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解　説

Views of the Periodic Heating Method

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Several e-mails were exchanged between Prof. Schick and I (YS) about our views of the periodic heating method. Prof. Schick has been working on the periodic heating method extensively and organized Lähnwitzseminar known as the leading conference in this field. I believe that the most suitable person gave contribution to this special issue. I hope that the readers will enjoy this discussion and I thank for the recent surprising development of the communication technology that enabled this discussion.

Dear Christoph

Thank you very much for your agreement to discuss with me about periodic heating method for the special issue of "*Netsu-Sokutei*". In this special issue five authors write papers about ac calorimetry, modulated temperature DSC, 3-omega method, temperature wave analysis and photo-acoustic method. Periodic heating (or alternating heating and cooling) utilized in these methods is distinct from the time independent technique used in the adiabatic or steady state measurement. As many authors pointed out the periodic heating method is not only another technique to measure the same quantities with the conventional methods but also a technique to get essentially new information. You have been working on the periodic heating method and organized Lähnwitzseminar* paying attention to this method. I would like to begin this discussion with asking you in what benefits of the periodic heating method you are interested.

Best regards,
Yasuo

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Dear Yasuo

Thank you very much for giving me the opportunity to share with you and the readers of the special issue of "*Netsu-Sokutei*" my thoughts about periodic heating methods in calorimetry.

One should always remember that there is no basic difference between dynamic measurements in time domain, *e.g.* relaxation mode in adiabatic calorimetry, and periodic measurements in frequency domain, *e.g.* AC-calorimetry, 3ω-method or temperature modulated DSC. This is due to the fact that all these methods are based on the linear response approach and the response in time domain can be transferred to frequency domain by Fourier transformation. Because we apply data treatments based on linear response we should always be aware that we have to check whether or not linearity holds for our measurements. In case linearity does not hold the results

* In the program leaflet of the 4th Lähnwitzseminar there is the next description; "Due to the spirit and tradition of the Lähnwitzseminar, the timing of the lectures is not fixed, to allow intensive (almost open end) discussions in the plenum and at the posters as well". Visit the next web page to know more about the Lähnwitzseminar. http://www.uni-rostock.de/fakult/manafak/physik/poly/polymerphysics.htm

obtained may be meaningless. After this very general statement I would like to discuss with you in more detail some general points as well as some applications of the periodic heating methods in calorimetry.

First of all I would like to know what is your personal view about the history of periodic heating methods in calorimetry and what you would like to add to the following.

Periodic perturbations are in use in calorimetry since 1910 when Corbino[1)] used the newer days so called 3ω-method to determine the heat capacity of electrically conducting wires. In the 1960's the AC-calorimetry was developed by Kraftmakher[2)] and Sullivan and Seidel.[3)] All these authors considered heat capacity as a real valued quantity although it was known from ultrasound propagation in gases that, in general, heat capacity should be considered as a frequency dependent complex quantity.[4)] The first direct measurement of the frequency dependent complex heat capacity was performed in 1971 by Gobrecht, Hamann and Willers[5)] at the glass transition of an inorganic polymer, namely amorphous selenium. Interestingly, they used for their experiments a differential scanning calorimeter. Therefore they did not only perform the first direct measurements of complex heat capacity but also they used, for the first time, a temperature modulated DSC (TMDSC). This idea, the combination of DSC and periodic temperature perturbations was reconsidered in 1993 by Reading *et al.*[6)] At that time it was possible to overcome the extreme limitations of the setup proposed by Gobrecht *et al.* because of the dramatic improvements of computer technology. Consequently TMDSC became available as a standard tool in thermal analysis and since then it is widely used in polymer characterization.

