ON APPROXIMATION OF THERMODYNAMIC DRIVING FORCE IN DEEPLY UNDERCOOLED MELTS

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The difference in Gibbs free energy between liquid and solid phases, usually expressed by authors as ΔG, appears in several theoretical formulations on nucleation and crystal growth. Approximations for ΔG are used extensively to gain an insight into the solidification phenomenon when thermophysical parameters are not known. In this work, the most commonly used models are applied to four bulk metallic glasses at temperatures starting from that of glass transition. An arithmetic mean of Thomson–Spaepen and Hoffman's approximations yield significant improvements over new models incorporating nonlinear relationships involving undercoolings.

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Introduction

The difference in Gibbs free energy between liquid and solid, usually expressed by authors as ΔG, appears in several theoretical formulations in phase transfer phenomena [1,2]. A notable example is the classical nucleation theory where the nucleation frequency is expressed as number density in the form

$$I = I_0 \exp\left(-\frac{16\pi\sigma^3 V_m^2}{3 k_B T \Delta G^2} - \frac{E_D}{RT}\right)$$, where k_B is the Boltzmann constant and σ is the

solid-liquid interface energy, V_m is the molar volume and I_0 is the pre-exponential factor and E_D is the energy threshold for diffusion. Another popular occurrence is

in solidification; crystal growth is shown as $V = fav\left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right]$, with f, a

and v being the fraction of attachment sites, jump distance and attempt frequency. Furthermore, a small driving force at larger undercooling could be indicative of a large glass forming ability [3].

Measurement of specific heats in highly supercooled liquids is difficult and often impossible, owing to which the direct determination of ΔG of a material from its basic thermodynamic parameters is rare. Approximations of ΔG are instead used extensively and to a good effect in thermodynamic and kinetic models when specific heat data in metastable liquid are not known. However, in heavily supercooled liquids, encountered in such physical problems as rapid solidification and in devitrification, significant errors can occur. In this paper, we assess the model approximations by applying them to four multi-component bulk glass alloys, $Pd_{40}Ni_{40}P_{20}$, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$, $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $La_{55}Al_{25}Ni_{20}$ with known heat capacities in deeply undercooled region.

Theory

By definition, the Gibbs free energy difference, ΔG, between liquid and crystal/glass is given by

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

This can be expanded using the well known expressions for ΔG and ΔS

$$\Delta G = \Delta H_m \frac{\Delta T}{T_m} - \int_T^{T_m} \Delta C_p dT + T\int_T^{T_m} \Delta C_p \frac{dT}{T} \tag{2}$$

While ΔH_L, the enthalpy of fusion, is readily available for most materials, the differential in solid-liquid specific heats, ΔC_p, is not, as it is experimentally difficult to measure for metastable liquids. Hence, often, approximations are used for a meaningful value of ΔG.

When ΔC_p can be neglected it is simply

$$\Delta G = \Delta H_m \frac{\Delta T}{T_m} = \Delta S_m \Delta T \tag{3}$$

This is the most convenient and widely used of all expressions and is attributed to Turnbull [4]. Equation (3) also holds at small undercoolings which are characteristic of conventional solidification processes like casting. It is easy to see that Eq.(3) overestimates ΔG. A slight improvement is attributed to Singh and Holz; the following expression underestimates ΔG to a less extent [5]

$$\Delta G = \Delta S_m \Delta T \frac{7T}{T_m + 6T} \tag{4}$$

Another relationship that found profound use by researchers was formulated by Thompson and Spaepen (TS) [6]. For a linear approximation of ΔC_p, $\Delta C_p = AT + B$, it can be seen that Eq.(2) simplifies to [6]

$$\Delta G = \Delta S_m \Delta T - \frac{1}{2} A \Delta T^2 + B \left[T \ln \frac{T_m}{T} - \Delta T \right] \tag{5}$$

