AC CALORIMETRY AT THE FIRST ORDER PHASE TRANSITION POINT

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A model is proposed for AC calorimetry (ACC) at the first order phase transition point. The model is compared with the results of ACC around the melting point of an n-paraffin ($C_{20}H_{42}$). The observed frequency dependence of ACC is consistent with the model. A harmonic component of the temperature modulation with a frequency equal to twice the heating frequency was observed at the phase transition point. It is shown that the harmonic component can be explained on the basis of the proposed model.

Keywords: AC calorimetry, first order phase transition, melting point of n-paraffin

Introduction

It has been known that the results of AC calorimetry (ACC) the first order phase transition point are essentially different from the results of DSC or those of adiabatic calorimetry. Two distinctive features of ACC have been pointed out. The first is that the latent heat accompanying the first order phase transition is excluded from the results of ACC [1, 2]. The second is that a phase shift of the temperature modulation is observed in the temperature range of coexistence of two phases [3, 4]. However, the origins of these features have not been studied in detail. In this report a model is proposed for ACC at the first order phase transition point to explain the exclusion of the latent heat and the phase shift. The model is compared with the results of ACC around the melting point of n-eicosane ($C_{20}H_{42}$).

Model

Figure 1 shows the basic idea of our model. Suppose that a sample is at the phase transition point and the low temperature phase and the high temperature phase are coexisting. A flash of light is incident to the sample at the time $t = 0$.

The total heat Q absorbed by the sample steps up as shown in Fig. 1(a). The fraction of the high temperature phase increases corresponding to the heat absorption. Since the phase transition often occurs slowly the delay of reaching the equilibrium after the incidence of the flash of light must be taken into account. The time dependence of the fraction x of the high temperature phase is schematically shown in Fig. 1(b). In this paper the polycrystalline sample is considered. Since the sample is composed of a large number of small regions of the low temperature phase and the high temperature phase, the phase transition takes place simultaneously at many points in the sample. Although the time dependence of the progress of the phase transition is different from point to point because of thermal fluctuation, the observed $x(t)$ is the average and characteristic of the material. The temperature T of the sample changes with time as shown in Fig. 1(c) where T is the temperature of the sample cell. Just after the incidence of the flash of light the temperature jumps up since the phase transition has not occurred yet and the absorbed heat has not been consumed as the latent heat. The low temperature phase is superheated. As the phase transition progresses the temperature becomes lower since the absorbed heat is progressively consumed as the latent heat.
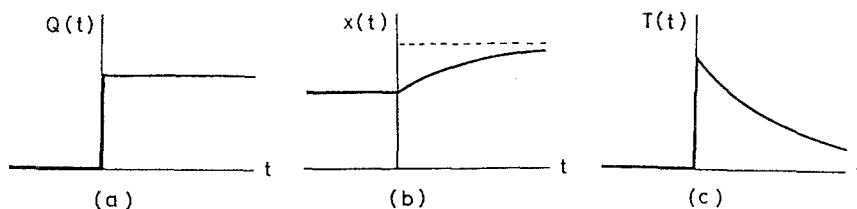

Fig. 1 Schematic drawings of the time dependence of (a) the heat adsorbed by the sample, (b) the fraction of the high temperature phase and (c) the temperature of the sample

Figure 1 suggests that if Q(t) of Fig. 1(a) and $T(t)$ of Fig. 1(c) are taken as the stimulus and the response, respectively, the formulation of the relaxation theory can be applied to ACC at the first order phase transition point.