As mentioned before information about the dynamics of a system can also be obtained from step or pulse response measurements instead of applying periodic perturbations. Such step response measurements were first performed at the glass transition using adiabatic calorimeters by Suga *et al.* in the 1970's, for a review see.[7)] Here the temperature drift of the sample under close to perfect adiabatic conditions was measured after applying a certain amount of heat. This method is, because of the large time constant of the adiabatic calorimeters, limited to very low frequencies below 10^{-2} Hz. In DSC stepwise increases of the temperature and measuring the heat flow rate response is known since the 1970's.[8)] Originally this technique was applied to purity determination based on the van't Hoff equation. But also the deconvolution of the signal obtained from such step heating measurements into a thermodynamic (reversible) and a kinetic component was proposed in 1988 by Claudy.[9)] Recently, this step technique was reconsidered and used in a commercial instrument for heat capacity measurements, StepScan™ DSC, PerkinElmer Instruments. The equivalence of the results obtained from frequency dependent measurements with that from step response measurements can be shown.[10)]

Please let me know your comments on my statement and let us continue our discussion with some thoughts regarding interesting applications of periodic heating methods in different field of calorimetry.

Best regards,
Christoph

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Dear Christoph

Thank you very much for the detailed explanation about your view of the periodic heating method. The historic description in your e-mail was very interesting, but it is regretful to say that my knowledge about the history is not sufficient to add something to your description. I would like to give some comment about the linearity below.

I agree to the point that linear response is very important in the periodic heating method. However, I think that we often use the term "linear response" in two meanings. The first meaning is linearity between the temperature modulation and the heat flow. This linear response can be checked experimentally. I have measured the complex heat capacity at the melting temperature of polyethylene crystals. As far as I experienced harmonic components of the observed signal were sufficiently small. This means that linear response of the first meaning held even at the melting temperature. The second meaning is the linear response theory. As you mentioned we can transfer the response in time domain to frequency domain on the basis of the linear response theory. This mathematical treatment by Fourier transformation is essential to combine the results from measurement using stepwise temperature change and the results from the periodic heating method. However, it should be remembered that this mathematical treatment of the linear response is based on the concept of the system with small deviation from the equilibrium state. Frequency dependent complex heat capacity just above the glass transition temperature is a typical case to be explained by the linear response theory. On the other hand phase transition can not be attributed to the small deviation from the equilibrium state. Therefore measurement of the melting of polyethylene crystals satisfies the linear response condition in the first meaning but does not in the second meaning.

Calorimetry and thermal analysis have been used as powerful tools to study phase transition. I hope that the periodic heating method can be applied to phase transition as well. A kinetic model for crystallization and melting of polymeric materials has been proposed.[11,12] Data analysis of the complex heat capacity at the crystallization and melting temperatures was carried out using this model instead of the linear response theory. The basic idea of the model is to consider small deviation from the steady state (crystallization or melting at a constant rate) instead of the equilibrium state. As far as I know there is not a systematic theory like the linear response theory applicable to this case. It should be splendid if the periodic heating method leads to a new field for theoretical studies as well as experimental studies.

Extension of the frequency range is important particularly to study the dynamics of materials around the glass transition temperature. Frequency dependent measurement around the glass transition temperature has been made for a long time using dielectric and mechanical methods. I would like to have your comments about the benefits of the thermal method comparing with the dielectric and mechanical methods. The glass transition and the phase transition are two typical phenomena studied by calorimetry and thermal analysis. To understand benefits as well as problems of the periodic heating method is important to utilize it successfully.

Best regards,
Yasuo

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Dear Yasuo

Thank you very much for your comments and interesting questions. Although I would not like to focus too much on the problems of linear response I have to make some additions to your e-mail. In my opinion linear response is the basic for all our measurements. As long as we apply Fourier analysis it is a prerequisite for the data treatment applied. I am not sure if it is necessary to distinguish between both kinds of linear response as you suggested. But I do not have very serious arguments to support my view beside that I wrote in my first e-mail. I would like to leave the question open at this point and to invite the readers to contribute in forthcoming papers to this very essential discussion.

Dielectric measurements actually allow for the broadest frequency range for the study of glass transition. Nevertheless a serious limitation of dielectric studies must be considered. Dielectric measurements are only sensitive to molecular processes related to electrical dipole fluctuations. Calorimetric measurements, on the other hand, are sensitive to all degrees of freedom not only to a single one as most of the other dynamic methods. This results sometimes in differences between dielectric and calorimetric relaxation times.[13] The reason for that is yet not understood but I believe this is another interesting field for the periodic heating method in calorimetry.