TS assumed a constant ΔC_p for which $A = 0$ and $B = \Delta C_p$ and further stated that for metallic glasses, $\Delta C_p \approx \Delta S_m \Delta T$, which leads to [6]

$$\Delta G = \Delta S_m T \ln \frac{T_m}{T} \tag{6}$$

Their approximation can be obtained by expanding $\ln(T_m/T)$ as $\ln \frac{(T_m + T)/2 + \Delta T/2}{(T_m + T)/2 - \Delta T/2}$. Noting the Taylor series expansion, $\ln \frac{1 + \delta}{1 - \delta} = 2\delta + \frac{2\delta^3}{3} + \frac{2\delta^5}{5} + ...$, one obtains

$$\Delta G = \Delta S_m \Delta T \frac{2T}{T_m + T} \tag{7}$$

Hoffman also assumed a constant ΔC_p and arrived at the following approximation [7]

$$\Delta G = \Delta S_m \Delta T \frac{T}{T_m} \tag{8}$$

Obviously, an estimation by Eq. (7) is greater than that of Eq. (8).

More recent attempts involve expansions involving higher powers of undercooling, and incorporating theoretical quantities like Kauzmann temperature [8]. A noteworthy example and one that is applied in this work is a simple looking expression obtained by Lad and co-workers used the series expansion,

$$\ln\left(1 - \frac{\Delta T}{T_m}\right) = \frac{\Delta T_m}{T_m} - \frac{\Delta T^2}{2T_m^2} - \frac{\Delta T_m^{\ 3}}{3T_m^3} \dots \text{ to obtain a parabolic approximation for}$$

ΔG [3]

$$\Delta G = \Delta S_m \Delta T \left(1 - \frac{\Delta T}{2T_m}\right) \tag{9}$$

More recently, Ji and Pan [8] obtained

$$\Delta G = 2\Delta S_m \Delta T \left(\frac{T}{T_m + T} - \frac{\Delta T^2 T_m}{3(T_m + T)^3}\right) \tag{10}$$

by incorporating the third order term in the TS approximation [9].

In this work present, the arithmetic mean of TS and Hoffman's predictions are used to obtain a new approximation

$$\Delta G = \Delta S_m \Delta T \left(\frac{T}{T_m + T} - \frac{T}{2T_m}\right) \tag{11}$$

Results and Discussion

The models were applied to four different alloys, $Pd_{40}Ni_{40}P_{20}$, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$, $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $La_{55}Al_{25}Ni_{20}$, referred in this section as alloys A, B, C and D, respectively, with published differential heat capacities known for a wide supercooling range. Table I shows the bulk metallic glass alloys

and their relevant physical properties. They are taken from a similar study involving BMGs [9]. Calculations were performed from T_g to the alloy liquidus temperature. For each alloy, thermodynamic driving force, $|\Delta G|$, was calculated as a function of temperature using the experimentally determined ΔC_p values given in Table I and then compared to the approximations using the aforementioned expressions. These comparisons are illustrated in Figs 1-4.

Table I   BMGs considered in present study and their thermophysical parameters used for determination of free energy

