass transition is one of the most fascinating open questions in materials science and condensed matter physics [2]. A hotly debated issue is whether the glass transition involves an underlying thermodynamic (static) or kinetic (dynamic) phase transition, which remains unsolved and controversial [3–5]. A thermodynamic first-order phase transition must involve abrupt changes in certain thermodynamic properties, such as volume. But no discontinuities of the thermodynamic properties are perceivable at the glass transition. According to the thermodynamic viewpoint, the experimentally observable glass transition is a kinetically controlled manifestation of an underlying thermodynamic transition. In contrast, the kinetic viewpoint explains the observed structural changes as the consequence of a dynamic transition in the relaxation of the supercooled liquid, which is not accompanied by abrupt changes in thermodynamic properties. Some models indicate that the change of heat capacity at T_g involves the vibrational and configurational degrees of freedom [5–8]. In other words, the glass transition involves both thermodynamic (static) and kinetic (dynamic) transition. But the configurational (or dynamic) contribution is difficult to be directly determined by experiment. Recently the experimental results determine the fraction of the configurational (or dynamic) heat capacity, which also depends on the liquid fragility *m* [9]. Trachenko et al. analyzed the thermodynamic properties of the glass formers near T_g and explained the heat capacity jump (ΔC_p) at T_g [10]. Their theories indicate that the ΔC_p at T_g in glass formers is correlated with the liquid fragility *m*.

The ΔC_p at T_g is the difference between the glass-forming supercooled liquid's heat capacity C_p^l and the relative solid glasses heat capacity C_p^g near T_g. Previous investigations of the ΔC_p at T_g have been focused on polymers and molecular liquids. According to the hole theory [11], the "bead" or the simplest molecular unit can describe the ΔC_p in the amorphous materials, and the value of the ΔC_p is an approximately constant around 11.2 J/mol-bead/K. Recently, the ΔC_p in the dense random packing metallic glasses is studied [12,13]. The ΔC_p in a variety of metallic glasses is almost an invariable value (13.69 J/mol/K), and is close to $3R/2$ (where *R* is gas constant), which can be quantitatively described by the atomic transitional diffusion. So the glass transition in metallic glasses is a pure dynamic or kinetic process.

In general, the heat capacity depends upon the temperature of the system and the way it is heated, for example, at constant-volume and constant-pressure. The former refers to C_v, and the latter to C_p. The heat capacity data are usually obtained under constant, generally atmospheric, pressure. So the experimental heat capacity usually refers to C_p. There is a known relationship between C_v and C_p: $C_p - C_v = VT\alpha^2B$, where *V* is the molar volume, α is the coefficient of thermal expansion, and *B* is the bulk modulus [14]. Due to both positive coefficient of thermal expansion and bulk modulus, C_p is always greater than C_v. The relationship is a general expression and applies to both solids and liquids. The difference

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between C_v and C_p near 0 K is negligible because of the very low coefficient of thermal expansion. But the ratio $(C_p - C_v)/C_p$ can be as large as 10% at the melting temperature T_m. In metallic glasses, the glasses transition temperature T_g is close to the melting temperature T_m, and the ratio T_g/T_m is about 0.7 [15]. So the difference between C_v and C_p cannot be negligible.

In this paper, we analyze the jump of heat capacity at T_g, and calculate the constant-volume heat capacity change at T_g in the common amorphous substances including polymers, oxides glasses, ionic glasses, metallic glasses, and elementary selenium glass. The experimental ΔC_p includes both dynamic and dilation's contributions. And the dynamic contribution is determined by constant-volume heat capacity, which is not correlated with the fragility.

2. Details of calculation

The relationship, $C_p - C_v = VT\alpha^2B$, which applies to both solids and liquids, can be used to study the constant-volume heat capacity change near T_g. The relationship in both glass and liquid at T_g can be written by the following two equations:

$$C_p^g - C_v^g = V_g T_g \alpha_g^2 B_g, \tag{1}$$

$$C_p^l - C_v^l = V_l T_g \alpha_l^2 B_l, \tag{2}$$

where subscripts l and g refer to the supercooled liquid and the glass. Here, the unit of heat capacity is J/mol/K or J/g-atom/K, and the unit of molar mass M is g/mol or g/g-atom. Due to no abrupt volume change near T_g, we set $V \approx V_l \approx V_g$. The volume change from room temperature to T_g is weak, and usually less than 1%. We then write the molar volume at T_g:$V = M/\rho$, where ρ is the room temperature density. The jump of the constant-pressure and constant-volume heat capacity at T_g is $\Delta C_p = C_p^l - C_p^g$ and $\Delta C_v = C_v^l - C_v^g$, respectively. Therefore, from Eqs. (1) and (2), the relationship between the ΔC_v and ΔC_p at T_g can be written as:

