

## THERMODYNAMICS OF METALLIC GLASS-TRANSITION TEMPERATURE

D. DUŽEVIĆ

*Institute of Physics of the University, 41000 Zagreb*

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In this work the Thompson's expression for the melting point temperature of a solid under a curved surface is applied for an estimation of metallic glass-transition temperature. Stress is laid on the basic difference between the Thompson's relation and the Clausius-Clapeyron differential equation which are particular derivatives of a more general two-phase thermal equilibrium differential equation.

### 1. Introduction

Metallic glasses are stable at temperatures below their glass-transition temperature point  $T_g$ , laying in the range 0.45—0.70 of the homologous temperature scale when quenched from the liquid phase, but considerably lower (0.30—0.45 of the homologous temperature scale) when condensed from vapour<sup>1)</sup>. In the temperature range below  $T_g$  the amorphous glassy structure is considered to be the ground state of the lowest energy, all the other structural forms occupying the higher energy levels<sup>2)</sup>.

The strategy of producing metallic glasses involves cooling the melts or vapours down to a temperature  $T < T_g$ , at a high enough rate to avoid the nucleation of crystalline phases. Because of its paramount importance for the glass formation process, the physical nature of the glass-transition temperature needs to be thoroughly understood. This work is an attempt to understand the glass transition within the framework of equilibrium thermodynamics used for normal melting.

## 2. Theoretical

When discussing the two-phase thermal equilibria in homogeneous systems one commonly starts by considering the well known Clausius-Clapeyron differential equation:

$$(v_1 - v_2) dp = - \frac{\Delta q_{12}}{T} dT, \quad (1)$$

correlating the common pressure variation ( $dp$ ) for both coexisting phases with the corresponding equilibrium temperature variation ( $dT$ ). In this equation  $\Delta q_{12}$  is the latent heat of transition from phase 1 to phase 2,  $v_1$  and  $v_2$  the respective specific volumes of the two phases. It has to be stressed that the Clausius-Clapeyron differential law assumes that both the phases are subject to the same equilibrium pressure  $p$  at the same temperature  $T$ . Formally this is because the law is derived from the two-phase equilibrium condition<sup>3, 4)</sup>:

$$\varphi_1(p, T) = \varphi_2(p, T). \quad (2)$$

$\varphi_1$  and  $\varphi_2$  denote the specific Gibbs potentials, of the two phases involved.

Relation (2) is not the most general two-phase thermal equilibrium condition for a homogeneous thermodynamic system. Circumstances may arise where the two phases are exposed to different external equilibrium pressures,  $p_1$  and  $p_2$ , while keeping the common equilibrium temperature  $T$  which is an essential prerequisite for any state of thermal equilibrium. Consequently, the most general two-phase thermal equilibrium condition for a homogeneous thermodynamic system may be expressed in terms of the Gibbs' potential the following way:

$$\varphi_1(p_1, T) = \varphi_2(p_2, T), \quad (3)$$

leading to the general two-phase equilibrium differential equation<sup>4)</sup>:

$$v_1 dp_1 - v_2 dp_2 = - \frac{\Delta q_{12}}{T} dT. \quad (4)$$

It is obvious from (4) that in the general case a change of the common equilibrium temperature ( $dT$ ) unequally reflects on the corresponding pressure variations of the phases involved.

The Clausius-Clapeyron equation (1) corresponds to the particular case for the constant phase pressure difference:

$$p_1 - p_2 = \text{const.}, \quad (5)$$

implying:

$$dp_1 = dp_2 = dp. \quad (6)$$

This includes the most frequently encountered case of equal phase pressures.

A particularly important form of equation (4) arises when the pressure of one of the phases, say phase 2, is constant:

$$p_2 = p_0 = \text{const.} \Rightarrow dp_2 = 0. \quad (7)$$

Inserting (7) in equation (4) yields after integration:

$$T = T_0 \exp \left[ - \frac{v_1}{\Delta q_{12}} (p_1 - p_0) \right], \quad (8)$$

correlating the two-phase equilibrium temperature ( $T$ ) with the variable pressure  $p_1$  of phase 1 and the constant pressure  $p_0$  of phase 2.  $T_0$  denotes the equilibrium phase transition temperature under the common pressure  $p_1 = p_0$ . Obviously,  $v_1$  and  $\Delta q_{12}$  are supposed to be independent of the variable  $p_1$  which is a fair approximation.

