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Melting and glass transitions of low molecular weight carbohydrates

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ABSTRACT

Glass-transition temperatures at various water contents (T_g) and in maximally freeze-concentrated solutions (T_g'), fusion temperatures (melting points, T_f), and heats of fusion (ΔH_f) were determined for pentoses, hexoses, disaccharides, and alditols, using differential scanning calorimetry. The T_g and T_g' values of the anhydrous compounds increased in the order pentoses < hexoses < disaccharides. The T_g values of the alditols were lower than those of the corresponding sugars. Compounds with high T_f/T_g ratios had high ΔH_f values and showed rapid crystallisation. The T_g and T_g' values allowed the prediction of T_g as a function of the water content and of the concentration of the maximally freeze-concentrated matrices (C_g'). The C_g' concentration was ~ 80% (w/w) for each carbohydrate. The results can be used to evaluate the physical stability of various carbohydrates at various water contents and in freeze-concentrated solutions.

INTRODUCTION

Most carbohydrates form amorphous structures in low-moisture and frozen biological materials, which are similar to those of other organic and inorganic amorphous compounds[1-9]. Amorphous materials may exist as solid "glasses" or liquid-like "rubbers" and the transition between these states is a second-order change in phase which occurs at the glass-transition temperature (T_g). When carbohydrate glasses are heated above T_g, noticeable changes in specific heat and viscosity occur, and amorphous carbohydrates can be classified as thermoplastics.

The properties of glucose glasses have been determined[1-3] and T_g values have been reported for fructose[8,10], lactose[11], maltose[12-15], galactose[16], glucitol[17], sucrose[4,5,11], and glucans[7]. These T_g values are affected by water, which is the main plasticiser of amorphous carbohydrates and other biological materials[4]. At low concentrations, water significantly decreases the T_g values[7,8,11]. The effect of temperature and water on the physical state of amorphous carbohydrates is

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particularly important in relation to the stability of dehydrated and frozen materials[9,18]. However, quantitative data on water plasticisation have been reported only for a few sugars[8,16,22], oligosaccharides[13], and polysaccharides[7,15].

Various thermal transitions were shown to occur[19,20] during the heating of carbohydrate solutions which had been cooled rapidly. The main transitions were the T_g of the freeze-concentrated solution, the formation of ice (devitrification) during rewarming, and the melting of the ice. The T_g values and ice-melting temperatures (T_m) had values that were independent of the initial concentration of the solution. Thus, during freezing, an initial concentration-independent unfrozen amorphous matrix with a constant solute and water content was formed as the maximum amount of water crystallised. T_g values (T_g') for various maximally freeze-concentrated carbohydrate solutions have been reported[9,21]. Roos and Karel[8,15,18,22] reported T_g' values lower than those reported by Levine and Slade[9,21] for common sugars and proposed that the onset temperatures of ice melting (T_m') in the maximally freeze-concentrated solutions were equivalent to the T_g' values[9,21].

Although T_g and T_g' values have been reported[9,21] for a wide range of carbohydrates together with C_g' data (solute concentration in the maximally freeze-concentrated matrix), only a few studies have reported T_g, T_g', and T_m' values for sugars at several water contents. Phase transitions of various pentoses, hexoses, disaccharides, and alditols, determined by differential scanning calorimetry, are now reported.

EXPERIMENTAL

Preparation of amorphous carbohydrates.—The mono- and di-saccharides and alditols in Table I, when analysed for melting point (T_f) and heat of fusion (ΔH_f), showed no evidence of a glass transition, and they were considered to be totally crystalline. Anhydrous amorphous sugars were produced by heating each crystalline compound (0.1–0.5 g) above the melting point. Dehydration during melting was assumed, since temperatures well above 100°C were necessary for preparation of the sugar melts. Materials that contained 70, 80 and 90% of solute were prepared from the crystalline compounds and the respective amounts of distilled water, and each was heated until a clear melt was obtained[8]. The water content of the materials was monitored by weighing. Solutions with concentrations of 20, 30, and 40% of sugar were prepared similarly, but without heating. The water in hydrates (Table I) was included in the total water contents.

