Viscous and thermodynamic behaviour of glass-forming organic liquids

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Abstract. The free energy difference (ΔG) between an undercooled liquid and its corresponding equilibrium solid has been evaluated on the basis of a method involving Taylor series expansion of ΔG around its value at the equilibrium melting temperature. The resultant expression is shown to be capable of correctly estimating ΔG at temperatures as low as the glass transition temperature. The method is then enlarged to obtain the configurational entropy and used in conjunction with the Adam and Gibbs model to derive a novel expression for the viscosity of undercooled liquids. Most commonly used expressions for the temperature dependence of viscosity are shown to be approximations of the equation obtained in this study.

Keywords. Viscosity; undercooled liquids; Kauzmann temperature; configurational entropy.

1. Introduction

An accurate thermodynamic description of the undercooled liquid state is essential for understanding the viscous behaviour, glass-forming ability, nucleation propensity and crystal growth tendency in many liquids. Often, the metastability of the liquids precludes thermodynamic measurements below the equilibrium melting temperature (T_m). Parameters like the free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid have so far been estimated by assuming some form of temperature dependence for the heat capacity difference (ΔC_p) between these phases (Turnbull 1950; Hoffman 1958; Jones and Chadwick 1971; Singh and Holz 1983). Models such as that due to Adam and Gibbs (1965) require a knowledge of the configurational entropy ΔS_c for an evaluation of the viscosity of an undercooled liquid. In this paper we demonstrate that a procedure recently proposed by Lele et al (1985) for estimating ΔG is well suited for the determination of many of these important properties of metastable liquids. Using this procedure and the Adam and Gibbs model, we derive a general expression for viscosity of an undercooled liquid that encompasses many other empirical relations as appropriate approximations.

2. Free energy and entropy of undercooled liquids

Following Lele et al (1985), we can expand the free energies of a liquid and the solid in equilibrium with it at the melting point (T_m) using Taylor series. The expansion extends the free energy versus temperature (G vs T) plot of each phase into their metastable regions. Considering the difference between the expressions for the liquid

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and the solid yields ΔG in the form

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{(T_m + T)} + \frac{1}{2}\left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \frac{\Delta T^3}{T_m + T} - , \cdots \tag{1}$$

where ΔC_p^m and ΔS_m are the specific heat and entropy differences between the liquid and the corresponding solid respectively at the melting temperature T_m. ΔT is the undercooling $T_m - T$. It may be noted that the first term in the above equation is the well-known Turnbull (1950) approximation for ΔG. At large values of ΔT and ΔC_p^m large corrections need to be made to the Turnbull expression. However, very often it may not be necessary to consider more than two terms in (1) as the contribution of the higher terms is invariably negligible. We shall demonstrate that the corrections to the Turnbull approximation to (1) are significant at large undercoolings.

A similar Taylor series expansion can be carried out with respect to the entropy (S) of both phases to get an expression for the entropy difference between the liquid and solid phases (ΔS) resulting in

$$\Delta S = \Delta S_m - 2\Delta C_p^m \frac{\Delta T}{T_m + T} + \left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \cdot \frac{\Delta T^2}{T_m + T}$$

$$-\frac{1}{4}\left[\frac{\partial^2 \Delta C_p}{\partial T^2}\right]_{T_m} \cdot \frac{\Delta T^3}{(T_m + T)} + \cdots \tag{2}$$

Kauzman (1948) pointed out the difficulties associated with a purely kinetic description of glass transition. One such problem is the likelihood of ΔS being negative at some low temperature. The paradox was resolved by Gibbs and DiMarzio (1958) when they considered glass transition as a truly second-order transition. ΔS goes to zero at an ideal glass transition temperature designated T_K. This temperature can be evaluated by setting (2) to zero at $T = T_K$. T_K can thus be expressed in terms of $\Delta S_m, \Delta C_p^m$ and its temperature derivatives at T_m as a solution to the transcendental equation of the form

$$\Delta S_m - T_m\left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} + \left\{\Delta C_p^m - T_m\left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m}\right\}\ln(T_K/T_m)$$

$$+ \left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \cdot T_K = 0. \tag{3}$$

In the derivation of (1) to (3) it is assumed that

$$\ln(T_m/T) = 2\Delta T/(T_m + T). \tag{4}$$

It may be noted that higher order derivatives of ΔC_p with respect to T at $T = T_m$ have been neglected due to their extremely small contributions. Under these approximations the above equation gives the value of T_K as

$$T_K = T_m - \left[\frac{(\Delta S_m + 2\Delta C_p^m) \pm \left\{(\Delta S_m + 2\Delta C_p^m)^2 - 8\Delta S_m \cdot T_m\left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m}\right\}^{1/2}}{2\left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m}}\right]. \tag{5}$$

Neglecting the term $[\partial \Delta C_p / \partial T]_{T_m}$ in (5), T_K is given by

$$T_K = T_m \left[\frac{2D - 1}{2D + 1} \right],$$

where $D = \Delta C_p^m / \Delta S_m$.

