

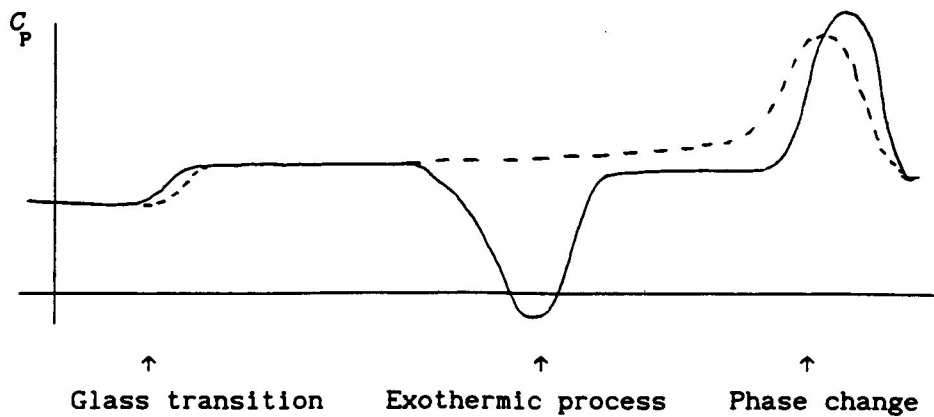
1. Introduction

A sample of material under investigation is subject to a controlled temperature within a furnace. The temperature is arranged to be an increasing ramp (as in conventional scanning calorimetry) plus a sinusoidal modulation:  $T = T_0 + bt + \beta \sin \omega t$ . The range of heating,  $\dot{Q}$ , is measured. The aim is to determine physical properties, or get a picture of what may be happening within the sample, by comparing the rate of change of temperature,  $\dot{T}$ , with  $\dot{Q}$ .

For a simple linear material heat content =  $Q C_p T$  where  $C_p$  is the (constant) specific heat. For a pure ramp ( $B = 0$  for normal calorimetry)  $\dot{T} = b$  and  $\dot{Q} = bC_p$  so  $C_p = \dot{Q}/\dot{T}$ . For the same material, assuming effectively no thermal lag in either the calorimeter or the sample,  $\dot{T} = b + \omega \beta \cos \omega t$  and  $\dot{Q} = C_p b + \omega B C_p \cos \omega t$  with the modulation. For both  $\dot{T}$  and  $\dot{Q}$  there are underlying measurements:  $b$  and  $C_p b$  respectively (these may be thought of as some "local" average); and cyclic measurements:  $B\omega \cos \omega t$  and  $C_p B \omega \cos \omega t$  respectively. The ratio of the underlying measurements gives the "underlying  $C_p$ " while the ratio of the amplitudes of the cyclic parts give the "cyclic  $C_p$ ". In general the cyclic measurements of temperature rise and heat input rates are given by the first terms in local Fourier series. The cyclic  $C_p$  is the ratio of the amplitudes of these first terms. Any phase difference may give extra information. In this special case both these " $C_p$ 's" will be the same value, namely the real specific heat.

This is a very idealized situation and in practice the specific heat generally depends upon temperature, exothermic processes will occur, and these might be phase changes. All these effects happen within the sample, additionally the measurements are not quite as straightforward as suggested. For a material of interest, polyethylene terephthalate (PET), both the underlying and cyclic  $C_p$ 's change during the experiment and, at times differ significantly from each other, see fig. 1 where they are sketched against temperature.

