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THE HEIGHT OF DSC PHASE TRANSITION PEAKS.
I. Theory

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A description of phase transitions as recorded by differential scanning calorimetry (DSC) is given. A new number N is defined as $N = h'/h$, where h is the height of a transition peak for a mass of sample m and a heating rate $\dot{T}_p$ and h' is the height of the same peak for a mass $2m$ or a heating rate $2\dot{T}_p$. N is theoretically derived in the case of isothermal and non-isothermal first order phase transitions and of a second order phase transition. The equivalence of mass and heating rate is proved. An example of the possible use of N is given.

Differential scanning calorimetry (DSC) is a widely used technique. Among the various potential applications, the study of transition peaks. such as melting peaks, is one of the most common. The usually available data are the transition temperature and enthalpy and sometimes an analysis of the shape of the peak (purity measurements, isothermal crystallizations). This paper is devoted to another parameter which is readily available from a transition peak· the variation of the height of the peak as a function of the sample mass or of the heating (or cooling) rate. Part I is a description of the theoretical basis of our analysis and part II is devoted to some applications to liquid crystalline systems.

Theoretical background

In this paper, a thermodynamical phase transition is studied using differential scanning calorimetry. This phase transition, which will be described according to the current thermodynamical theories as a first order or a second order one, is recorded on the DSC trace as an anomalous change in the differential power ΔP, different from the normal ΔP variation only due to the heat capacity of the material. This variation, sharp or smooth, will be called the "transition peak". We define the height h of the peak as the distance between the heat capacity trace, or baseline, and the maximum ΔP during the course of the phase transition. In the case of a pure second order phase transition, this height is the difference between the heat capacities before and after the transition. In the case of a pure first order phase transition, it is simply the maximum height of the peak above the baseline.

A number N is defined as $N = h'/h$, h' being the height of the transition peak when the mass or the heating rate are multiplied by two. The theoretical values of N will be determined in the case of an isothermal first order phase transition, a second order phase transition and a non-isothermal first order phase transition (case of an impure material). Two very simple applications (melting of a pure metal, glass transition of an amorphous polymer) will be given for checking the validity of our theoretical analysis and a more complicated example will illustrate a possible use of this new parameter.

Isothermal first order phase transition

Several models have been developed for explaining the shape of a DSC melting peak of a pure material [1–4]. These models are valid for any isothermal first order phase transition. In this paper, only the simplest expressions describing the melting peak will be used [1]. The basic assumption for using these expressions is that the temperature of the specimen remains constant during the transition. This is a good approximation as far as the thermal resistance of the specimen can be considered as negligible. O'Neill [2] has proposed a more sophisticated model taking the thermal resistance of the specimen into account. However, it has been shown that this model reduces to the simple one described in reference 1 provided that:

$$\frac{r\dot{T}_p(t_2 - t_1)^2}{R_0^2 A^2 \rho \Delta h} << 1 \tag{1}$$

where $\dot{T}_p$ is the heating rate, $(t_2 - t_1)$ is the melting time, r, ρ and Δh are the thermal resistivity, the specific mass and the heat of fusion per unit mass of the specimen, respectively, A is the contact area of the sample with the oven and R_0 is the thermal resistance between the sample and the oven.

If the sample temperature is assumed to be constant during melting, the theoretical melting curve has the general shape shown in Figure 1. The equations describing such a melting curve are the following:

(i) For $t \leqslant t_1$, i.e. before the beginning of melting, the differential power $\Delta P(t)$ is only due to the heat capacity of the solid material. So:

$$\Delta P(t) = mC_{ps}\dot{T}_p \tag{2}$$

where m is the sample mass and C_{ps} the specific heat of the solid material.