The assumption of $\Delta S = 0$ at $T = T_K$ facilitates expression of ΔS in terms of only T_K, ΔC_p and its derivatives at T_m. Thus we have

$$\Delta S = \Delta C_p^m \ln(T/T_K) - \left[\frac{\partial \Delta C_p}{\partial T} \right]_{T_m} [T_m \ln(T/T_K) - \Delta T_K] + \ldots, \tag{6}$$

where $\Delta T_K = T_m - T_K$. Equation (6) can be used to estimate the viscosity of undercooled liquids using the Adam and Gibbs (1965) model.

3. Viscosity of undercooled liquids

According to the molecular-kinetic theory of Adam and Gibbs (1965), the viscosity of an undercooled liquid can be expressed as

$$\eta = A \exp[C/T \Delta S_c], \tag{7}$$

where A and C are constants and ΔS_c, the configurational entropy is given by

$$\Delta S_c = \int [C_p(\text{liquid}) - C_p(\text{glass})] \, d\ln T. \tag{8}$$

Often, the experimentally determined value of C_p (glass) is very close to that of the crystal and exhibits similar temperature dependence (Wong and Angell 1976). Hence the expression for ΔS given by (6) can be used in place of ΔS_c. Consideration of higher order derivatives of ΔC_p and use of (4) yield an expression for η of the form

$$\ln \eta = \ln A + \frac{B(l + T_K/T)}{(T - T_K)[1 + A_1(T - T_K) + A_2(T - T_K)^2 + A_3(T - T_K)^3 + \ldots]}. \tag{9}$$

In case ΔC_p varies linearly with temperature

$$\ln \eta = \ln A + \frac{C}{2 \Delta C_p^m} \frac{1}{(T - T_K)} \left(1 + \frac{T_K}{T} \right) \frac{1}{\left\{ 1 - \frac{\alpha \Delta T_K}{T_m} \left(1 - \frac{T - T_K}{2 \Delta T_K} \right) \right\}}, \tag{9a}$$

where

$$\alpha = T_m \frac{\partial}{\partial T} [\ln \Delta C_p]_{T_m} \text{ and } \Delta T_K = T_m - T_K,$$

where $B = C/2 \Delta C_p^m, A_1, A_2, A_3$, etc are constants and depend on ΔC_p^m and its derivatives with respect to T at $T = T_m$ and T_K. When ΔC_p is independent of temperature (9) reduces to

$$\ln \eta = \ln A + \frac{C'}{2(T - T_K)} \left(1 + \frac{T_K}{T} \right) \tag{10}$$

with $C' = C/\Delta C_p^m$. In the vicinity of the glass transition temperature T_g, T_K/T is

approximately 0·75 (see §4) and (9) reduces to the frequently used Vogel-Fulcher equation (Vogel 1921; Fulcher 1925)

$$\ln \eta = \ln \eta_0 + \frac{C''}{(T - T_0)} \tag{11}$$

with $T_0 = T_K$ and $C'' = 0.875C'$.

In general, C'' of the Vogel-Fulcher equation (11) should be temperature-dependent at least to the extent of

$$C = \frac{C'}{2}\left[1 + \frac{T_K}{T}\right].$$

Our analysis shows that the Vogel-Fulcher equation is in fact an approximate expression arising from the more general equation of the form given by (9). The complexity of the viscous behaviour and consequently the curvature in the ln η vs $1/T$ plots will thus depend upon the temperature dependence of ΔC_p. It should be stressed that (9) derived by us has *less number of adjustable parameters* than in the case of the Vogel-Fulcher expression. All other constants (9) except A and B are derivable from thermodynamic data and are not adjustable. They are dependent on ΔC_p and its temperature dependence. Further, (9) with a single set of constants A and B should be applicable over the entire temperature range of interest. Equation (9) of our analysis is to be preferred when ΔC_p is a strong function of ΔT and should have a definite advantage over the Vogel-Fulcher equation.

