

The Kauzmann Paradox at Constant Volume

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The entropy of *o*-terphenyl in the liquid and crystalline state heated at constant volume in the range 250–310 K is calculated from calorimetric data at a pressure of 0.1 MPa and equation of state data. The specific heat is found to fit the same functional form as that at 0.1 MPa and leads to a vanishing of the excess entropy at essentially the same Kauzmann temperature as that under isobaric conditions. This adds confirmation to the significance of the Kauzmann extrapolation and contradicts the expectation that constant volume heating would show qualitatively different behavior from isobaric heating.

Introduction

That the vibrational frequencies of a supercooled liquid may change with its structural state has been known since the calorimetric studies of Chang and Bestul in the 1960s.¹ Recent landscape calculations have shown that the vibrational frequencies increase upon heating at constant volume, in contrast to their decrease upon heating at constant pressure.^{2,3} The landscape model assumes inherent structures of various energies; the higher energy structures are favored at higher temperatures because there are more of them (they have more configurational entropy). The higher entropy of the lower vibrational frequencies for the structures explored at constant pressure provides an additional favoring. The fact that the frequencies increase upon heating at constant volume has the opposite effect, with the decreasing vibrational entropy of the higher energy structures detracting somewhat from their increasing configurational entropy.⁴ This implies at least that the specific heat at constant volume will be diminished by this effect, but whether its qualitative behavior, specifically the behavior that gives rise to the Kauzmann paradox,⁵ will be different or otherwise much the same is less obvious.

I have reported quantitative assessments of the magnitude of the vibrational contribution to the excess entropy^{6,7} and suggested an explanation of the Kauzmann paradox in terms of this effect and the related increase in anharmonicity of vibrations as the supercooled liquid moves upon isobaric heating to higher potential energy inherent structures of the energy landscape.⁸ It is therefore of some interest to calculate the course of the excess entropy and the status of the Kauzmann paradox under isochoric conditions. In this paper, I use equation of state data for the fragile glass former *o*-terphenyl to examine this question.

The Kauzmann Paradox and Isobaric Heating

The Kauzmann paradox, the apparent vanishing of the extrapolated excess entropy of the liquid over that of the crystal at a temperature, T_k , not far below the glass temperature, T_g , has been a source of controversy ever since its discovery.⁵ Kauzmann suggested it may not be a real crisis, as the liquid would cease to be even metastable with respect to the crystal before T_k is reached, while Gibbs and DiMarzio⁹ proposed a theory predicting a type of second-order phase transition to a

zero entropy state at T_k . More recently, Stillinger¹⁰ suggested on the basis of energy landscape considerations that the vanishing of the excess entropy above absolute zero is only a failure of the extrapolation to represent reality in the vicinity of T_k , and a gradual and continuous decrease in the experimentally inaccessible region below T_g is more plausible.

The paradox derives its force from the fact that not only is the extrapolation often over a not very large temperature range (40–50 K for fragile liquids) but the slope of the entropy–temperature curve is increasing as the liquid is cooled to T_g , below which temperature the equilibrium liquid properties can no longer be observed. The isobaric excess specific heat is often fit empirically to the form $C_{p,exc} = a/T$ (which is the case for *o*-terphenyl¹¹). If there is to be a more gradual continuous decrease in the excess entropy below T_g , $C_{p,exc}$ must have a fairly sharp maximum in the inaccessible sub- T_g region, followed by a rapid but continuous falloff. (Here and in what follows, the subscript “exc” denotes a property of the liquid minus that of the crystal.)

I have previously suggested a scenario consistent with this behavior arising from the decrease of vibrational frequencies and increase of anharmonicity upon isobaric heating,⁸ which cause a more rapid rise in entropy as vibrations are thermally excited and become more nearly classical. This effect was postulated to give rise to a maximum in $C_{p,exc}$ below T_g , but no sharp phase transition, a picture consistent with Stillinger’s.

As heating at constant volume leads to higher rather than lower frequencies, and probable decreases rather than increases in anharmonicity, the scenario I proposed implies that at constant volume heating the entropy–temperature curve would follow a different course from that for isobaric heating, and the vanishing of excess entropy might be considerably displaced below its isobaric value at T_k , or conceivably might not be at all noticeable.