Let phase 1 be the solid, and phase 2 the corresponding melt of a homogeneous system. When compressed (that is  $p_1 - p_0 > 0$ ), in circumstances allowing the liquid phase to be exposed to a constant equilibrium external pressure  $p_0$  the melting point of the solid phase drops. Conversely, when subjected to a tensile stress (that is  $p_1 - p_0 < 0$ ), under the same conditions regarding the liquid phase pressure, the solid melting point temperature gets increased. The first conclusion quoted above apparently directly contradicts the prediction of the Clausius-Clapeyron equation (1). The reason for this discrepancy is because the two sets of basic conditions, (5/6) and (7), are not the same.

There is apparently no direct experimental evidence which can be quoted in support of equation (8). Some indirect evidence will be reviewed in the next paragraph.

### 3. Discussion

A common physical situation, where the condition (7) applies and which is consequently controlled by the relation (8), arises when melting a solid under a curved external surface. The coexisting equilibrium melt, being itself exposed to a constant, say atmospheric pressure  $p_0$ , loads the solid portion under the curved interface with the net Laplace's stress<sup>4)</sup>:

$$\Delta p_L \equiv p_1 - p_0 = \frac{2\gamma_{12}}{r}, \quad (9)$$

where

$\gamma_{12}$  = solid-liquid interface energy,

$r$  = interface radius of curvature.

In this case  $T_0$  corresponds to the nominal bulk melting point of the system under atmospheric pressure. Using simplified symbols:

$$v_1 \rightarrow v, \quad q_{12} \rightarrow h, \quad \gamma_{12} \rightarrow \gamma, \quad (10)$$

and by inserting (9) in (8), one readily obtains Thompson's expression for the melting temperature of a solid under a curved surface<sup>5)</sup>:

$$T = T_0 \exp \left( - \frac{2v\gamma}{hr} \right). \quad (11)$$

According to (11) the melting point of a solid under the convex external surface falls down below the material bulk melting point ( $r > 0 \Rightarrow T < T_0$ ), while solid solid portions under the concave surfaces ( $r < 0 \Rightarrow T > T_0$ ) melt at temperatures superseding it. From the numerical values of the parameters involved one estimates that this effect becomes observable only for extremely high curvatures, i. e. for an extraordinarily small radius of curvature of up to several tens nanometers.

Equation (11) was experimentally substantiated by observations of the decrease in melting point of fine powders and thin films. Actually, in 1908. Pavlow<sup>6)</sup> already proposed a qualitative conclusion on the reciprocity relation between the decrease in melting point and the diameter of the small particles. Very fine copper and silver powders (down to one nanometer particle diameter) were observed to melt at up to 400 degrees below the bulk melting point temperature<sup>7, 8)</sup>, in quite a good quantitative agreement with formula (11). Turnbull and Hollomon<sup>9)</sup> warned about the considerable undercooling ability of finely dispersed metallic melt droplets. Using the low-energy electron diffraction method, Henrion and Rhead<sup>10)</sup> determined the melting point temperature decrease of the single-atom lead layer, precipitated onto a copper single-crystal 100 plane substrate, of up to 100 degrees. The authors drew from there the general conclusion that surface layers of all the solids get melted at temperatures considerably inferior to their nominal bulk melting point temperatures. Adequate phenomena were recorded for thin layers of tin and bismuth<sup>11)</sup>, as well as for the very thin organic layers by means of nuclear magnetic resonance method<sup>12)</sup>. In contrast to this, except for a slight overheating of ice by 0.3 K in very special experimental conditions<sup>13)</sup>, no overheating of solids, corresponding to negative radius of curvature (convex surface), has yet been reported. This was explained by the inherent microscopic convexity of matter elsewhere<sup>14)</sup>.

Suppose now a melt, undercooled or overheated before the solidification takes place to a temperature  $T \neq T_0$ . By inversion of the equation (11) one obtains the surface curvature radius of the resulting solid portion (portions):

$$r(T) = \frac{2v\gamma}{h \ln \frac{T_0}{T}}. \quad (12)$$

Larger particles would get solidified at higher temperatures, the smaller ones should still be liquefied. Consequently, if a liquid is supercooled to a temperature  $T > T_0$  the expression for  $r$  represents the uniform grain size of the solid phase, resulting from subsequent solidification at that temperature. Let now be remembered that formula (11) applies quantitatively in the very deep dispersion level of matter, as quoted previously. So, by substituting in (11) for the curvature radius ( $r$ ) the

lattice parameter ( $a$ ), for the most common cubic metals one calculates the melting point in the temperature range 0.45—0.70 of the homologous temperature scale, i. e. just in the very range of the corresponding glass-transition temperature. Higher temperature would result, according to (12), in bigger radii of curvature, i. e. larger solid grains containing enough room for subsequent nucleation and crystallization processes. At lower temperatures, conversely, formula (12) predicts formation of solid grains smaller than elementary cell, with no room for the crystalline ordering. Consequently, supercooling the melts to temperatures lower than 0.45—0.70 of the homologous temperature scale is a necessary prerequisite for the solidification of amorphous metallic glasses.