Differential scanning calorimetry (DSC).—DSC was used to determine melting points (T_f), heats of fusion (ΔH_f), glass-transition temperatures, and for 20, 30, and 40% solutions, the T_g' and T_m' values. A Mettler TA 4000 analysis system was used with a DSC30 low-temperature cell, a TC10A TA processor, and GraphWare TA72AT.2 thermal analysis software. The instrument was calibrated[22] using hexane, distilled water, and indium. Analyses in triplicate involved 40-μL hermetically sealed aluminium pans (Mettler) heated at 5°C/min.

TABLE I

Onset values for the glass-transition temperatures of solutions with various solute concentrations (% solute) without ice formation (T_g) and with maximum freeze-concentration (T_g')

Compound	T_g (°C)				T_g' (°C)		
	melt	90%	80%	70%	40%	30%	20%
D-Arabinose	−2	[b]	[b]	[b]	[b]	−67	−66
D-Ribose	−20	−52	−70	−85	−67	−69	−67
D-Xylose	6	[b]	[b]	[b]	−65	−65	−66
D-Fructose	5	−33	−55	−73	−57	−57	−57
α-D-Fucose	26	–	–	–	–	–	–
D-Galactose	30	[b]	−61	[b]	[b]	−57	−56
D-Glucose	31	−28	−56	−74	−56	−56	−56
D-Mannose	25	−35	−58	−78	−58	−58	−58
α-L-Rhamnose (monohydrate)	−7	[b]	[b]	[b]	−59	−60	−62
L-Sorbose	19	[b]	[b]	[b]	−57	−57	−57
α-Lactose (monohydrate)	101 [a]	[b]	[b]	[b]	−41	−41	−41
Maltose (monohydrate)	87 [a]	−18	−44	−67	−41	−43	−42
α-Melibiose (0.5 g H_2O/mol)	85		[b]	[b]	−42	−42	−42
Sucrose [a]	62	[b]	−46	−68	−46	−46	−46
α,α-Trehalose (dihydrate)	100	[b]	[b]	[b]	−42	−42	−40
Maltitol	39	[b]	−56	−72	−47	−48	−47
D-Glucitol	−9	−46	−65	−77	−63	−63	−64
Xyliol	−29	[b]	−72	−85	−72	−72	−73

[a] Values reported by Roos and Karel[11,15,22]. [b] Rapid crystallisation.

Melting points (T_f) *and heats of fusion* (ΔH_f).—Crystalline compounds (3–10 mg) in hermetically sealed pans were scanned from $T_f - 30$°C to $T_f + 30$°C. Each thermogram was analysed for the onset of fusion (T_f), peak temperature of the melting ($T^p{}_f$), and the heat of fusion (ΔH_f), which was obtained by integration of the melting endotherm. The average values of triplicate measurements were obtained.

Glass-transition temperature (T_g).—Carbohydrate melts (3–20 mg) were transferred immediately after preparation into DSC pans by using glass capillaries, the pans were sealed hermetically, and scanned from $T_g - 30$°C to $T_g + 30$°C for the determination of onset temperature of the glass-transition region (T_g), endset temperature of the glass-transition region ($T^e{}_g$), and change of specific heat at the glass-transition region (Δc_p)[22]. The glass-transition midpoint value was obtained as an average of the T_g and $T^e{}_g$ values. The T_g values reported are averages of triplicate measurements.

Glass transition and ice melting in frozen solutions.—Carbohydrate solutions (10–20 mg) were transferred into DSC pans as above, and the 20 or 40% solutions were scanned initially from −100°C to 20°C in order to locate T_m'. Thereafter, each solution was cooled to −100°C, heated at 10°C/min to $T_m' - 1$°C, annealed for 15 min at $T_m' - 1$°C, cooled at 10°C/min to −100°C, and scanned from −100°C to 20°C for the determination of T_g' and T_m'. Annealing was necessary[8,15,22] in order