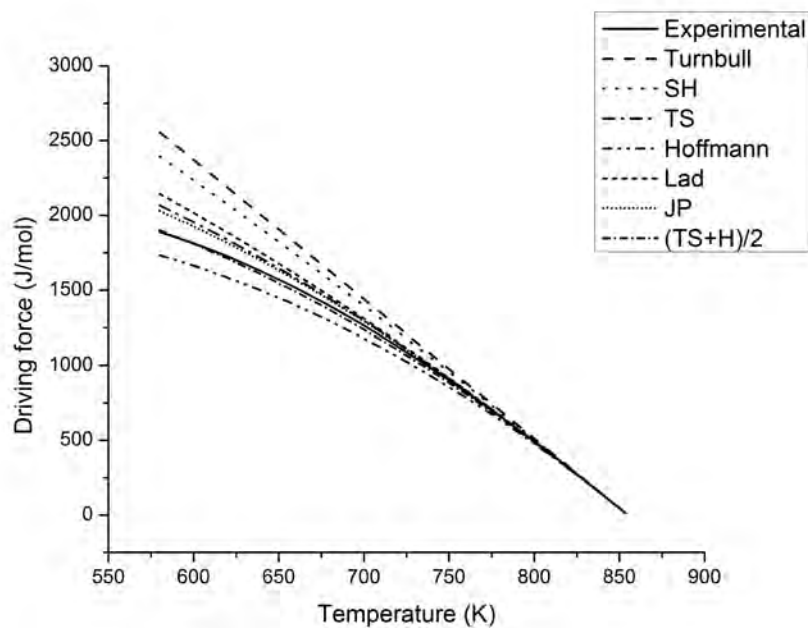| Ref.	Composition	T_m K	T_g K	ΔC_p J mol^{-1} K^{-1}	ΔH_m kJ mol^{-1}
A	$Pd_{40}Ni_{40}P_{20}$	855	580	$39.96 - 3.51 \times 10^2 T$	7.95
B	$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$	1072	675	$1.98 \times 10^{-2} T + 6.43 \times 10^6 T^{-2} - 1.68 \times 10^{-5} T^2$	8.2
C	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	1109	657	$19.84 - 8.89 \times 10^{-3} T$	10.3
D	$La_{55}Al_{25}Ni_{20}$	712	491	$2.19 \times 10^{-2} T + 1.24 \times 10^6 T^{-2} - 1.01 \times 10^{-5} T^2$	7.48

Fig. 1 Thermodynamic driving force, $|\Delta G|$, as function of melting temperature for alloy A. Curves were calculated for temperature range from T_g to T_m

Clearly, the Turnbull relationship was rather poor at large undercoolings, overestimating ΔG in all cases. Estimations by Eq. (7), SH, also showed large deviations in all compositions. TS and Hoffman's relationships offered reasonable approximations, respectively overestimating and underestimating in all cases. Both

the newer models, Eqs (8) and (10), offer improved results. Nevertheless, the best results were obtained by using Eq. (10).
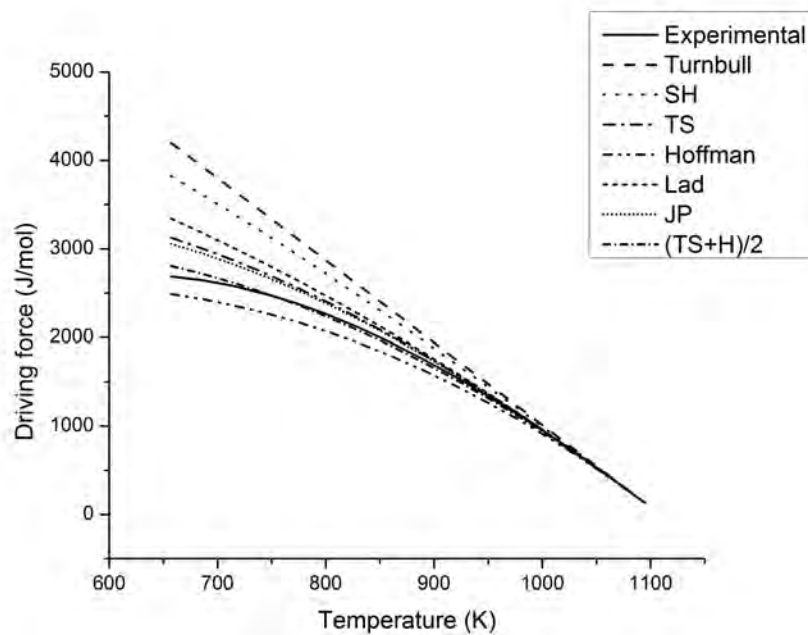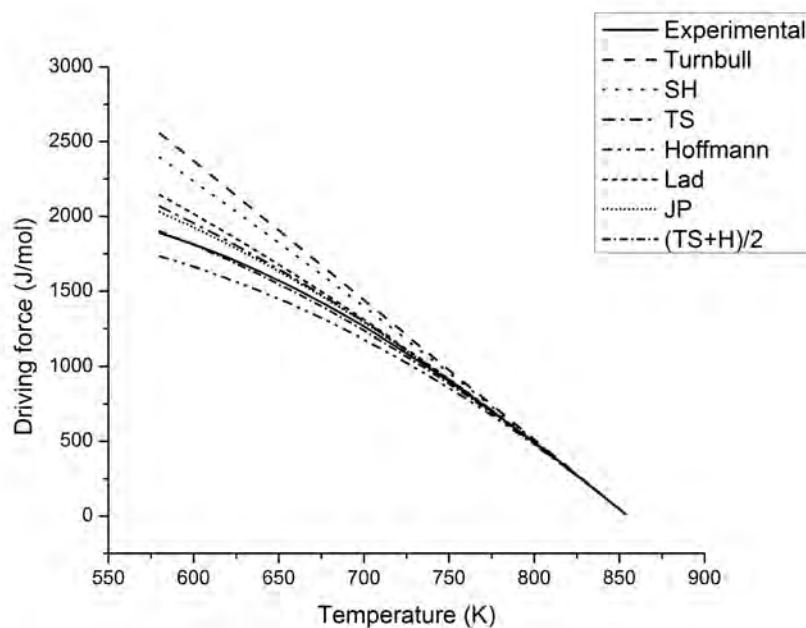