(ii) Between times t_1 and t_2, melting of the sample occurs at a constant temperature, and $\Delta P(t)$ is given by:

$$\Delta P(t) = \frac{\dot{T}_p}{R_0}(t - t_1) + mC_{ps}\dot{T}_p \tag{3}$$

(iii) At the end of melting, the sample is still at the melting temperature, whereas the programmed temperature is much higher. So, the sample has to reach the programmed temperature, which implies the following variation of $\Delta P(t)$:

$$\Delta P(t) = mC_{pl}\dot{T}_p + \left[m(C_{ps} - C_{pl})\dot{T}_p + \frac{\dot{T}_p}{R_0}(t_2 - t_1)\right] \exp \frac{t_2 - t}{mR_0C_{pl}} \tag{4}$$

where C_{pl} is the specific heat of the liquid sample.

From a mathematical point of view, equation (4) shows that the ΔP curve reaches the baseline for an infinite time. Practically, it will be considered that the sample reaches the programmed temperature at a time t_3 which is taken when it is impossible to measure the difference between the baseline and the ΔP curve.

(iv) For $t \geqslant t_3$

$$\Delta P(t) = mC_{pl}\dot{T}_p \tag{5}$$

The transition enthalpy $m\Delta h$ is given by:

$$\begin{aligned} m\Delta h &= \int_{t_1}^{t_2} \left[mC_{ps}\dot{T}_p + \frac{\dot{T}_p}{R_0}(t - t_1)\right] dt = \\ &= mC_{ps}\dot{T}_p(t_2 - t_1) + \frac{\dot{T}_p}{2R_0}(t_2 - t_1)^2 \end{aligned} \tag{6}$$

As defined in Figure 1, the height h of the peak has the following expression:

$$h = \frac{\dot{T}_p}{R_0}(t_2 - t_1) \tag{7}$$

The combination of equations (6) and (7) leads to:

$$h = - mC_{ps}\dot{T}_p + \left(m^2C_{ps}^2\dot{T}_p^2 + \frac{2m\Delta h\dot{T}_p}{R_0}\right)^{\frac{1}{2}} \tag{8}$$

It is easy to see from equation (8) that multiplying by two m or $\dot{T}_p$ is equivalent. N is defined as h'/h, where h' is the height of the peak for a mass $2m$ or a heating rate $2\dot{T}_p$. So:

$$N = \frac{2\left[-1 + \left(1 + \dfrac{\Delta h}{mC_{ps}^2R_0\dot{T}_p}\right)^{\frac{1}{2}}\right]}{-1 + \left(1 + \dfrac{2\Delta h}{mC_{ps}^2R_0\dot{T}_p}\right)^{\frac{1}{2}}} \tag{9}$$

When m or $\dot{T}_p$ tends to zero, N tends to $\sqrt{2}$ and when m or $\dot{T}_p$ tends to infinity, N tends to 1. The function being without extremum,

$$1 < N < \sqrt{2} \tag{10}$$

These limits are only a mathematical consequence of equation (9) and their physical significance has to be examined. The upper limit is valid and can be understood in a simple way. When $\dot{T}_p$ or m tends to zero, it means that Δh is important and the heat capacities negligible. Thus, the transition peak is a triangle (area $B = 0$ in Figure 1) and $N = \sqrt{2}$. On the contrary, the lower limit cannot be reached since the basic assumption of this model is that the melting curve has the shape shown in Figure 1, which implies that $\dot{T}_p$ and m are small. The exact limits for $\dot{T}_p$ and m depend on the nature of the sample and its geometry. For instance, in the case of a specimen of pure indium with $m = 100$ mg, the melting curve has the shape described in Figure 1, if $\dot{T}_p$ is lower than 1.25 deg min^{-1}.

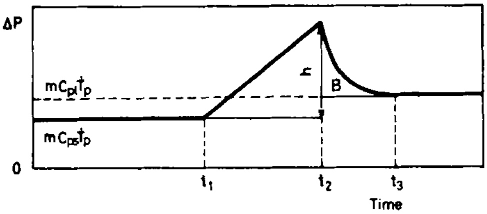

Fig. 1 Theoretical DSC melting curve of a pure material. ΔP is the power difference between the sample holder and the reference holder. The heating rate $\dot{T}_p$ is constant

It is much better to multiply $\dot{T}_p$ by two rather than m. The first reason is experimental, since it is easier to run twice the same sample than to run two different samples. Secondly, this model assumes that the thermal resistance R_0 is independent of mass. This is true only when special case is taken to ensure that the specimen geometry, particularly the contact with the pan, and its position remain constant (the same requirements are necessary for an accurate determination of temperature).