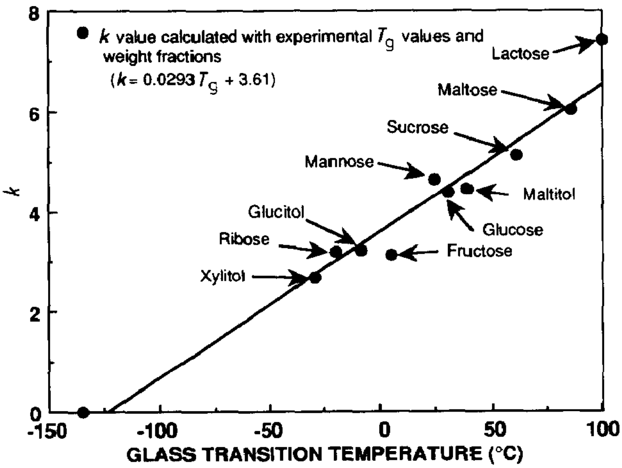

Fig. 1. The k value (eq *1*) of various sugars as a function of their anhydrous glass-transition temperature (T_g). The correlation coefficient was 0.959 and the regression equation was used to calculate the k value for each compound (Table IV).

to achieve maximum freeze-concentration and eliminate the devitrification typical of non-annealed carbohydrate solutions. Since T_g' and T_m' were independent of the initial concentrations, the values reported for each compound are average values of the total number of measurements.

Effect of water on the glass-transition temperature.—Equation *1*, originally reported by Gordon and Taylor[23] for the calculation of T_g values of binary polymer mixtures, was used to predict the T_g values of carbohydrates at various water contents,

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (1)$$

where w_1 and w_2 are the weight fractions of the solute and water, respectively, T_{g1} is the T_g of the anhydrous solute, T_{g2} is the T_g of water[24,25] (-135°C), and k is a constant.

Although eq *1* predicts the T_g values of carbohydrates at various water contents, several experimental weight fractions and T_g values must be used[8,18,22] in order to determine k. The values of k calculated for sugars with T_g values at several water contents are shown in Fig. 1. The plot of T_g for the anhydrous materials against k was linear (Fig. 1). The regression equation obtained was then used to estimate the k values for the solutions (Table IV). The C_g' values were predicted on the basis of the estimated k values and the experimental T_g' values (Table IV).

RESULTS AND DISCUSSION

Glass-transition temperatures.—The T_g values for the compounds studied are given in Table I. Each anhydrous compound could be rapidly cooled to below T_g

TABLE II

Glass-transition temperatures (T_g) and change of specific heat at T_g (Δc_p)

Compound	T_g (°C)					Δc_p (J/g)	
	onset	midpoint	endset	I [a]	II [a]		II [a]
Arabinose	−2	3	8		4	0.66	0.80
Ribose	−20	−13	−6	−10	−11	0.67	0.94
Xylose	6	14	21	9.5	13	0.66	0.95
Fructose	5	10	16	100	7	0.75	0.84
Fucose	26	31	35				
Galactose	30	38	46	110	32	0.50	0.85
Glucose	31	36	41	31	38	0.63	0.88
Mannose	25	31	38	30	36	0.72	0.97
Rhamnose	−7	0	6		27	0.69	1.00
Sorbose	19	27	34			0.69	
Lactose	101						
Maltose	87	92	98	43	95	0.61	0.79
Melibiose	85	91	97		95	0.58	0.65
Sucrose	62	67	72	52	70	0.60	0.77
α,α-Trehalose	100	107	115	79		0.55	
Maltitol	39	44	49			0.56	
Glucitol	−9	−4	1	−2		0.96	
Xylitol	−29	−23	−17	−18.5	−19	1.02	1.52

[a] Literature values: I, Slade and Levine[9]; II, Orford et al.[14].

without crystallisation. The T_g values generally increased with increasing molecular weight[9], i.e., pentoses < hexoses < disaccharides, but the T_g values of the alditols were lower than those of corresponding sugars. The drastic decrease of T_g with increasing water content accorded with the findings in previous studies[3,7–9,12–17,22]. The decrease of T_g with increasing water content also decreased the viscosity[9,22], which facilitated crystallisation[11]. Thus, anhydrous compounds with low T_g values and poor water solubilities crystallised rapidly (Table I). Rhamnose, lactose, melibiose, and α,α-trehalose, the anhydrous forms of which have high T_g values, probably crystallised as hydrates in the presence of water. Only arabinose and galactose showed rapid crystallisation at 40% concentrations.