It is a well known fact that interfacial energy of a pure substance diminishes with increasing impurity level. Due to the fractional evaporation effect, metallic vapour condensates are of the much higher purity level than rapidly quenched melts, their interfacial energies of higher numerical values than corresponding literature figures, determined mostly by measuring the liquid drop contacting angle. With these higher  $\gamma$ -values inserted in (11) one obviously arrives at lower melting points for condensates, corroborating experimental finding of their lower glass-transition temperatures, laying in the range 0.30—0.45 of the homologous temperature scale.

There remains to be discussed the question of temperature hysteresis during the reverse heating of metallic glasses. While the crystallization temperatures  $T_c$  of amorphous rapidly quenched melts supersede their glass-transition temperatures  $T_g$  by some 50 K or so, corresponding hysteresis accompanying the heating of the condensates is practically negligible<sup>1)</sup>. This means that strain fields around foreign atoms present in liquid-quenched amorphous structures make them more inert for ordering movements than is the case in pure condensates, thus requiring more energy to be consumed and, consequently, higher transition temperature. The friction with the strain field of foreign atoms is also responsible for the series of intermediate transient Ostwald structures, appearing sequentially during the crystallization.

#### References

- 1) M. G. Scott and B. Madin, in N. J. Grant and B. C. Giessen (Eds.), *Rapidly quenched metals I, MTI*, Cambridge (USA), 1976., p. 249;
- 2) B. C. Giessen, in N. J. Grant and B. C. Giessen (Eds.), *Rapidly quenched metals I, MTI*, Cambridge (USA), 1976., p. 19;
- 3) L. Landau i E. Lifšic, *Statističeskaja fizika*, OGIZ, Moskva/Leningrad, 1951.;
- 4) V. A. Kirilin,, V. N. Sicev and A. E. Sheindlin, *Engineering thermodynamics*, Mir, Moscow, 1976.;
- 5) J. E. Geguzin, *Fizika spekanja*, Nauka, Moskva, 1967.;
- 6) S. J. Peppiat, Proceedings of the Royal Society A **345** (1975) 1642;
- 7) M. J. Takagi, Journal of the Physical Society of Japan **9** (1954) 737;
- 8) N. Gladkich, R. Niedermayer and K. Spiegel, Physica Status Solidi **15** (1966) 181;
- 9) D. Turnbull and J. H. Hollomon, in W. E. Kingston (Ed.), *The Physics of powder metallurgy*, McGraw-Hill, New York/Toronto/London, 1951., p. 109;
- 10) J. Henrion and G. A. Rhead, Surface Science **29** (1972) 20;
- 11) L. S. Palatnik i J. F. Komnik, Fizika metallov i metallovedenie **9** (1960) 374;
- 12) G. Karagounis, E. Papayannakis and C. I. Stasinopulos, Nature **221** (1969) 655;
- 13) M. Käs und S. Magun, Zeitschrift für Kristallographie **116** (1961) 354;
- 14) D. Dužević, Science of Sintering **10** (1978) 191.

## TERMODINAMIČKA POZADINA TEMPERATURE PRIJELAZA U METALNO STAKLO

D. DUŽEVIĆ

*Institut za fiziku Sveučilišta, 41000 Zagreb*

UDK 538.953

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Razmatranje izuzetnih slučajeva taljenja svodi se uglavnom na raspravu Clausius-Clapeyronove diferencijalne jednačbe, po kojoj se tališta normalnih sistema povišuju s porastom tlaka. U ovome se radu trag Clausius-Clapeyronove jednačbe slijedi do njezina izvorišta i podsjeća, da je ona samo poseban slučaj opće diferencijalne jednačbe dvofazne termičke ravnoteže za uvjet, da su obje faze izložene istome tlaku. Sasvim suprotan odnos kretanja tlaka i temperature ravnoteže iziskuje okolnost, u kojoj se mijenja samo tlak čvrste faze, dok se tlak taljevine održava stalnim. Uvažanjem Laplaceove relacije za kapilarni tlak iz ove varijante proistječe Thompsonova relacija između temperature tališta tvari i zakrivljenosti njezine vanjske površine. Primjena ove relacije na minimalne kristalne entitete veličine elementarne stanice vodi neposrednome proračunu temperature prijelaza u metalno staklo.