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A SIMPLE AND EFFECTIVE METHOD FOR SMOOTHING DSC CURVES

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All known procedures of smoothing are limited by the beginning of falsification of the signals. We suggest a simple modification of the moving average of the polynomial smoothing procedure. The signal curve is smoothed to the best degree and independently of the special problem within an interval calculated from the n-th multiple of the standard deviation of the noise.

All types of heat flux or power-compensated scanning calorimeters usually contain the necessary electronics and/or the corresponding software filters to keep the signal-to-noise (S/N) ratio as high as possible. Most of the typical calculation routines can be solved without further smoothing procedures. However, some additional enhancement of the S/N ratio is required in the following cases:

– Improvement of the accuracy of C_p measurements
– Detection and estimation of very weak thermal events (liquid-crystalline transformation; C_p changes around T_g, including the relaxation phenomena)
– Derivation of signals
– Deconvolution of very fast signals

The first situation is a very simple one. It is known that the C_p function can be approximated by one of the following polynomia (dependent on the investigated substance and the desired temperature range):

$$C_p = a + bT; \qquad C_p = a + bT + cT^2; \qquad C_p = a + bT + cT^2,$$

where a, b and c are the polynomial coefficients.

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By fitting the experimental curve to one of these "theoretical functions", the "true" signal curve may be restored. The result of the linear regression yields not only the smoothed signal curve, but also the best analytical function for all further thermodynamic calculations. In all the other cases mentioned above, the analytical functions of the signals are unknown. Signal enhancements are possible by smoothing in the original signal domain or by digital filtering, that is signal processing in the Fourier domain [1-3]. The advantages and disadvantages of these methods are discussed in detail in [1].

In general, the better the S/N ratio, the larger the distortion of the peak; in filtering techniques, there is also sometimes a risk of a unidirectional distortion of the peak position. Furthermore, each new problem requires careful optimization of the smoothing procedure (type, window size, number of repeated smoothing cycles, and so on). Smoothing by spline functions [4] is subject to the same restrictions.

The aim of this paper is to present an algorithm which operates very effectively in the original signal domain. The proposed solution is very straightforward and free of any marked peak distortions.

Experimental

All experiments were carried out with Perkin-Elmer DSC 2C/TADS 3600 equipment. A self-made UV-irradiation device permits the investigation of light-induced reactions too [5]. The multi-tasking software package we have developed allows the simultaneous running of samples and the performing of any application tasks. The software for the data acquisition and large parts of the calculation routines are written in Assembly language.

The smoothing algorithm

As a rule, we use the simplest way to smooth data, i.e. the moving average technique. As usual, we replace the central point of a window with three, five or generally a fixed odd number of points by the calculated average of the window. Using the Golay-Savitzky filters in our algorithm yields the same result in the end. Time saving is significant only in the case of point number ≥ 5 of the window size, but this is not a typical case.

Our basic, new idea is shown schematically in Fig. 1. Table 1 demonstrates the course of calculation for the same example, using a three-point window. The central point is replaced by the calculated average if the difference is not larger than a given threshold value (±2 in our example). Otherwise, the smoothed new value is taken as the signed sum of the original value and this threshold (compare rows 3 and 4 in Table 1). For calculations in the subsequent cycle, the starting values of these points are used. Similarly as in the removal of spikes [1], we define the threshold as some multiple of the estimated standard deviation of the noise. The standard deviation can be calculated from ranges of temperature or time without liberation or adsorption of heat. The main advantage of our procedure is that the smoothing can be amplified by applying it repeatedly on the same curve (row 5 in Table 1). This is normally very critical, because the distortion of the signal is proportional to the number of calculation cycles, strongly dependent on the chosen window size. Our method is free of this disadvantage. The more frequent the calculation cycles, the better the S/N ratio of the original curve in a strip built by the threshold ($n*s$) on both sides of it. The real tuning parameter is the multiple n of the standard deviation s. If the data density is high compared with the changes in the experimental signal, a frequently repeated smoothing cycle with a narrow window width yields the same result as a few iterations using a larger window width. If the data density is decreased, this condition is no longer fulfilled. Therefore, we calculate as a matter of routine 20 or more smoothing cycles with a three-point window. Using a computer with a slow microprocessor (Motorola 6800 in the TADS 3600), the smoothing of 600 data points takes about 60 seconds.

Table 1 The results of the first and the last smoothing cycle, using a three point window, ten arbitrary original values and a threshold of ±2

point number	1	2	3	4	5	6	7	8	9	10
orig. val.	2	4	2	6	2	3	4	–1	2	1
calculated values 1)	3.33	2.67	4.00	3.33	3.67	3.00	3.00	1.67	0.67	2.33
calculated values 2)	3.33	2.67	4.00	4.00	3.67	3.00	2.00	1.00	0.67	2.33
calculated values 3)	2.80	3.20	3.60	4.00	3.33	2.67	2.00	1.00	1.33	1.67

1) in the result of the 1st cycle

2) corrected values, using the corresponding threshold (compare the point numbers 4 and 8)

3) smoothed points after more than 15 cycles

If an n-point window is used, the $n/2–1$ limiting points on both ends of the signal curve should be calculated as suggested by Gorry [6]. This should be done again after each smoothing cycle. Spikes should be removed by using the known procedures [1] before smoothing starts.