We shall now test (1) for ΔG and (9a) for viscosity on five well-studied organic glass-forming liquids. In each case the experimentally determined ΔC_p can be expressed by

$$\Delta C_p = a + bT \tag{12}$$

and the experimental value of ΔG can be evaluated by integrating

$$\Delta G = \left[\Delta H_m - \int_T^{T_m} \Delta C_p \, dT\right] - T\left(\Delta S_m - \int_T^{T_m} \Delta C_p \, d\ln T\right). \tag{13}$$

The materials and their constants are shown in table 1.

Table 1. Parameters used for the evaluation of ΔG of the materials under study.

Material	T_m (K)	T_g (K)	ΔS_m (J/mol/K)	Constants in (12)	
				a (J/mol/K)	b (J/mol/K^2)
Glycerol	293	186	62·70	90·8646	$-3·906 \times 10^{-2}$
Ethanol	158·5	91	31·64	51·5810	$-1·673 \times 10^{-1}$
2-Methyl pentane	119·55	79·5	52·36	146·8710	$-7·985 \times 10^{-1}$
o-terphenyl	328	243·15	56·01	241·1280	$-4·933 \times 10^{-1}$
1,3,5-Tri-α-naphthyl benzene	472	342	90·02	311·4250	$-4·673 \times 10^{-1}$

(Kelly 1929; Parks *et al* 1930; Douslin and Huffmann 1946; Wunderlich 1960; Magill 1967; Angell and Rao 1972)

4. Results and discussion

Table 2 shows the ΔG values obtained from (1) and compares the same with the values calculated from (13) and shown as the experimental values. For the sake of brevity these are evaluated at normalized undercooled temperature (T/T_m). In all cases, the agreement between the calculated and experimental values of ΔG is excellent. Even at the glass transition temperature T_g, the difference is always less than 4% of the value obtained from (13). A comparison of the present results with those arrived at by the use of several expressions in current use [(14)–(17)] clearly brings out the utility and accuracy of (1). In table 3 are compared the ΔG values for glycerol estimated from (1) and the following expressions at various temperature from T_m to T_g

$$\Delta G = \Delta S_m \cdot \Delta T \text{ (Turnbull 1950)}, \tag{14}$$

$$\Delta G = \Delta S_m \cdot \Delta T \cdot \frac{T}{T_m} \text{ (Hoffman 1958)}, \tag{15}$$

$$\Delta G = \Delta S_m \cdot \Delta T \frac{2T}{T_m + T} \text{ (Thompson and Spaepen 1979)} \tag{16}$$

$$\Delta G = \Delta S_m \cdot \Delta T \frac{7T}{T_m + 6T} \text{ (Singh and Holz 1983)}. \tag{17}$$

In all cases the values derived from (1) are the closest to the experimental values (obtained from (13)). All other expressions result in considerable error at large undercoolings. Such errors are most detrimental in estimating quantities like nucleation frequency and growth rate of crystal in undercooled liquids. In view of this we strongly advocate the use of (1) which is derived from mathematical concepts without reference to any model. A temperature dependence of ΔC_p is, however, inherent in (1) and enters through the use of ΔC_p^m, $\partial \Delta C_p / \partial T$, etc. at T_m. It also enters in the required form by the very nature of Taylor series expansion since the second

Table 2. Free energy difference between the liquid and equilibrium solid phase (1) of various materials. The experimental value was obtained by the use of (12).

	ΔG(J/mol)									
	Glycerol		o-terphenyl		1,3,5-Tri-α-Naphthyl benzene		2-Methylpentane		Ethanol	
T/T_m	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
0·95	889	889	883	884	2066	2068	305	305	246	246
0·90	1713	1716	1686	1693	3996	4009	591	592	480	480
0·85	2470	2478	2390	2415	5757	5802	854	859	700	703
0·80	3150	3169	2977	3036	7313	7422	1090	1103	905	911
0·75	3747	3786	3425	3543	8626	8843	1295	1320	1093	1105
0·70	4253	4322	—	—	—	—	1462	1508	1261	1282
0·65	4659	4772	—	—	—	—	—	—	1406	1440
T_g/T_m	4761	4890	3487	3619	9185	9479	1554	1619	1575	1640

Table 3. Free energy difference between the liquid and equilibrium solid of glycerol evaluated from various available expressions and compared with that calculated using (1) of the present investigation.