Fig. 2 Thermodynamic driving force, $|\Delta G|$, as function of melting temperature for alloy B. Curves were calculated for tempersature range from T_g to T_m

Fig. 3 Thermodynamic driving force, $|\Delta G|$, as function of melting temperature for alloy C. Curves were calculated for temperature range from T_g to T_m

It is also worthwhile to calculate the errors in approximation. Absolute percentage errors were determined as $100\left|(\Delta G_{exp} - \Delta G_{model})/\Delta G_{exp}\right|$ for the temperatures ranging from that of glass transition to melting. The plots, Figs 5-8, show the maximum errors for the aforementioned conditions varied from 27 % for

alloy A to 57 % for alloy C. Both the Thompson–Spaepen and Hoffman relationships yielded less than 16 % error for all compositions. The equations pro-
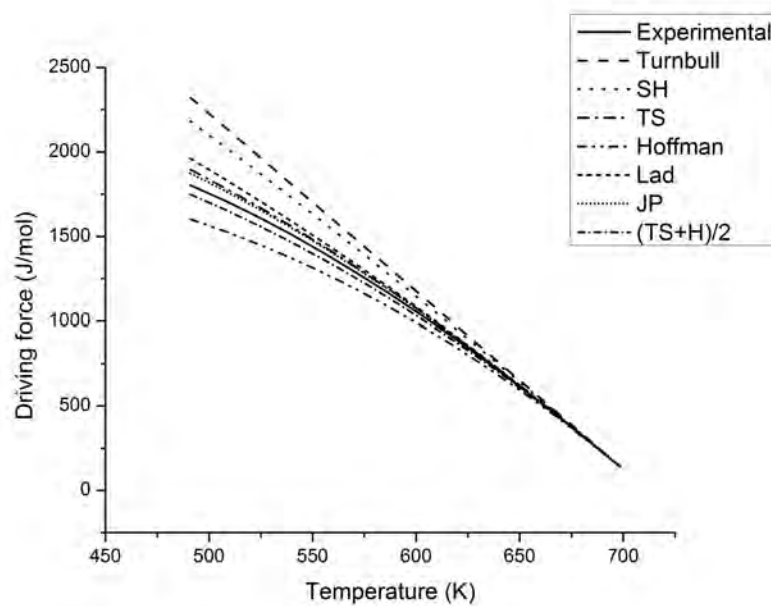