$$\Delta C_v = \Delta C_p - \Delta C, \tag{3}$$

$$\Delta C = VT_g(\alpha_l^2 B_l - \alpha_g^2 B_g). \tag{4}$$

From Eq. (3), one can see that the term ΔC is due to the thermal expansion effect or the anharmonic vibration effect.

3. Results and discussion

The survey results of the density ρ, T_g, volume expansion coefficient α_l of the supercooled liquid and α_g of the glass, molar mass M, bulk modulus B_l of the supercooled liquid and B_g of the glass, ΔC_p at T_g and fragility m are listed in Table 1 [3,10,12,13,16–29]. The investigated glass formers contain polymers, ionic glasses, metallic glasses, oxide glasses, and amorphous Se. The α_l and B_l of the metallic supercooled liquids are not known for most metallic glasses. The experimental thermal expansion ratio α_l/α_g in the Pd, Zr, and Fe-based metallic glasses is about 1.6 [30–33]. So here we assume $\alpha_l \approx 1.6\ \alpha_g$ for those metallic glasses. Similarly, the bulk modulus in Pd-based, Zr-based and Ce-based metallic glasses change weakly with the temperature [34–37], and we suppose $B_l \approx B_g$ in those metallic glasses.

From the experimental values of $\rho, \alpha_l, \alpha_g, M, B_l, B_g, \Delta C_p$ listed in Table 1, we calculate ΔC and ΔC_v using Eqs. (3) and (2), and the results are listed in Table 2. Wunderlich suggested that the "bead" or the simplest molecular unit can describe the approximately constant of ΔC_p in the amorphous materials [11]. For the strong glass GeO_2, when we set the simplest molecular unit is GeO_2, the change of heat capacity for the GeO_2 unit is 5.49 J/mol–GeO_2/K, which is also far below the constant 11.2 J/mol-bead/K. Similarly, the ΔC_p of the $NaAlSi_3O_8$ and B_2O_3 glasses cannot be simply described by the "bead" unit.

The calculated ΔC, exhibited in the Fig. 1a, changes from 0.20 to 5.46 J/mol/K. This means that the ΔC is markedly different for different glass formers. Fig. 1b shows the ΔC_p and the calculated ΔC_v. vs. fragility m. The values of the experimental ΔC_p and the calculated ΔC_v are also significantly different for different glass formers. The results indicate that the heat capacity jump at T_g in glass formers is not directly correlated with the m. The ratio $\Delta C_v/\Delta C_p$ for the typical amorphous materials is calculated and exhibited in Table 2.

Table 1

Room temperature density ρ, glass transition temperature T_g, volume expansion coefficient α_l of the supercooled liquid and α_g of the glass, molar mass M, bulk modulus B_l of the supercooled liquid and B_g of the glass, jumps in heat capacity ΔC_p at T_g, and fragility m.