T(K)	Exp.	Equation (1)	Equation (1) $[\partial \Delta C_p/\partial T]_{T_m} = 0$	ΔG (J/mol) Equation (14) Turnbull (1950)	Equation (15) Hoffman (1958)	Equation (16) Thompson and Spaepen (1979)	Equation (17) Singh and Holz (1983)
293(T_m)	0	0	0	0	0	0	0
290	187	187	187	188	186	187	188
280	792	792	792	815	779	797	810
270	1368	1367	1368	1442	1329	1383	1425
260	1975	1911	1913	2063	1836	1946	2032
250	2430	2423	2426	2696	2300	2483	2631
240	2914	2899	2905	3323	2722	2993	3222
230	3363	3338	3347	3950	3101	3474	3801
220	3776	3737	3752	4577	3437	3926	4370
210	4152	4095	4116	5204	3730	4345	4926
200	4489	4406	4438	5831	3980	4731	5468
190	4784	4670	4714	6458	4188	5081	5994
186(T_g)	4890	4761	4811	6709	4259	5210	6199

Table 4. Constants for use in (9a) for the viscosity of undercooled melts.

Material	T_m(K)	T_K(K)	A(poise)	C(poise K)	α	Viscosity range	Correlation (r)
1,3,5-Tri-α Nephthyl benzene	472	255·4	$3\cdot6392 \times 10^{-10}$	4484·7590	$-2\cdot4273$	$10^{13}\text{–}10^{-1}$	0·9989
o-terphenyl	328	200·2	$1\cdot0088 \times 10^{-7}$	1692·4021	$-2\cdot0353$	$10^{13}\text{–}10^{-1}$	0·9977
2-Methyl pentane	119·55	60·9	$2\cdot4049 \times 10^{-4}$	716·0881	$-1\cdot8569$	$10^{11}\text{–}10^{4}$	0·9911
Glycerol	293	137·5	$3\cdot6144 \times 10^{-4}$	513·0195	$-0\cdot1441$	$10^{4}\text{–}10^{0}$	0·9994

and higher temperature derivatives of ΔG are related to ΔC_p and its temperature dependence.

The temperature dependence of the viscosity can also be arrived at from the ΔC_p data of table 1 in conjection with (9a). Towards this end we have estimated the Kauzmann temperature T_K from ΔC_p data and (3). Experimentally measured viscosity values (Plazek and Magill 1966; Ling and Williard 1968; Laughlin and Uhlmann 1972; Cuckerman et al 1973; Weast 1988) were then plotted against a temperature function,

$$f(T) = \frac{1 + (T_K/T)}{(T - T_K)\left[1 - \frac{\alpha\Delta T_K}{T_m}\left\{1 - \frac{T - T_K}{2\Delta T_K}\right\}\right]}.$$ (18)

In each case, the Kauzmann temperature T_K and the constants A and B derived from the best fit straight line are shown in table 4 together with the correlation coefficients (r) for the straight line. The calculated and observed viscosity values for three of the materials discussed are shown in figure 1. As can be seen from the figure and the values of the correlation coefficients (table 4) (9a) with only two parameters is obeyed over a wide range of temperatures.

We have also noticed that there is a linear relationship between the reduced glass transition temperature (T_g/T_m) and the reduced Kauzmann temperature (T_K/T_m) for all the materials studied here (figure 2). Analytically the straight line is represented by

$$T_g/T_m = 0\cdot832(T_K/T_m) + 0\cdot25$$ (19)

with a correlation of 0·9948. Consequently

$$T_g = 0\cdot832\,T_K + 0\cdot25\,T_m.$$ (20)

As a rule of thumb, T_q/T_m is about 1/2. In the present instance, T_K/T_m of materials studied varies from 0·6 to 0·4 and (20) is still well obeyed.