Figure 1  $C_p$ 's as a function of temperature



The key features shown by these graphs are:

- (i) The values are initially nearly constant and are very close to each other.
- (ii) Around the glass transition  $C_p$  increases and the cyclic value is somewhat below the underlying one.
- (iii) The values are again nearly constant and close.
- (iv) The exothermic process is shown as a large dip in the underlying (apparent)  $C_p$ , in this case it goes negative, but does not exhibit itself in the cyclic measurement.
- (v) The underlying measurement is roughly constant while the cyclic  $C_p$  is significantly larger and gradually rises. It was suggested that this was due to some type of crystal rearrangement effected by the oscillation of temperature in the vicinity of the phase changes.
- (vi) The phase change is smeared out due to different melting points for different sized crystals. Rather than have a delta function for  $C_p$  (size = latent heat) there is instead a large bump. The cyclic measurement peaks a little earlier and lower than the underlying one.
- (vii) Again the values are close to each other. They are similar to that of (iii) and the underlying  $C_p$  of (v).

We shall first discuss the calorimeter in a little more detail to find the implications of the actual measurements made. We shall then examine some simple models for the material, under the original assumption of specified sample temperature to try to find out what sort of physical effects give rise to observed experimental results. Finally we show the outcome of some numerical calculations done for an ad hoc model for a changing distribution of types of crystals.

To get an accurate quantitative representation of the experiment it will eventually be necessary to combine different approaches so both the internal structure and the calorimeter are considered fully.

## 2. Experimental procedure

Analysis of the experimental output is easiest if we can make the assumptions that the sample temperature is controlled to be a linear ramp plus sinusoidal oscillation and that the measured lower input,  $\dot{Q}$ , is the rate of heating of the sample. In practice this is difficult to carry out especially when either a phase transition or an exothermic reaction occurs. For the former it becomes difficult to change the temperature while the latter prompts a sudden increase in temperature.

Here we discuss the implications of a different method of control. The sample is contained in a crucible within the furnace and a second, identical but empty, crucible acts as a reference. The power supplied to the sample and its crucible is  $k_F(T_F - T_S) + k_C(T_R - T_S)$  while that supplied to the reference crucible is  $k_F(T_F - T_R) + k_C(T_S - T_R)$ , the first term in each case is the heat supply from the furnace into the crucible while the second terms are the rates of heat transfer directly between the crucibles. Here  $k_F$  and  $k_C$  are heat transfer coefficients while  $T_F, T_S$  and  $T_R$  are the temperatures of the furnace, sample (and its crucible), and the reference respectively.

Absorbing mass into specific heat we then have

$$(C_c + C_s)\dot{T}_s = k_f(T_f - T_s) + k_c(T_r - T_s) + f$$

$$C_c\dot{T}_r = k_f(T_f - T_r) + k_c(T_s - T_r)$$

where  $C_c$  is the specific heat of each crucible and  $C_s$  is that of the sample, also  $f$  represents the rate of heat production in the sample due to some internal process ( $f > 0$  for an exotherm,  $f < 0$  for an endotherm).

Writing  $\dot{Q} = k(T_r - T_s)$ , where  $k = k_f + 2k_c$ ,  $\dot{Q}$  is a measure of power supply and satisfies  $\lambda\dot{Q} + \dot{Q} = C_s\dot{T}_r - f$ . Here the time constant  $\lambda$  is given by  $(C_c + C_s)/k$ . The constant  $k$  is determined during calibration of the calorimeter using a sample with known, simple properties. (If  $k_f$  is "large" then to leading order  $T_f$ ,  $T_r$ , and  $T_s$  are all the same and  $\dot{Q}$  is the rate of heat supply from the furnace to the sample. Also for  $k_c = 0$ , that is, no direct interaction between the two crucibles,  $k = k_f$  and a linear ramp with oscillation of the reference temperature is equivalent to a linear ramp with oscillation of the furnace temperature, with different phase and amplitude.)

The furnace is now controlled so that  $T_r = bt + B\sin \omega t$  while  $\dot{Q}$  is measured and is taken to be of the form  $\bar{Q} + \tilde{Q}_0 \cos(\omega t - \delta)$ . The underlying  $C_p$  is  $\tilde{C} = \tilde{Q}_0/\omega B$  ( $\omega B =$  amplitude of the cyclic part of  $T_r$ ).