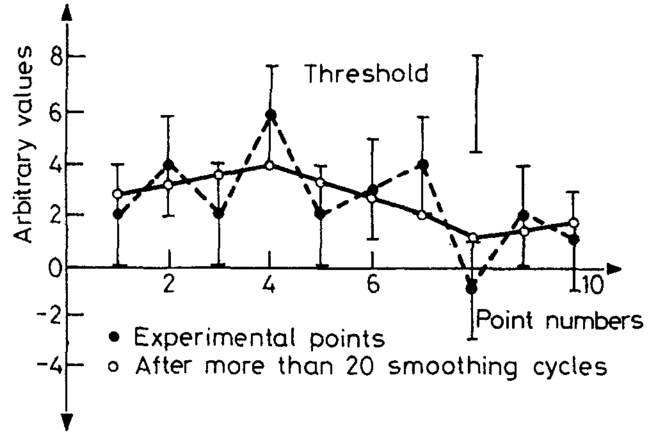

Fig. 1 Schematic representation of the smoothing procedure

Finally, if the shape of a thermal event is very sensitive to changes in outstanding points (e.g. the peak maximum in the case of a lower data density), we have created the possibility to fix the corresponding heat flows by using a cursor routine. However, this less-than-ideal solution is better replaced by signal curves with a larger data density.

Examples

The derivation of signals is rarely used in DSC but it is a very important operation in other techniques. Figure 2 shows the phase transformation monoclinic/orthorhombic for Ti_3O_5 (curve 1). If the derivation subroutine from the original Perkin-Elmer software is used, neither the signal height nor the temperatures of the derivative are correct. To demonstrate the validity of our procedure, we have first calculated the correct but noisy derivative (curve 2, normally no separated step) and then the smoothed curve 3. Both the peak height and the shape of the derivative (compare the characteristic points of the original and the derivated curve on the dotted lines) are unchanged.

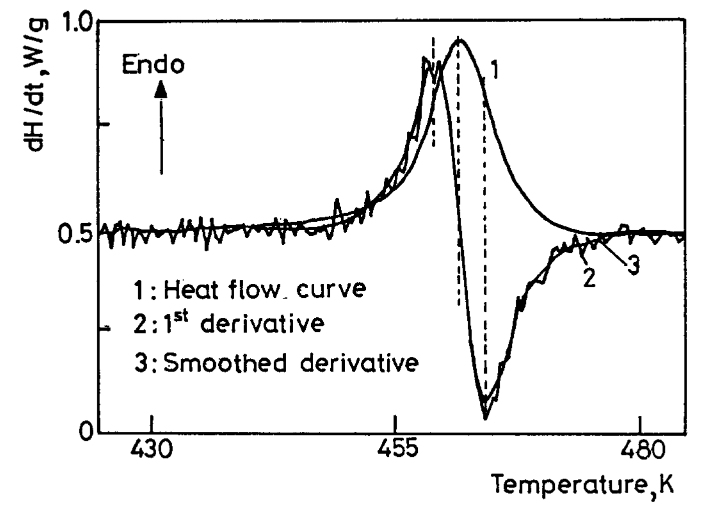

Fig. 2 The smoothing of the first derivative of a weak endothermic effect in case of the monoclinic/orthorhombic phase transformation of Ti_3O_5. Heating rate: 10 deg/min

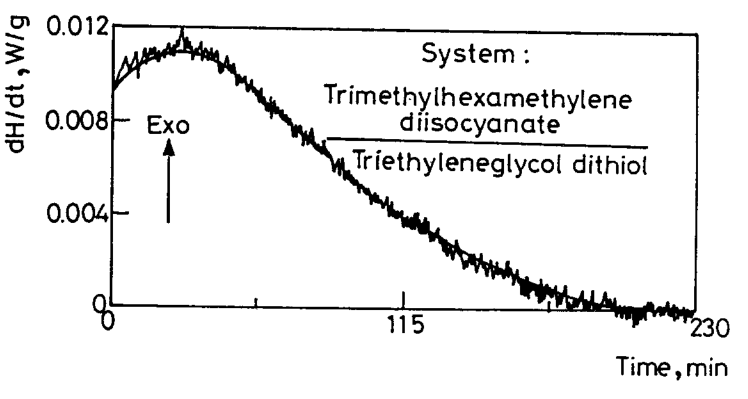

Fig. 3 The smoothing of an isothermal reaction curve, T = 383 K

Very frequently, we investigate extreme situations of isothermal reaction curves in our laboratory, as shown in Fig. 3 for a dithiol/diisocyanate system. The reaction rate is no longer much higher than the thermal noise. Kinetic model processing of such curves should not be done without preliminary smoothing. Owing to the large ratio of the data density compared with the relative signal change, the smoothing can be made very effective by using a larger threshold value (±3 s to±5 s). To demonstrate the above-mentioned fact that the risk of "overfiltering" [2] is not present in our procedure, we have calculated the smoothing curve of Fig. 2 as a result of 500 cycles. The result is excellent and convincing.