The T_g values with Δc_p values are given in Table II. T_g values for several carbohydrates have been reported[7,9,14,21] as *midpoints* values (Table II). In this study, T_g values are reported generally as *onset* values because most mechanical properties change[22] above the *onset* value of T_g, e.g., the viscosity decreases. This value is particularly important for carbohydrate materials, which may become sticky and crystallise above the *onset* temperature[11,18,22]. The T_g *midpoint* values obtained in the present study were in good agreement with the literature values[9,14,16,17]. A few degrees in variation may reflect the method of sample preparation and the residual water contents in different studies. Levine and Slade[7,9,21] have discussed the high T_g value (100°C) of anhydrous fructose in comparison with other hexoses. However, the T_g value of fructose seems to be

TABLE III

Onset temperature of melting (T_f), peak temperature of the melting endotherm (values in parentheses), and heat of fusion (ΔH_f)

Compound	T_f (°C) [a]			ΔH_f (J/g) [a]		T_f/T_g [a]	
	I	II	III	I	II	I [e]	III
D-Arabinose	150 (160)			238		1.56 (1.60)	
D-Ribose	70 (86)	60 (90)	87	146	150	1.36 (1.42)	1.37
D-Xylose	143 (157)	135 (150)	153	211	280	1.49 (1.54)	1.51
D-Fructose	108 (127)	80 (115)	124	169	180	1.37 (1.44)	1.06
α-D-Fucose	133 (145)	115 (130)		186	190	1.36 (1.40)	
D-Galactose	163 (170)	140 (165)	170	243	280	1.44 (1.46)	1.16
D-Glucose	143 (158)	135 (150)	158	179		1.37 (1.42)	1.42
D-Mannose	120 (134)		139.5	137		1.32 (1.37)	1.36
α-L-Rhamnose [b]	86 (99)	85 (100)		191	210		
L-Sorbose	153 (163)	140 (160)		245	250	1.46 (1.49)	
α-Lactose [b]	(214)	160 (195)				(1.30)	
Maltose [b]	104 (123)		129 [f]	126			1.27
α-Melibiose [c]	138						
Sucrose	173 (190)	160 (185)	192	118	120	1.33 (1.38)	1.43
α,α-Trehalose [d]	91 (97)		203	127			1.35
Maltitol	139 (149)	115 (150)		147	150	1.32 (1.35)	
D-Glucitol	85 (99)	60 (95)	111	154	150	1.36 (1.41)	1.42
Xylitol	89 (95)	65 (100)	94	226	250	1.48 (1.51)	1.44

[a] I, This study; II, Raemy et al.[28]; III, Slade and Levine[9]. [b] Monohydrate. [c] 0.5 mol H_2O/mol. [d] Dihydrate. [e] Values calculated with onset values of T_f and T_g; values in parentheses are those calculated with peak values of T_f and onset values of T_g. [f] Anhydrous.

substantially lower (5°C), as also was reported by others[10,13]. Similarly, the T_g value of galactose was ~ 80°C below that reported by Slade and Levine[9]. Viscosity data for amorphous fructose[10] support the lower T_g values of these sugars, which probably reach the typical viscosity of the glassy state (10^{12} Pa s) below the lower T_g. The T_g values of disaccharides were higher than those reported[9]. The T_g values of α,α-trehalose and lactose are comparable. Although these findings support the proposed dehydration protection of amorphous α,α-trehalose without crystallisation in biological materials[12], its T_g value does not significantly differ from those of other disaccharides. α,α-Trehalose crystallised rapidly at low water contents, but crystallisation may become significantly delayed in biological materials[26].

Fusion temperatures (melting points).—Amorphous materials reach equilibrium conditions above the melting point (T_f). In the polymer literature, T_g and T_f values are often related. The T_f values are given in Table III. The relationship between T_f and T_g is usually given as the ratio T_f/T_g (Table III). For most sugars, this ratio was 1. 35 ± 0.02 (for onset temperatures), which indicated $T_f - T_g$ to be ~ 100°C as also reported by Slade and Levine[9]. Higher values were obtained for arabinose, xylose, galactose, sorbose, and xylitol. Polymers with high T_f/T_g ratios are considered to be readily crystallisable[9], as found also for the compounds in Table I. The anomalous low T_f/T_g values of fructose and galactose[9] were not confirmed.