When it is not possible to run twice a sample, the following equation gives N in the case of two masses m_1 and m_2 leading respectively to two peak heights h_1 and h_2:

$$N = \exp\left[\frac{0.69 \ln\left(\frac{h_2}{h_1}\right)}{\ln\left(\frac{m_2}{m_1}\right)}\right] \tag{11}$$

Second order phase transition

As a DSC curve is the recording of the differential power ΔP versus time t, it is possible to write:

$$\Delta P = \frac{\mathrm{d}\Delta W}{\mathrm{d}t} = \frac{\mathrm{d}\Delta W}{\mathrm{d}T_p}\frac{\mathrm{d}T_p}{\mathrm{d}t} \tag{12}$$

where T_p is the programmed temperature. This equation is valid only when no first order phase transition occurs. Thus:

$$\frac{\mathrm{d}\Delta W}{\mathrm{d}T_p} = mC_p \quad \text{and} \quad \frac{\mathrm{d}T_p}{\mathrm{d}t} = \dot{T}_p \tag{13}$$

Equation (12) is then the same as equation (2):

$$\Delta P = mC_p\dot{T}_p \tag{14}$$

When m or $\dot{T}_p$ are multiplied by two, ΔP is also multiplied by two. A second order transition is recorded by DSC as a change of heat capacity, without involving a transition energy. Equation (14) is so valid for describing such a transition. In this case, $h = m\dot{T}_p|C_{p2} - C_{p1}|$ where C_{p1} and C_{p2} are the specific heats before and after the transition. As a consequence, $N = 2$.

Impure material (non-isothermal first order transition)

When the material is impure, the first order phase transition is generally not isothermal. The presence of impurities lowers the melting point and broadens the melting peak. If the impurity is soluble at any quantity in the material, one can describe the melting curve using the Van't Hoff equation. This equation is commonly used in the DSC technique for measuring the purity of samples [5]. It can be written as:

$$\frac{dW}{dT_s} = \frac{m\Delta h(T_f - T_m)}{(T_f - T_s)^2} \tag{15}$$

where T_f is the melting temperature of the pure material, T_m the melting temperature of the impure material, Δh the specific enthalpy of transition, T_s a temperature where a certain amount of material has melted. dW/dT_s is related to the power ΔP involved in the transformation at the temperature T_s by:

$$\Delta P(T_s) = mC_p(T_s)\dot{T}_p + \frac{dW}{dT_s}\dot{T}_p \tag{16}$$

At the melting temperature T_m:

$$\frac{dW}{dT_s} = \frac{m\Delta h}{T_f - T_m} \tag{17}$$

The height of the peak h is:

$$h = \Delta P(T_m) - mC_p(T_m)\dot{T}_p = \frac{dW}{dT_s}\dot{T}_p \tag{18}$$

$$h = \frac{m\Delta h\dot{T}_p}{T_f - T_m} \tag{19}$$

When m or $\dot{T}_p$ are multiplied by two, h is multiplied by two, and so $N = 2$. It is the same result as for a second order transition, where only heat capacities are involved. This can be explained by using the theoretical model of Gorter for a second order transition [6]. In this model, a second order phase transition is described as the end of a non-isothermal first order transition. This is exactly what happens in the case of the melting of an impure material as described by the Van't Hoff equation.

Practical use of number N

Table 1 is a summary of the different N values for the theoretical cases described above. How can these theoretical results be used in the case of an experimental melting?