Assuming a linear relationship between Q(t) and $T(t)$ the response to periodic heating is given by the following Boltzmann's equation of superposition:

$$T(t) = \int_{-\infty}^{t} L_t(t - t')J(t')\, dt' \qquad (1)$$

where L_t is the time response function of the material shown in Fig. 1(c) and J is the heat flow to the sample given by dQ/dt. The Fourier component of $T(t)$ written as T_{ac} is given by

$$T_{ac}(\omega) = \frac{1}{i\omega} L_f(\omega) J_{ac}(\omega) \qquad (2)$$

where ω and J_{ac} are the angular frequency of heating and the Fourier component of J, respectively. L_f is the frequency response function given by

$$L_f(\omega) = i\omega \int_0^\infty L_t(t) \exp(-i\omega t)\, dt .$$ (3)

Similarly to the mechanical or the dielectric frequency response function L_f must satisfy the requirement of the causality and the second law of thermodynamics. They require that L_{fe} given by $L_f(\omega \rightarrow 0)$ is smaller than L_{fg} given by $L_f(\omega \rightarrow \infty)$. The values of L_{fe} and L_{fg} are real and positive numbers. L_{fe} is equal to the inverse of the apparent heat capacity containing the contribution of the latent heat; the apparent heat capacity can be measured by DSC or adiabatic calorimetry. L_{fg} is equal to the inverse of the true heat capacity excluding the contribution of the latent heat. Furthermore, the causality and the second law of thermodynamics require that the imaginary part of L_f is positive. This means that the phase shift of T_{ac} is in the positive direction.

The ω dependence of L_f is explained as follows. If ω is much smaller than the rate of the phase transition the system can stay almost in equilibrium and the results of ACC contain a large contribution of the latent heat. In this case the amplitude of the temperature modulation is small. As ω becomes larger and compatible with the rate of the phase transition, the system falls out of equilibrium because of the delay of the phase transition. The amplitude of the temperature modulation becomes larger because of the decrease of the contribution of the latent heat. The delay of the phase transition makes the phase of the temperature modulation shift to the positive direction. If ω is much larger than the rate of the phase transition, the contribution of the latent heat becomes negligible. The amplitude of the temperature modulation reaches a maximum and the phase shift tends to zero. Thus both of the two features of ACC at the first order phase transition point, the exclusion of the latent heat and the existence of the phase shift, are explained. In Ref. [1] the exclusion of the latent heat is attributed to the unstable nature of the endothermic and the exothermic process at the first order phase transition point. According to the present model the exclusion of the latent heat is attributed to the delay of the phase transition and complete exclusion occurs only in the case of large ω.

The formulation of the present model is equivalent to that of used by Birge [5] to apply ACC to the study of the relaxation phenomena in the temperature range near the glass transition. Similar formulation can be used to apply ACC to studies of the slow dynamics of pretransition phenomena, critical phenomena, phase separation and so on.

Experimental

The sample used in this work is n-eicosane (Nakarai Tesque, Inc.). The ACC equipment made in our laboratory was used. The sample was held between two polymer films of 6 μm thickness in order to keep the shape of the sample in the liquid state. The thickness of the sample was 12 μm. Copper-constantan thermocouple was formed on one of the polymer films by vacuum evaporation technique as the detector of the temperature modulation [6]. The thermocouple was at the lower surface of the stack of the polymer films and the sample and the light is incident to the upper surface.

The average temperature of the sample over one period of heating was changed steadily at a rate of 0.5 deg/min from 285 K up to 320 K then down to the starting temperature. The scanned temperature range contains the melting point of n-eicosane. Such a heating and cooling cycle was repeated a few times before measurement to confirm reproducibility. The heating frequency was 2.5 Hz, 5 Hz, 10 Hz, 20 Hz, 40 Hz and 80 Hz. Uniformity of temperature within the sample was confirmed both in the solid state and in the liquid state by the observation that the amplitude of the temperature modulation is proportional to the inverse of the heating frequency. At the phase transition point the uniformity of temperature cannot be directly confirmed by the above method because of the dependence of L_f on ω. However, the fact that the product of ω and the amplitude of the temperature modulation increases with increasing ω as shown in the next section suggests that the uniformity of temperature is not broken down at the phase transition point.