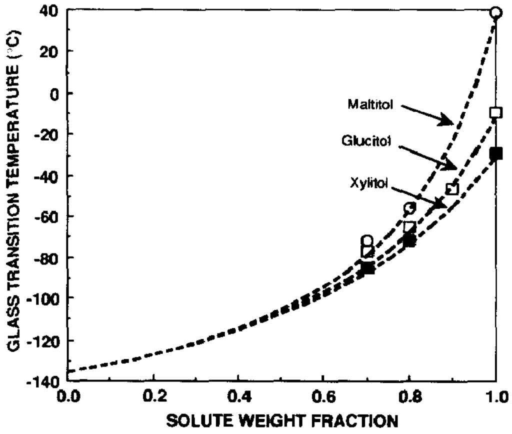

Fig. 2. Glass-transition temperature of alditols as a function of concentration. The dashed lines indicate the calculated T_g values.

Although most of the materials were considered to be anhydrous, traces of water would have decreased T_f and ΔH_f values[27]. Most of the T_f values were higher than those reported by Raemy et al.[28], but lower than those reported by Slade and Levine[9]. The ΔH_f values were mostly in accord with those reported by Raemy et al.[28]. Compounds with high T_f/T_g ratios also showed high ΔH_f values. The ΔH_f and T_f values are also dependent on the polymorphic form of the material. Examples of such materials are glucose[12], lactose[28], and α,α-trehalose[12] for which only the ΔH_f and T_f values of the anhydrous crystalline forms may be related to the T_g value of the anhydrous amorphous material. The T_f/T_g values were not calculated for lactose, maltose, melibiose, rhamnose, and α,α-trehalose (Table III).

Water plasticisation and freeze-concentration.—Each of the sugars studied was plasticised significantly by water. The T_g values of the alditols were the lowest and they are shown as a function of water content in Fig. 2. The T_g lines were calculated from eq *1* and the *k* estimates (Fig. 1). The predicted and experimental T_g values showed good correlation for the alditols (Fig. 2), monosaccharides (Fig. 3), and disaccharides (Fig. 4). A comparable water plasticisation was assumed to be typical of each compound studied, and the *k* estimates were used to calculate the C_g' value for each compound (Table IV).

Roos and Karel[8,22,27] reported that the maximum freeze-concentration of carbohydrate solutions is achieved by annealing at a temperature above T_g' but below T_m'. The rate of ice formation decreases with increasing initial solute concentration. The annealed solutions showed thermal behavior similar to those of annealed fructose, glucose, and sucrose solutions[8,22]. The annealed solutions had an initial concentration-independent T_g' and T_m' value (Table I and IV), which indicated that annealing for 15 min at $T_m' - 1$°C allowed ice formation and maximum freeze-concentration of the solutes. The T_m' values of monosaccharides were

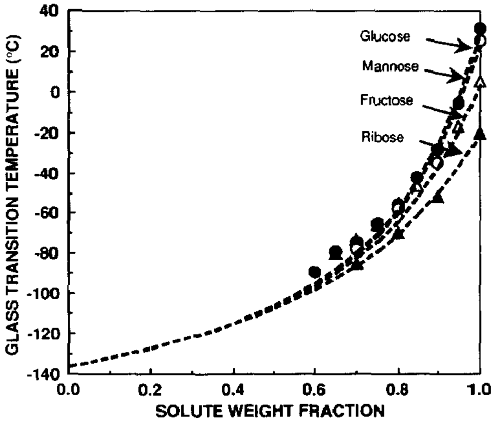

Fig. 3. Glass-transition temperatures of pentoses and hexoses as a function of concentration. The dashed lines indicate the calculated T_g values.

slightly above the endset temperatures of the T_g' values, but melting of the ice in most disaccharide solutions occurred at the completion of the T_g' range. The T_g' midpoint values determined by Slade and Levine[9] were above the T_m' values in Table IV. Levine and Slade[7,9,21] have considered an endothermal step change typical of DSC scans of freeze-concentrated carbohydrate solutions, defined[8,15,22] here as T_m', as T_g', which seems to result in the higher T_g' values.