Usually, a baseline under the melting peak is plotted by drawing a straight line between the beginning and the end of the peak, since the real baseline is unknown (except for very pure sample). The value of N can then give at least two results. The first one is to give a qualitative measurement of the relative importance of a second order component in a first order phase transition. This will be studied in the part II of this paper. The second result is that an anomalous N number may be found. It indicates that the transition is not a simple one, but that another phenomenon is hidden, as for instance two transitions, very close together, and giving only one peak. An example of such a mechanism will be given in the experimental section.

Table 1 Summary of theoretical N parameters for various phase transitions

Transition	N
Isothermal first order phase transition	$1 < N < \sqrt{2}$
Impure material	
First order phase transition	2
Second order phase transition	2

Experimental section

Materials

The indium sample used in this work was supplied by Perkin–Elmer Co. Commercial atactic polystyrene was supplied by BASF. The preparation of *N*-methylmorpholine *N*-oxide monohydrate is described in reference [8]. DSC measurements were performed with a Perkin–Elmer DSC 2 calorimeter.

Results

Isothermal first order transition: Indium

Indium melts at 156.6°. The melting peak recorded by DSC (Fig. 2) agrees very well with the theoretical melting peak of a pure sample, as described above (Fig. 1). Table 2 shows that $1 < N < \sqrt{2}$ (see equation (10)), N decreasing when $\dot{T}_p$ increases. This reflects the increasing importance of area B, as seen by looking at $t_2 - t_1$. This leads to a temperature lag $\Delta T = T_{\text{programmed}} - T_f$ at the end of the melting which is more important when $\dot{T}_p$ increases. There is a good agreement between the experimental and theoretical values of N.

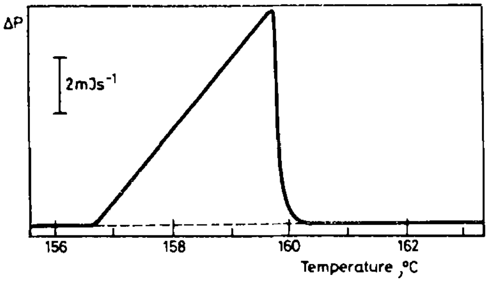

Fig. 2 Experimental DSC melting curve of indium

Table 2 *N* parameters for the melting of pure indium. ΔT: temperature difference between the sample temperature and the programmed temperature at time t_2

$\dot{T}_p$, deg min^{-1}	$t_2 - t_1$, s	ΔT, °C	*N*
1.25	9	0.19	–
2.5	5.2	0.22	1.27
5	3.8	0.32	1.22
10	3.4	0.57	1.14

Second order transition: Polystyrene

The glass transition of amorphous atactic polystyrene was chosen as an example of a second order transition. Figure 3 shows the DSC trace recorded for a heating rate $\dot{T}_p = 20$ deg min^{-1}. In a conventional way, the glass transition temperature is taken as the mid-point in the thermogram as measured from the extensions of the pre- and post transition baselines [7]. As shown in Figure 3, *h* is defined as the difference between the two extrapolated baselines at T_g. For all the investigated heating rates, a small endothermic peak was observed in the transition region. This phenomenon, which is classical for polystyrene, was not taken into account: the post transition baseline is extrapolated through the peak and T_g measured in the conventional manner (Fig. 3). Table 3 gives the values of *N* determined for such a transition. These values are close to 2, as predicted by the theory.

Anomalous first order transition: N-methylmorpholine N-oxide monohydrate [8]

N-methylmorpholine *N*-oxide (MMNO) is an organic compound with a melting temperature of 75.6°. When prepared from acetone, the first melting peak and the following runs have different shapes (Fig. 4). The textures as observed by optical microscopy are different, since the first peak corresponds to the melting of lath-like crystals and the following to the melting of MMNO spherulites. The first peak has a *N* value of 1.49. But the next ones have a *N* value of about 6 showing that something else