Results and discussion

Figures from 2(a) to 2(f) show the temperature dependence of the absolute value (the upper curves) and the phase (the lower curves) of T_{ac}. The heating frequency increases from (a) to (f). The upper curves show the product of the absolute value of T_{ac} and the heating frequency. The absolute value has a valley at the temperature range of the phase transition. The rather broad distribution of the phase transition point is due to the impurity in the sample. It can be clearly seen that comparing the absolute values at a fixed temperature in the range of the phase transition the absolute value becomes larger as the heating frequencies increases. This is consistent with our model. The lower curves show that there is a phase shift in the positive direction in the temperature range of the phase transition. This is consistent with our model, too. The phase shift becomes smaller as the frequency increases. This shows that the heating frequencies are rather large and the phase shift is tending to zero. However, since the lower curve in Fig. 2(f) still has a small peak, 80 Hz is not large enough to exclude completely the latent heat.
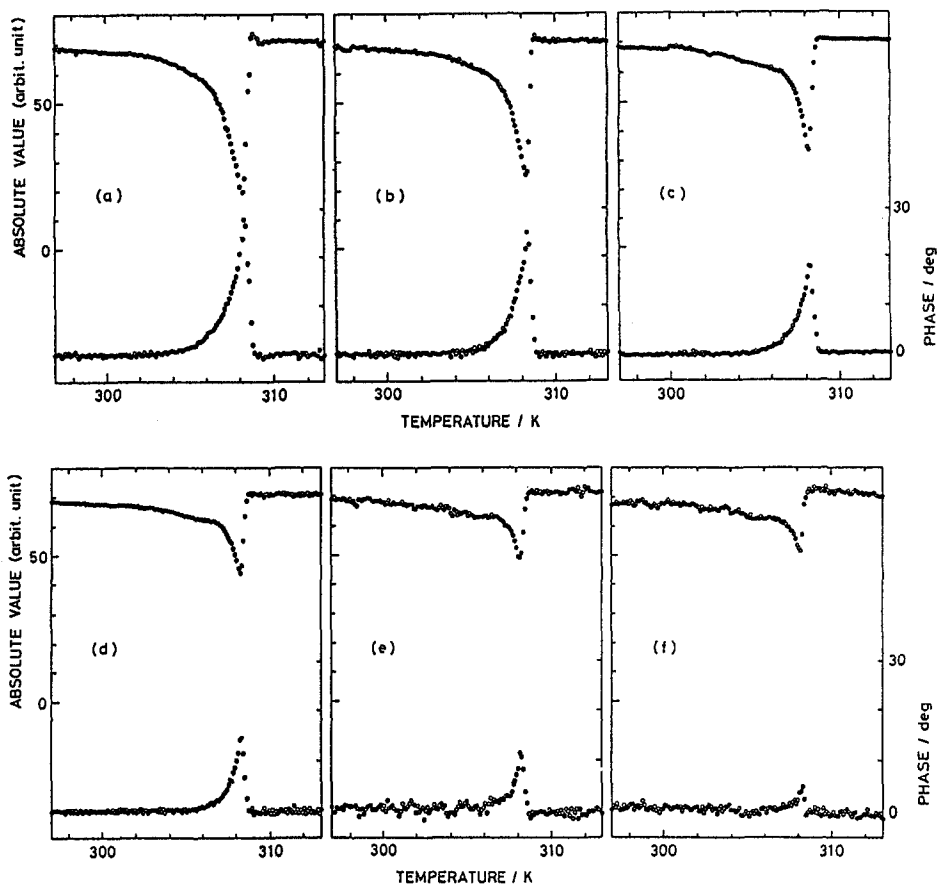
Fig. 2 Temperature dependence of the absolute value (upper curves) and the phase (lower curves) of T_{ac}. Heating frequency: (a) 2.5 Hz, (b) 5 Hz, (c) 10 Hz, (d) 20 Hz, (e) 40 Hz and (f) 80 Hz