The solute concentration in the maximally freeze-concentrated matrices (C_g') could be calculated from the T_g' and k values[8,22,27], The C_g' values (Table IV) were each ~ 80%, similar to those reported for fructose[8], glucose[8], lactose[8], maltose[8], and sucrose[22,29,30]. Most C_g' values reported by Slade and Levine[9] are significantly different from 80%, probably because their method did not consider

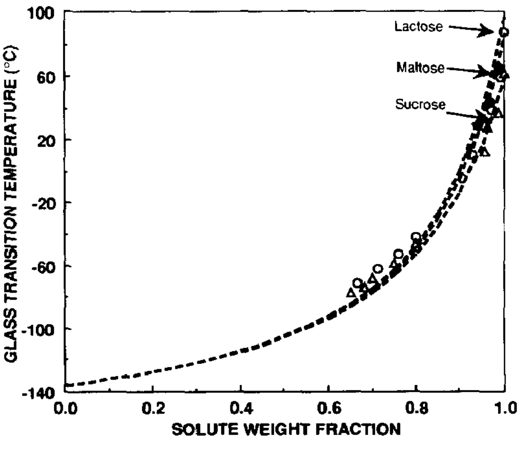

Fig. 4. Glass-transition temperatures of disaccharides as a function of concentration. The dashed lines indicate the calculated T_g values.

TABLE IV

Glass-transition temperatures of maximally freeze-concentrated solutes (T_g') and the amount of unfrozen water in the maximally freeze-concentrated matrix (C_g'); the estimated C_g' values were obtained with eq. *1* and the estimated k value

Compound	T_g' (°C)				T_m' (°C)	k	C_g' (%)	
	onset	midpoint	endset	Lit. [a]			Estimate	Lit. [a]
Arabinose	−66	−61	−55	−47.5	−53	3.55	79.3	44.8
Ribose	−67	−62	−57	−47	−53	3.02	81.4	67.1
Xylose	−65	−60	−54	−48	−53	3.78	78.9	69.0
Fructose	−57	−53	−50	−42	−46	3.76	82.5	51.0
Fucose	−62	−57	−51	−43	−48	4.37	78.4	47.4
Galactose	−56	−51	−46	−41.5	−45	4.49	80.5	56.5
Glucose	−57	−53	−50	−43	−46	4.52	80.0	70.9
Mannose	−58	−53	−47	−41	−45	4.34	80.1	74.1
Rhamnose	−60	−55	−49	−43	−47	3.40	82.8	52.6
Sorbose	−57	−52	−46	−41	−44	4.17	81.0	69.0
Lactose	−41	−36	−30	−28	−30	6.56	81.3	59.2
Maltose	−42	−37	−32	−29.5	−32	6.15	81.6	80.0
Melibiose	−42	−37	−32	−30.5	−32	6.10	81.7	
Sucrose [b]	−46	−41	−36	−32	−34	5.42	81.7	64.1
α,α-Trehalose	−40	−35	−30	−29.5	−30	6.54	81.6	83.3
Maltitol	−47	−42	−37	−34.5	−37	4.75	82.9	62.9
Glucitol	−63	−57	−51	−43.5	−49	3.35	81.7	81.3
Xylitol	−72	−67	−61	−46.5	−57	2.76	80.2	57.1

[a] Slade and Levine[9]. [b] Roos and Karel[22].

the time dependence of the formation of ice (annealing), the latent heat of ice melting decreases with decreasing melting temperature[22], and the latent heat of ice melting was determined by peak integration from a temperature below T_m'. C_g' values have also been determined using the heat of ice melting in samples having various initial concentrations of solute. A plot of the ratio of the heat of ice melting and the weight of solute against the ratio of weight of water and weight of solute results in a straight line which can be extrapolated to the unfrozen water content[16,22]. This method also gives lower C_g' values than the method used in this study[16,22], and it does not consider the heat of dilution of the solute during ice melting[30].

Thus, the T_g, T_g', and T_m' values can be used to calculate the T_g values of various carbohydrates and the compositions of maximally freeze-concentrated carbohydrate matrices. These values allow evaluation of the physical state of various sugars and alditols at various water contents and temperatures. This information is useful in the determination of the cryoprotective and cryostabilisation[9] properties of the compounds as well as the stability of the amorphous materials at low water contents and varying conditions. The T_f, T_g, and ΔH_f data can be used to evaluate such physical properties as crystallisation kinetics of the compounds above T_g.

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