As you mentioned in your previous e-mail melting in general and especially of polymers seems to be a very interesting field of periodic heating calorimetry. To the best of my knowledge there are two fields of application of periodic heating calorimetry to polymer melting and crystallization. The first, as mentioned in your last e-mail, is related to the influence of the temperature perturbation on the melting and crystallization process. As shown by Toda and your self one can obtain very useful information about the dynamics of melting and crystallization. TMDSC seems to be a very appropriate method to check the superheating of polymer crystals and the temperature dependence of this effect. The second process I have in mind, and my research is focused on, is the reversible melting. Surprisingly, one observe some reversing melting-crystallization process in polymers within a fraction of a degree although it is well known that ordinary polymer crystallization needs a sufficient super cooling in the order of 10 K.[14] Most interestingly these reversing melting crystallization processes show a serious frequency dependency. Basically two processes are considered to be responsible for the reversible melting. Surface melting as discussed in detail by Strobl *et al.*[15] which requires some mobility inside the polymer crystal. For polymers not showing such mobility inside the crystals some detachment attachment process as discussed by Wunderlich[16] and us[17] may be responsible. Because this effect exhibits a strong frequency dependency there is, as in the case of glass transition, a need to broaden the frequency window available for heat capacity measurements. If we want to study melting this is a promising task because we are dealing with systems which dramatically change thermal conductivity and thermal contacts during the phase transition. The broadest frequency range available for calorimetric measurements is provided by the 3ω-method which is discussed in detail in this issue. Another approach is that of photo-acoustic detection and related techniques as discussed by Thoen *et al.*[18] But unfortunately all these methods measure a combination of heat capacity and thermal conductivity. To get true heat capacity often knowledge about thermal conductivity is needed. I would not like to go into details here but this is one of the promising questions around high frequency heat capacity measurements.

Frequency dependence of heat capacity and its interpretation is one of the still open questions in calorimetry. But also in regions where heat capacity is not frequency dependent one can obtain very useful information. As an example I would like to mention the opportunity to measure base line heat capacity in the melting or crystallization range of polymers. Following the definition of base line heat capacity given by Mathot,[19] base line heat capacity is related to the heat needed to change the temperature of a sample without changing the phase distribution (absence of all latent heats). As shown[20] it seems to be possible to measure base line heat capacity of polymers at the high frequency limit. The "high frequency" much depends on the sample under investigation. For polycarbonate or polyhydroxybuterate, as an example, we were able to measure baseline heat capacity by TMDSC and to obtain information about vitrification and devitrification of the fraction of the polymers which is detected as rigid amorphous at the glass transition. I mention this to demonstrate that frequency dependent heat capacity measurements provide not only information about the glass transition, the dynamics of melting, crystallization and reversible melting but also very interesting information in the limits of high and low frequencies.

Concluding, my message to the readers of this special issue of Netsu-Sokutei is to make use of the surprising possibilities of periodic temperature calorimetry as much as possible and appropriate. But one has always to take care for the prerequisite of the data treatment, namely linearity and stationarity, as well as the possible frequency dependence of heat capacity during complex transitions like glass transition and melting.

Best regards,
Christoph

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Dear Christoph

Many thanks for your contribution to this special issue. I agree to the concluding remark that one should pay attention to both the surprising possibility and importance of linearity and stationarity. I presume that only a small portion of the "surprising possibility" of the periodic heating method has been utilized. Every researcher has a chance to open a new field of application. Since the way to interpret the experimental results has not been established particularly in such new fields, it will be very important to make detailed discussion with other researchers. Linearity and stationarity should always be checked. I expect that Lähnwitzseminar will provide an opportunity for such discussion in future as it has done up to now. I wish to be there again.

Thank you very much again for your kind collaboration.

Best regards,
Yasuo

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要　旨

Rostock大学のSchick教授と猿山の間で，周期加熱法についての意見交換を，e-mailによって行った。Schick教授は周期加熱法による研究を活発に行ってこられ，この分野での指導的な研究会となっているLähnwitzseminarの世話人を長年にわたって務めてこられた方である。この特集のテーマについて意見をうかがうには最もふさわしい方である。この意見交換を楽しんで読んでいただければ幸いである。

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