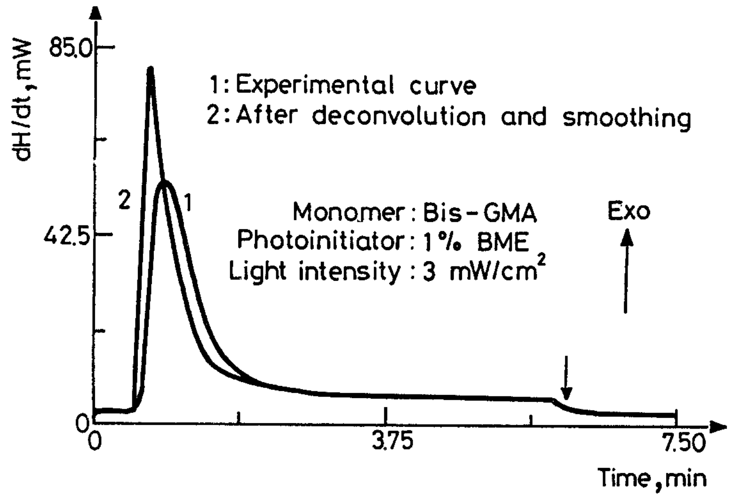

Fig. 4 The experimental and the smoothed deconvoluted reaction curves for the light-induced polymerization of Bis-GMA, T = 298 K

The last example concerns the smoothing of a curve which was produced by a deconvolution procedure. As regards the noise, the deconvolution acts like a derivation of the original curve. Figure 4 shows experimental and deconvoluted reaction curves for the very rapid light-induced polymerization of Bisphenol-A-diglycidyl ether-dimethacrylate (Bis-GMA). 1% of benzoin methyl ether (BME) is used as photoinitiator. The experimental technique and the algorithm of deconvolution [7] have already been published. It should be mentioned that, in contrast with other solutions [8, 9], we illuminate only the sample side of the sample holder. Switching off the UV light after completion of the reaction yields the point-spread function (the arrow in Fig. 4). The step response in our case reflects the total of all influences of the device and the individual sample. The latter fact is particularly important and worth mentioning. Figure 5 shows an enlarged part of the deconvoluted and distinctively noisy curve from Fig. 4, together with the smoothed curve.

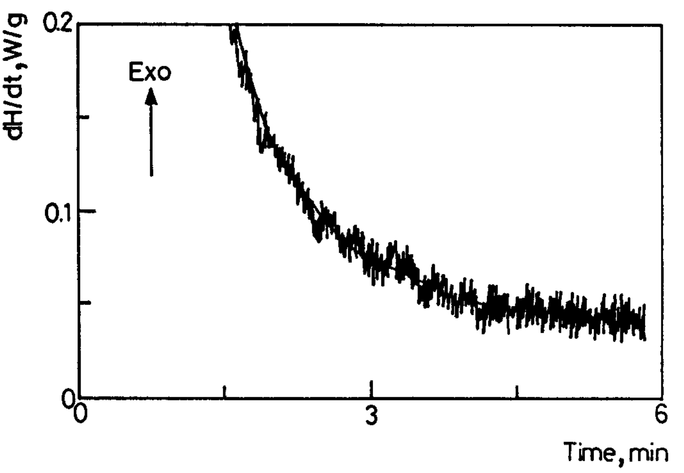

Fig. 5 Increased part from Fig. 4, showing the smoothing of the noisy deconvoluted reaction curve, $T = 298$ K

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Zussammenfassung — In einigen Fällen (Bildung von Ableitungen, Entschmierungsrechnungen, Auswertung schwacher Effecte) ist auch bei der DSC-Technik eine Glättung des primären Signals angebracht. Alle bekannten Verfahren beinhalten immer einen Kompromiß zwischen erreichter Glättung und beginnender, nicht mehr zu vernachlässigender Verfälschung der Analysenergebnisse. Zudem erfordert jedes Problem seine eigenen optimalen Glättungsparameter. Wir schlagen eine einfache und universell anwendbare Modifikation des Verfahrens mit gleitender Mittelwertsbildung bzw. unter Verwendung der Golay-Sawitzky-Filter vor. In einem Streifen, der aus einem vorgebbaren Vielfachen der Standardabweichung des Rauschens gebildet wird, erhält man so eine optimale Glättung.