It was found that there is a small harmonic component of the temperature modulation for a frequency equal to twice the heating frequency. Figure 3 shows the absolute value of the 20 Hz component of the temperature modulation for 10 Hz heating. The heat flow to the sample does not contain 20 Hz component as can be seen from Fig. 3 in which the 20 Hz component of the temperature modulation is almost zero outside the temperature range of the phase transition. The 20 Hz component exists only in the temperature range of the phase transition. If the observed 20 Hz component were due to the 20 Hz component of the heating, the observed 20 Hz component would, similarly to Fig. 2, have a large value outside the temperature range of the phase transition and a minimum in the

temperature range of the phase transition. Thus the 20 Hz component should be attributed to the phase transition.
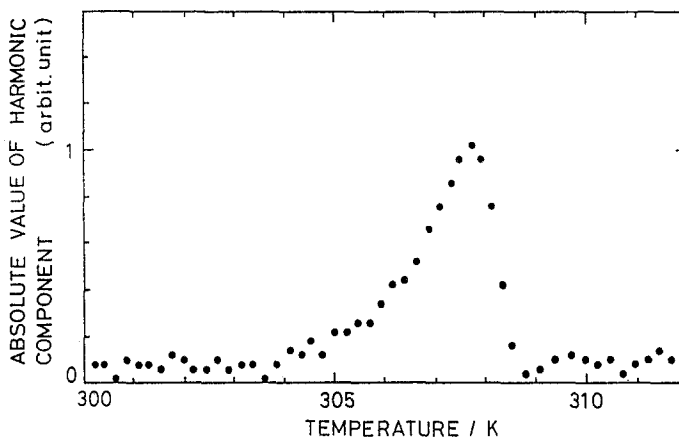

Fig. 3 Absolute value of the harmonic component of the temperature modulation. The frequency of the harmonic component is 20 Hz and the heating frequency is 10 Hz

The outline of a possible extension of our model to explain the 20 Hz component is as follows. The heat flow to the sample is composed of two parts; one is the incidence of the chopped light and the other is the steady flow from the sample to the sample cell. Since the average of the total heat flow over one period of heating is zero, the total heat flow, written as J in Eq. (1), becomes positive and negative alternately. At the moment of positive J the response function L_t in Eq. (1) corresponds to melting. On the other hand at the moment of negative J L_t corresponds to crystallization. It is conceivable to assume an asymmetric response which means that the time response function for melting is different from the time response function for crystallization. In that case L_t in Eq. (1) depends on the sign of J and $T(t)$ is not linear with respect to $J(t)$. The 20 Hz component can be attributed to the non-linear relationship between $T(t)$ and $J(t)$.

Conclusions

A model was proposed for ACC at the first order phase transition point. The model can explain the exclusion of the latent heat from the ACC data and the phase shift at the phase transition point. The results of ACC for n-eicosane are consistent with the model. The existence of a harmonic component of the temperature modulation was found. Asymmetric response was proposed to explain the harmonic component. Detailed studies of the harmonic component will be reported elsewhere.

References

1 I. Hatta and A. J. Ikushima, Jpn. J. Appl. Phys., 20 (1981) 1995.
2 M. Futatsugi, T. Fukuzono and Y. Saruyama, Polymer Comm., 30 (1989) 22.
3 G. B. Kasting, K. J. Lushington and C. W. Garland, Phys. Rev., B22 (1980) 321.
4 K. J. Lushington, G. B. Kasting and C. W. Garland, J. Phys. Lett., 41 (1980) L419.
5 N. O. Birge, Phys. Rev., B34 (1986) 1631.
6 Y. Haikawa and Y. Saruyama, Netsu Sokutei, 18 (1991) 170. (in Japanese)

Zusammenfassung — Es wird ein Modell für die AC-Kalorimetrie (ACC) von Phasenumwandlungen erster Ordnung vorgeschlagen. Das Modell wird mit den Ergebnissen von ACC in Nähe des Schmelzpunktes des n-Paraffins $C_{20}H_{42}$ verglichen. Die beobachtete Frequenzabhängigkeit von ACC stimmt mit dem Modell überein. Im Phasenumwandlungspunkt kann eine harmonische Komponente der Temperaturmodulation mit einer Frequenz festgestellt werden, die doppelt so hoch wie die Heizfrequenz ist. Es wird gezeigt, daß die harmonische Komponente anhand des vorgeschlagenen Modelles erklärt werden kann.