Equation of State Data for *o*-Terphenyl

Naoki and Koeda¹² have provided equation of state data on *o*-terphenyl in the liquid, crystal, and glassy states in the form of polynomials in T (kelvins) and P (megapascals) for the specific volume, V (cubic centimeters per gram). As will be seen, the integral of $(\partial V/\partial T)_P$ needed to calculate the entropy under high pressures extends to pressures somewhat in excess of the range for which their data was obtained. It is desirable

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TABLE 1: Tait Parameters of *o*-Terphenyl Used for the Extrapolation

	b_1 , MPa	b_2 , K ⁻¹	C
liquid (Comez ¹³)	710	4.45×10^{-3}	9.8×10^{-2}
crystal	1202	4.16×10^{-3}	8.46×10^{-2}

therefore to fit their data to a form more appropriate for extrapolation to higher pressures, specifically the Tait equation:¹³

$$V(T,P) = V_0[1 - C \ln(1 + P/B)]$$

in which $V(T,P)$, the volume at a given T and P , is equal to the volume, V_0 , at zero pressure at the temperature T , multiplied by the function of P in square brackets, in which C is a constant and B a function of temperature of the form $B = b_1 \exp(-b_2 T)$. Comez et al.¹³ have fit the Naoki and Koeda data on liquid *o*-terphenyl to this form but not the crystal.

To obtain a similar fit for the crystal, and as a check on the values of the constants found by Comez et al., I expressed the Tait equation as a Taylor series in powers of P starting from $P = 0$:

$$V(T,P) = V_0 - (V_0 C/B)P + (V_0 C/2B^2)P^2 - (V_0 C/3B^3)P^3 + \dots$$

and then rearranged the Naoki and Koeda polynomials as a power series in P with temperature dependent coefficients. By equating these coefficients with the corresponding terms in the above Taylor series, values of B and C could be found at various temperatures in the range of the Naoki and Koeda data. The temperature dependence of the resulting B values were well fit by a relation of the form used in the Tait equation; C varied somewhat with temperature, so an average value was taken. The results agreed quite well for the liquid with Comez's parameters, so the latter were used for the liquid. The parameters for liquid and crystal are given in Table 1.

Calculation of S

The reference states for the equilibrium liquid and the crystal used in this calculation were the states reached at T_k and a pressure of 0.1 MPa. The volumes in these states were those calculated from the Naoki and Koeda polynomials at $P = 0.1$ MPa and $T_k = 204.2$ K, the calculated Kauzmann temperature for isobaric cooling.¹¹ At this temperature, the extrapolated entropy of the liquid equals that of the crystal.⁵

The entropies of the compressed phases were calculated at 10° intervals from 210 to 310 K. The entropies at 0.1 MPa are the measured values for the crystal over the whole temperature range and for the liquid at 250 K and above.¹ Below T_g (about 245 K^{1,11}), the liquid excess entropies were those obtained by assuming $C_{p,exc}$ below T_g obeys in this temperature range the relation given earlier.¹¹

The pressure, P_v , at each temperature necessary to keep the volume equal to its value at T_k is easily found by inverting the Tait equation:

$$P_v = B\{\exp[(1 - V_k/V_0)/C] - 1\}$$

In the above, V_k is the extrapolated volume of the phase, liquid, or crystal at the Kauzmann temperature and V_0 is the volume of the phase at the temperature T and a pressure of 0.1 MPa.

The integration of $(\partial V/\partial T)_P$ with respect to P has been found from the Tait equation by Casalini et al.¹⁴ to result in the

TABLE 2: Entropy of *o*-Terphenyl Liquid, J/(K·mol); $S(0)$, the Entropy at 0.1 MPa Is from Chang and Bestul^{1 a}

T , K	P_v	$S(0)$	$S(P_v) - S(0)$	$S(P_v)$
210	12.42		-1.75	
220	32.72		-4.51	
230	52.55		-7.11	
240	71.95		-9.51	
250	90.94	274.83	-11.87	262.96
260	109.55	288.26	-14.06	274.20
270	127.82	301.40	-16.14	285.26
280	145.78	314.29	-18.13	296.16
290	163.46	326.95	-20.04	306.91
300	180.89	339.39	-21.87	317.52
310	198.09	351.64	-23.65	327.99

^a The change in entropy on increasing the pressure to P_v in this and the following tables is calculated from eq 1.

TABLE 3: Entropy of *o*-Terphenyl Crystal, J/(K·mol)

T , K	P_v , MPa	$S(0)$	$S(P_v) - S(0)$	$S(P_v)$
210	7.11	213.13	-0.27	212.86
220	18.61	222.25	-0.70	221.55
230	29.66	231.37	-1.13	230.24
240	40.30	240.49	-1.54	238.95
250	50.52	249.62	-1.95	247.67
260	60.35	258.77	-2.34	256.43
270	69.79	267.93	-2.72	265.21
280	78.87	277.11	-3.08	274.03
290	87.60	286.30	-3.44	282.86
300	95.98	295.51	-3.78	291.73
310	104.04	304.74	-4.11	300.63

TABLE 4: Excess Entropy, S_{exc} , J/(K·mol)^a

T , K	$S_{exc}(0)$	$S_{exc}(P_v)$	$S_{exc}(P_v)$ (eq 2)
210	(3.79)	(2.31)	3.46
220	(9.87)	(6.06)	6.85
230	(15.41)	(9.43)	9.94
240	(20.50)	(12.48)	12.76
250	25.21	15.29	15.37
260	29.49	17.77	17.77
270	33.47	20.05	20.00
280	37.18	22.13	22.06
290	40.65	24.05	23.99
300	43.88	25.79	25.78
310	46.90	27.36	27.46