No.	Material name	ρ (g/cm^3)	T_g (K)	α_l (10^{-6}K^{-1})	α_g (10^{-6}K^{-1})	M (g/mol)	B_l (GPa)	B_g (GPa)	ΔC_p (J/mol/K)	m	Refs.
1	GeO_2	4.25	818	76	27	34.9	8.08	23.9	1.83	20	[10,16,17]
2	$NaAlSi_3O_8$	2.62	1100	54	23	32.8	20	40	2.46	24.4	[10,17,18]
3	$La_{55}Al_{25}Ni_{20}$	5.91	465		45.9	95.6		44[a]	13.4	28[a]	[12,13,19,20]
4	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	6.61	653		33.9	78.3		106.7[b]	12.5	30[b]	[12,19,20]
5	B_2O_3	2.46	550	400	50	13.9	2.6	10	8.77	30.6	[10,17,18,21]
6	$Mg_{65}Cu_{25}Y_{10}$	2.27	380		77.4	40.6		44.7[c]	12.9	41	[12,13,19,20]
7	Glycerol	1.26	190	500	100	6.58	5.5	9.9	8.8	48	[10,16,22]
8	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	6.09	623		29.7	59.9		112	12.9[d]	50	[12,19,20]
9	$Pd_{77.5}Cu_6Si_{16.5}$	10.6	625		41.1	90.9		167	12.7	52	[13,19,20]
10	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	9.31	525		53.4	73.7		151.8	13.7	52	[13,19,20]
11	Glucose	1.54	300	350	90	7.507	6.49	10.8	5.66	52	[3,23]
12	$Pd_{40}Ni_{40}P_{20}$	9.51	551		47.1	72.2		185	13.7	54	[13,19,20]
13	$Zr_{55}Al_{10}Ni_5Cu_{30}$	6.79	653		33.9	74.9		115[e]	12.8	72[f]	[13,19,20]
14	O-terphenyl	1.16	241	720	300	7.20	2.1	3.7	10.24	81	[10,16,24]
15	$Pt_{60}Ni_{15}P_{25}$	15.1	478		37.5	133		202	20	86	[19,20,25]
16	Selenium	3.99	300	420	170	78.96	3.31	4.1	14.88	87	[3,26]
17	Polyvinyl acetate	1.19	304	710	280	7.17	2	3.5	3.59	88	[10,21,27]
18	$0.4Ca(NO_3)_2$-$0.6KNO_3$	2.19	340	360	120	19.1	7.6	15.9	10.33	93	[10,16,21]
19	Polystyrene	1.05	355	600	250	6.51	1.5	2	8.75	97	[10,28,29]

[a] Value for $La_{55}Al_{25}Ni_5Cu_{10}Co_5$.

[b] Value for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$.

[c] Value for $Mg_{65}Cu_{25}Tb_{10}$.

[d] Value for $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$.

[e] Value for $Zr_{55}Al_{19}Cu_7Co_{19}$.

[f] Value for $Zr_{55}Al_{22.5}Co_{22.5}$.

Table 2
Calculated values of ΔC [$=MT_g(\alpha_l^2 B_l - \alpha_g^2 B_g)/\rho$], $\Delta C_v(=\Delta C_p - \Delta C)$, and $\Delta C_v/\Delta C_p$, and the experimental values of ΔC_p at T_g and fragility *m*.

No.	Material name	ΔC (J/mol/K)	ΔC_p (J/mol/K)	ΔC_v (J/mol/K)	$\Delta C_v/\Delta C_p$	*m*
1	GeO_2	0.20	1.83	1.63	0.89	20
2	$NaAlSi_3O_8$	0.51	2.46	1.95	0.79	24.4
3	$La_{55}Al_{25}Ni_{20}$	1.09	13.4	12.31	0.92	28
4	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	1.48	12.5	11.02	0.88	30
5	B_2O_3	1.22	8.77	7.55	0.86	30.6
6	$Mg_{65}Cu_{25}Y_{10}$	2.84	12.9	10.06	0.78	41
7	Glycerol	1.26	8.8	7.54	0.86	48
8	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	0.95	12.9	11.95	0.93	50
9	$Pd_{77.5}Cu_6Si_{16.5}$	2.37	12.7	10.33	0.81	52
10	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	2.81	13.7	10.89	0.80	52
11	Glucose	1.03	5.66	4.63	0.82	52
12	$Pd_{40}Ni_{40}P_{20}$	2.68	13.7	11.02	0.80	54
13	$Zr_{55}Al_{10}Ni_5Cu_{30}$	1.48	12.8	11.32	0.88	72
14	O-terphenyl	1.13	10.24	9.11	0.89	81
15	$Pt_{60}Ni_{15}P_{25}$	1.87	20	18.13	0.91	86
16	Selenium	2.76	14.88	12.12	0.81	87
17	Polyvinyl acetate	1.34	3.59	2.25	0.63	88
18	$0.4Ca(NO_3)_2$-$0.6KNO_3$	2.25	10.33	8.08	0.78	93
19	Polystyrene	0.91	8.75	7.84	0.9	97