5. Conclusion

Equation (1) derived by us for evaluating the ΔG of an undercooled liquid has been shown to yield correct estimates even at large undercoolings. The expression for the entropy difference (ΔS) between the undercooled liquid and the solid in thermodynamic equilibrium with it (2) can be used to determine the Kauzmann glass transition temperature and yields values which are in close agreement with values reported earlier
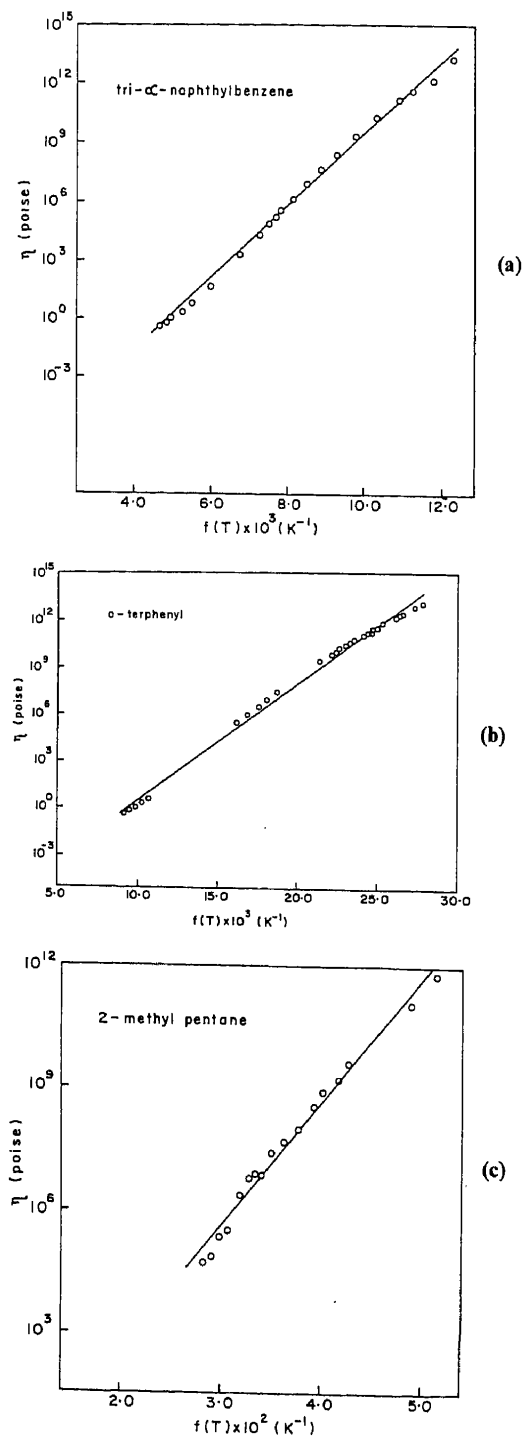
Figure 1. A comparison of the temperature dependence of the viscosity of undercooled liquids as predicted by equation (9a) (——) with the experimental values (0). (a) 1,3,5-Tri-α-Naphthylbenzene (Plazek and Magill 1966), (b) o-terphenyl (Laughlin and Uhlmann 1972; Cuckerman *et al* 1973) and (c) 2-methylpentane (Ling and Williard 1968).
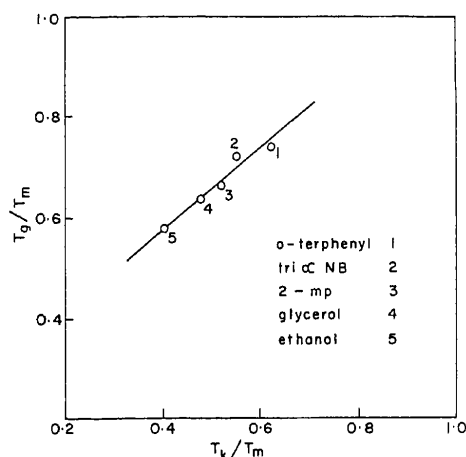
Figure 2. Linear relation between reduced T_g and reduced T_K for different glass forming liquids (equation (19)).

for a number of organic liquids. Both ΔG and ΔS are, as expected, strongly dependent on the temperature dependence of heat capacity and the values of the heat capacity and entropy difference (ΔC_p^m and ΔS_m respectively) between the melt and the crystal at equilibrium melting temperature (T_m). Both (1) and (2) require a knowledge of these parameters and the temperature dependence of C_p^L and C_p^S only in the temperature ranges where the two phases are stable i.e. for $T < T_m$ (near T_m) in the case of solid and $T > T_m$ (near T_m) in the case of liquid. Use of (2) in conjunction with the Adam and Gibbs model for viscous behaviour of undercooled liquids leads to a novel expression for the temperature dependence of viscosity of liquids. The new expression does not involve any more adjustable parameters than the Vogel-Fulcher equation but modifies the latter in a significant fashion. Applicability of our equation for viscosity with a single set of constants over a wide range of viscosity (10^{-1} to 10^{13} P) establishes its great utility.

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