Fig. 4 Thermodynamic driving force, $|\Delta G|$, as function of melting temperature for alloy D. Curves were calculated for temperature range from T_g to T_m
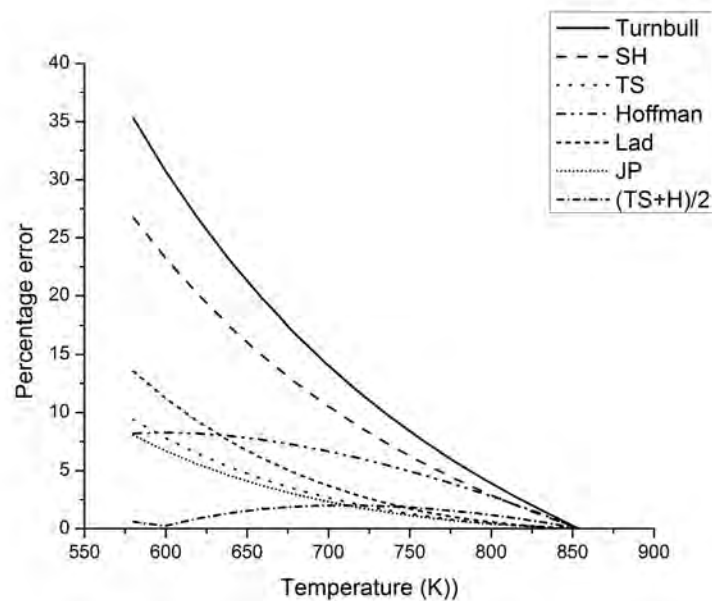

Fig. 5 Percentage errors determined relative to experimental values for different approximations for alloy A. The curves were calculated for temperature range from T_g to T_m

posed by Lad *et al*., and Ji and Pan increased the accuracy only marginally. The suggestion by the authors, though without a sound physical foundation, offers the best results, yielding less than 5% error in all the cases investigated.

The integrals of ΔC_p, being nonlinear, tend to vary at greater rates at large

undercoolings. The satisfactory results obtained by applying Eq. (10) are due to the fact that both TS and Hoffman's relationship appear to diverge from the expected ΔG values.
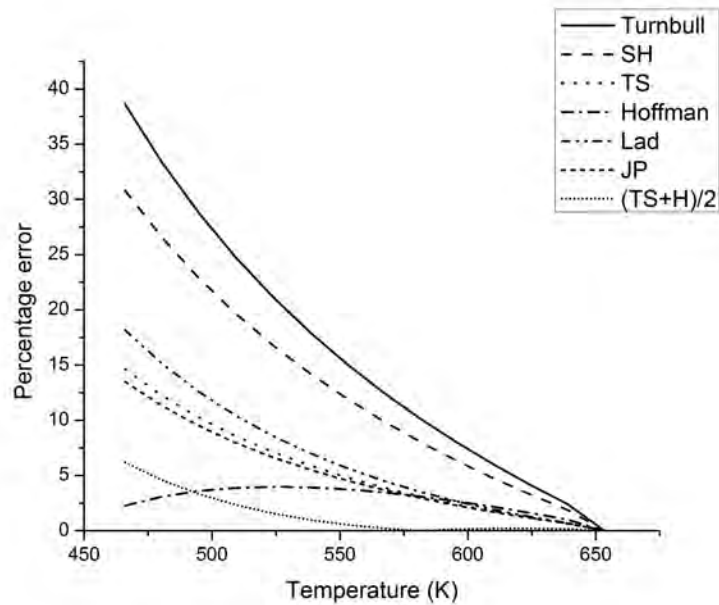