^a In the second column, the first four figures, displayed in parentheses, are calculated from the Richert and Angell formula¹¹ and the remaining figures are from Chang and Bestul.¹ The third column gives the calculated excess entropies at P_v . The fourth column gives the results from eq 2 for comparison.

following equation for $S(P_v) - S(0)$ (the distinction between $P = 0.1$ MPa and $P = 0$ will be ignored in what follows):

$$S(P_v) - S(0) = P_v V_0 C b_2 - P_v (dV_0/dT)(1 + C) + [(dV_0/dT)C(P_v + B) - V_0 C b_2 B] \ln(1 + P_v/B) \quad (1)$$

In the above, I have used a notation different from Casalini et al.

Results

Tables 2–4 give the results of the calculation, including $P_v(T)$, $S_{liq}(T, P_v)$, $S_{liq}(T, 0)$, $S_{cryst}(T, P_v)$, and $S_{exc}(T, P_v)$. The values for S_{exc} below T_g are displayed in parentheses to mark the fact that not only did I use the Tait parameters determined from measurements at higher temperatures but also the 0.1 MPa values of the excess entropy are themselves a result of

extrapolation to temperatures below T_g using the Richert and Angell expression:¹¹

$$S_{\text{exc}} = S_0(1 - T_k/T)$$

Upon substituting the numerical value 137.4 for S_0 and setting $T_k = 204.2$,¹¹ one obtains:

$$S_{\text{exc}} = 137.4 - 2.8057 \times 10^{-4}/T$$

and

$$C_{p,\text{exc}} = 2.8057 \times 10^{-4}/T$$

for *o*-terphenyl under isobaric heating.

The excess entropy curve on the isochore is very similar in form to that on the 0.1 MPa isobar. In fact, it could be fit reasonably well in the range 250–310 K by assuming the same empirical form for S_{exc} as that used by Richert and Angell, with T_k as a free parameter. Table 4 compares the calculated excess entropy with the fit obtained for the following equation:

$$S_{\text{exc}} = 77.865 - 1.5624 \times 10^4/T \quad (2)$$

The differences are probably within the errors of the various extrapolations involved. The excess specific heat at constant volume, C_v , is found from the fit to be $1.5624 \times 10^4/T$, and T_k is found to be 200.7 K.

Discussion

The expectation that under constant volume conditions the entropy–temperature relationship would be qualitatively different from that at constant pressure is strongly contradicted by these results. It appears therefore that while dependence of vibrational frequencies on structural state influence the magnitude of the change in energy with temperature (with the isobaric and isochoric specific heats having a temperature independent ratio of 1.8 in the temperature range 250–310 K), the qualitative course is much the same whether at constant pressure or constant volume. It should be noted that the enthalpy change upon isobaric heating at 0.1 MPa is essentially equal to the energy change, with the difference between enthalpy and energy for condensed phases being negligible at 0.1 MPa.

At the suggestion of an anonymous reviewer, I have calculated the ratio $C_{p,\text{exc}}/C_{v,\text{exc}}$ at 204.2 K, where the isobar and isochore cross, using the well-known thermodynamic equation for $C_p - C_v$ in the form $C_{p,\text{exc}} - C_{v,\text{exc}} = (TV\alpha^2/\kappa)_{\text{exc}}$ (α = thermal expansivity and κ = isothermal compressibility) and the value of $C_{p,\text{exc}}$ extrapolated from the Richert and Angell equation. The result for the ratio was 1.6, in good enough agreement with its value in the higher temperature range, given the uncertainties in the extrapolations involved. I have also calculated this ratio at 250 K, where the Tait parameters and specific heats are known with more confidence; the result was 1.82. The large values of the ratio may seem surprising when the ratios for the two pure phases are considered (1.22 for the liquid and 1.05 for the crystal at 250 K), but $C_{p,\text{exc}}$ is less than one-third that of the liquid C_p , and $(TV\alpha^2/\kappa)$ of the liquid is about 5 times that of the solid.

In the analysis presented here, the excess entropy on the isochore was assumed to vanish at the isobaric T_k value, so it is to be expected that it should decrease to a value near this upon cooling. However, it is less obvious that, when extrapolated down from the isochoric values in the temperature range 250–310 K, the temperature at which it appears to vanish would be so embarrassingly close to that observed on isobaric cooling. That this indeed happens strengthens the case for the Kauzmann temperature being a point of real significance for the supercooled liquid state. This is consistent either with a phase transition there or a narrowly avoided one.^{8,10} How this is to be reconciled with the question I have raised elsewhere¹⁵ about whether the configurational entropy really vanishes at the Kauzmann temperature is a topic for further investigation.

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