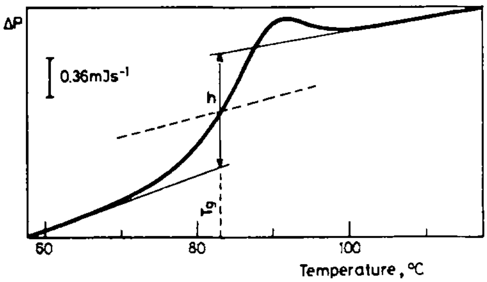

Fig. 3 Glass transition of atactic polystyrene. $\dot{T}_p = 20$ K min^{-1}

Table 3 N parameters for the glass transition of polystyrene

$\dot{T}_p$, deg min^{-1}	T_g, °C	N
5	79	–
10	81	2
20	83	2.07
40	86	1.97

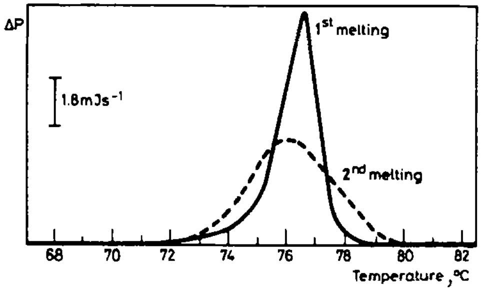

Fig. 4 Experimental DSC melting curve of *N*-methylmorpholine *N*-oxide. $\dot{T}_p = 10$ K min^{-1}

than a simple melting process occurs. What probably occurs is that the recorded melting peak is composed of two or more superposed peaks. This can be seen by looking carefully at the melting curves obtained for very slow heating rates: an inflexion of the curve can be observed at a temperature higher than the temperature of the peak maximum. Even at 10 deg min^{-1}, this effect is slightly detectable (see Fig. 4 or Fig. 8 in reference [8]). So, when changing m or $\dot{T}_p$, the relative position of these peaks changes and gives this very high value of N.

Conclusion

The measurement of N is very simple to do, and can give useful information, e.g. showing the importance of the second order component in a first order phase transition, or detecting anomalies in the transition (see part II and the example given in part I). The equivalence of m and $\dot{T}_p$ for determining N has been shown. The theoretical expression of N was derived and studied in the case of first order transitions, both isothermal and non-isothermal, as well as in the case of second order transitions. The use of $\dot{T}_p$ is much easier and more precise than the use of m, since the material, the capsule and the thermal resistance R_0 are the same, but is restricted to perfectly reversible phase transition (not the use of m). The use of a melting rather than a freezing curve avoids problems associated with supercooling of samples, instability in the melt, crystallization mechanisms varying with thermal histories (e.g. in polymer crystallization).

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Zusammenfassung — Eine Beschreibung von Phasenübergängen, registriert durch DSC, wird gegeben. Eine neue Zahl N wird eingeführt und als $N = h'/h$ definiert, wobei h die Höhe des Übergangspeaks für die Probenmasse m und die Aufheizgeschwindigkeit $\dot{T}_p$ und h' die Höhe des gleichen Peaks für die Masse $2m$ oder die Aufheizgeschwindigkeit $2\dot{T}_p$ sind. N ist im Falle isothermer und nichtisothermer Übergänge erster Ordnung und eines Phasenübergangs zweiter Ordnung theoretisch ableitbar. Die Äquivalenz von Masse und Aufheizgeschwindigkeit wurde überprüft. Ein Beispiel für eine mögliche Anwendung von N wird angegeben.

Резюме — Приведено описание фазовых переходов, установленных методом ДСК. Новый параметр N определяется выражением $N = h'/h$, где h-высота пика перехода для образца с массой m и скорости нагрева $\dot{T}_{\text{п}}$, а h'-высота того же самого образца с массой $2m$ и скорости нагрева $2\dot{T}_{\text{п}}$. Величина N теоретически выведена в случае изотермических и неизотермических фазовых переходов первого порядка и фазового перехода второго порядка. Доказана эквивалентность массы и скорости нагрева. Приведен пример возможного использования параметра N.