Fig. 6 Percentage errors determined relative to experimental values for different approximations for alloy B. Curves were calculated for temperature range from T_g to T_m
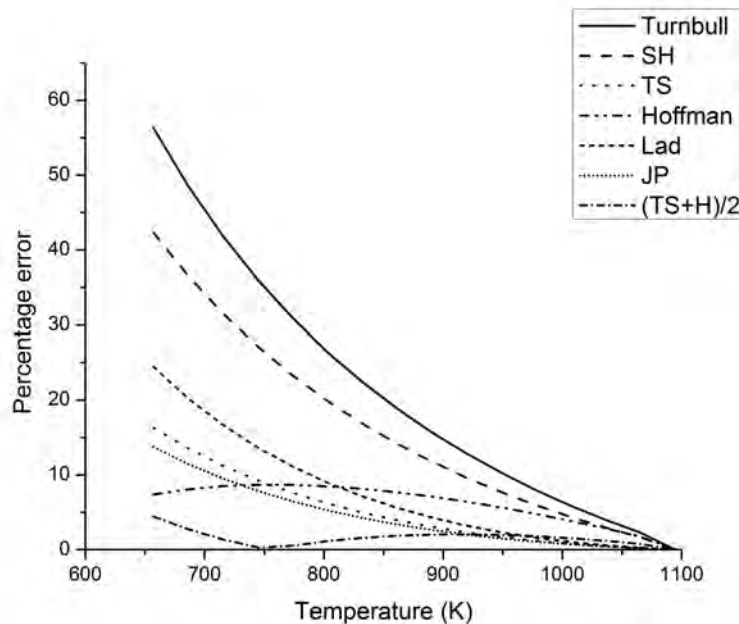

Fig. 7 Percentage errors determined relative to experimental values for different approximations for alloy C. Curves were calculated for temperature range from T_g to T_m
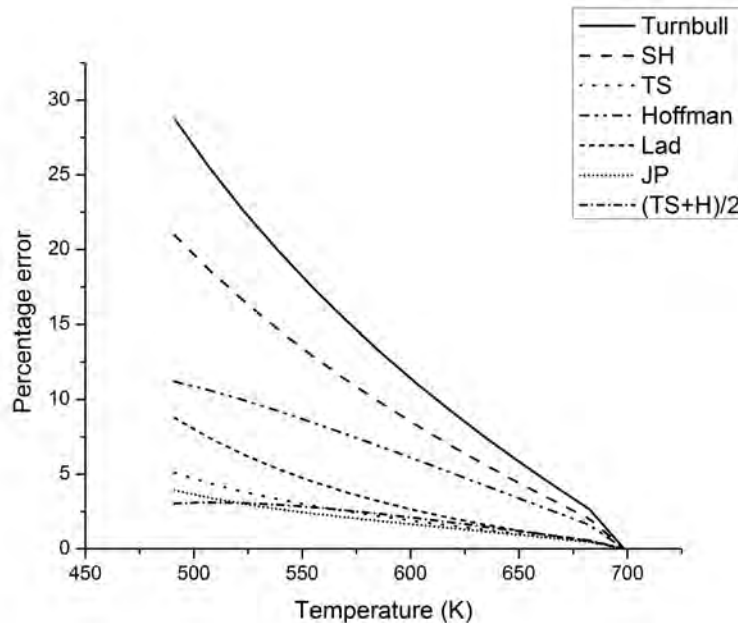
Fig. 8 Percentage errors determined relative to experimental values for different approximations for alloy D. Curves were calculated for temperature range from T_g to T_m

Conclusion

Different models were considered for the estimation of free enegy between solids and liquids. For small undercoolings, the simplest form, Turnbull approximation can be readily used. When the liquid is heavily undercooled, TS or better approximations should be used. When the liquid is undercooled to the glass transition temperature or lower, care should be taken in using the appropriate expression in physical models. The use of Turnbull approximation in such cases is incorrect and may be avoided. The authors recommend the arithmetic mean value of TS and Hoffman's approximation as a possible solution. Of all the compositions and temperatures studied, the largest relative error obtained was only 6 %, a better result compared to some of the recent models. The validity of the proposed approximation for other compositions and a theoretical investigation of its feasibility are subjects of a future investigation.

Acknowledgement

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