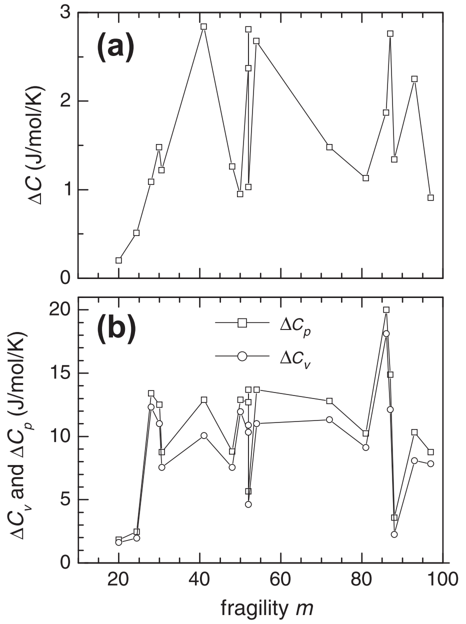

Fig. 1. (a): Correlation between the calculated ΔC and *m* for the amorphous materials listed in Table 2. (b): ΔC_v (or ΔC_p) vs. *m* for the amorphous materials.

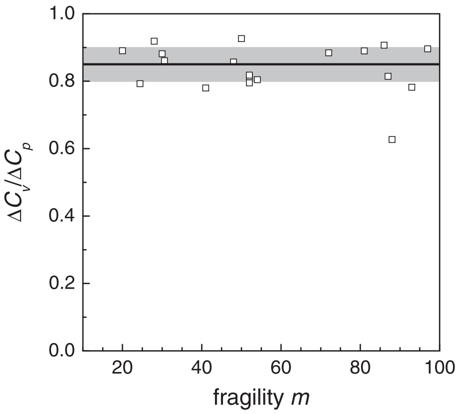

Fig. 2. Ratio of $\Delta C_v/\Delta C_p$ for the amorphous materials listed in Table 2. The solid line is the meaning value of the ratio, and the shadow is the error of the meaning value.

The ratio $\Delta C_v/\Delta C_p$ for the several common glass formers (the exception is the glass former polyvinyl acetate with the ratio 0.63) is close to a value 0.85 with the error of ±0.05, as shown in Fig. 2.

There is no abrupt density or volume change in glass formers near glass transition. So the C_v in glass formers should keep a constant if there is not the dynamic contribution near glass transition. Yet the experimental results show that there is an obvious jump of C_v near glass transition in these glass formers. So the heat capacity of the glass or supercooled liquid usually includes the vibrational, anharmonic, and dynamic (or configurational) parts [9,38–43]. In the relationship $C_p - C_v = VT\alpha^2B$, the term of $VT\alpha^2B$ refers to the anharmonic contribution to the measured heat capacity C_p, which is due to the thermal expansion effect. So the anharmonic vibration effect can be determined by the relationship and the constant-volume heat capacity C_v of the glass or supercooled liquid only includes the vibrational and dynamic parts. The dynamic heat capacity is difficult to access by experiment. As far as known at present, only the high electric field impedance experiment and the temperature-modulated scanning calorimetry can be used to directly determine the dynamic heat capacity [9,38–40]. The results by temperature-modulated calorimetry show that the vibrational heat capacity of the glass is almost as same as that of its supercooled liquid [40–43]. Therefore, the ΔC_v $(= C_v^l - C_v^g)$ in the glass formers removes both vibrational and anharmonic contributions, and only refers to the dynamic contribution. The ratio $\Delta C_v/\Delta C_p$ in glass formers is the fraction of the dynamic contribution. In the high electric field impedance experiment [9], the fraction of the dynamic heat capacity for the glass former Glycerol is determined to be 0.81. Our analysis results show that the ratio $\Delta C_v/\Delta C_p$ at T_g for the Glycerol is 0.86, and is very close to that by the high electric field impedance experiment, which also proves that the ratio $\Delta C_v/\Delta C_p$ just is the fraction of the dynamic contribution in glass formers. So the glass transition is mainly a dynamic process, and the fraction of the dynamic transition is about 0.85.

4. Summary

In conclusion, the heat capacity jump at T_g is analyzed in the typical amorphous substances with markedly different fragility. The ΔC_v at T_g removes both vibrational and anharmonic contributions, and only refers to the dynamic contribution. The ratio $\Delta C_v/\Delta C_p$ in the glass formers, or the fraction of the dynamic contribution, almost keeps a constant of 0.85 and does not change with the liquid fragility *m*. The results are essential for understanding the nature of glass transition.

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