Three points should be stressed:

(i) For nonlinear materials  $\tilde{Q}$  may be written as a Fourier series

$$\tilde{Q} = \sum_{n=1}^{\infty} (\alpha_n \cos(\omega t) + \beta_n \sin(\omega t)) \quad \text{and} \quad \tilde{Q}_0 = \sqrt{\alpha_1^2 + \beta_1^2}$$

(ii) For these definitions to make sense  $\omega$  must be large enough for the period of oscillation must be small compared to any time scale over which properties of the sample change :  $\frac{b}{\omega\psi} \frac{d\psi}{dT} \ll 1$  for any  $\psi$  describing some property (e.g.  $C_s$ ).

(iii) These definitions of  $C_p$  use variation of the reference temperature not the sample temperature.

The simplest possible situation is again where specific heat is constant and no reactions or phase changes occur so  $f \equiv 0$ . After any transient decays the solution to  $\lambda \ddot{Q} + \dot{Q} = C_s(b + B\omega \cos \omega t)$  is

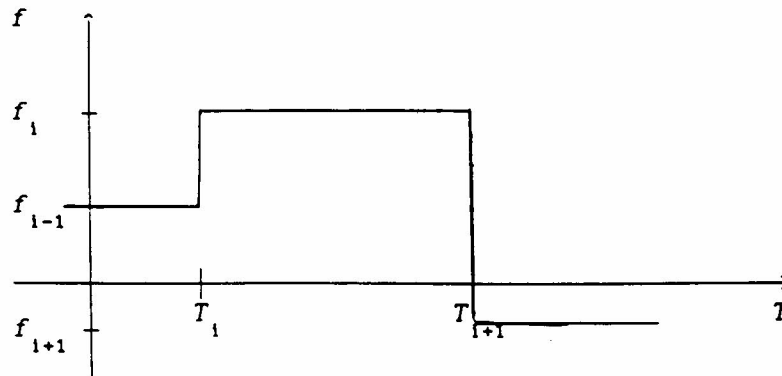
$$\dot{Q} = bC_s + C_s B \omega (\cos \omega t + \lambda \omega \sin \omega t) / (1 + \lambda^2 \omega^2)$$

so  $\bar{Q} = C_s b$  and  $\tilde{Q} = C_s B \omega \cos(\omega t - \delta) / \sqrt{1 + \lambda^2 \omega^2}$  with  $\delta = \tan^{-1}(\lambda \omega)$ . Thus  $\bar{C} = C_s$  and  $\tilde{C} = C_s / \sqrt{1 + \lambda^2 \omega^2}$  the phase lag is  $\tan^{-1}(\lambda \omega)$ . ( $\lambda \omega$  is small and  $\tilde{C} \approx C_s$  for  $\omega \lesssim 1 \text{ min}^{-1}$ .)

Now consider the possibility of  $f \neq 0$  but, for simplicity, a step function of temperature :  $f = f(T_s)$ , constant except at some value(s)  $T_c$  at which it jumps. We still assume that  $C_s = \text{constant}$ .

Now  $\lambda \ddot{Q} + \dot{Q} = C_s \dot{T}_R - f(T_R - \dot{Q}/k)$  (recalling that  $\dot{Q} = k(T_R - T_s)$ ). First suppose that  $B = 0$  so that reference temperature is a pure ramp :  $T_R = bt$ . Take  $f(T) = f_1$  for  $T_1 < T < T_{1+1}$ , see fig. 2.

Figure 2. Reaction rate = step function of temperature



While  $T_S < T_1$ ,  $f = f_{i-1}$ , and assuming an absence of transients,  $\dot{Q} = C_S b - f_{i-1}$  and  $T_S = T_R - \dot{Q}/k = T_R - C_S b/k + f_{i-1}/k$ .  $T_S$  reaches the critical  $T_1$  when  $T_R = T_1 + C_S b/k - f_{i-1}/k$  (again note that for  $k$  large  $T_R \approx T_S$ ).

We have two cases to consider.

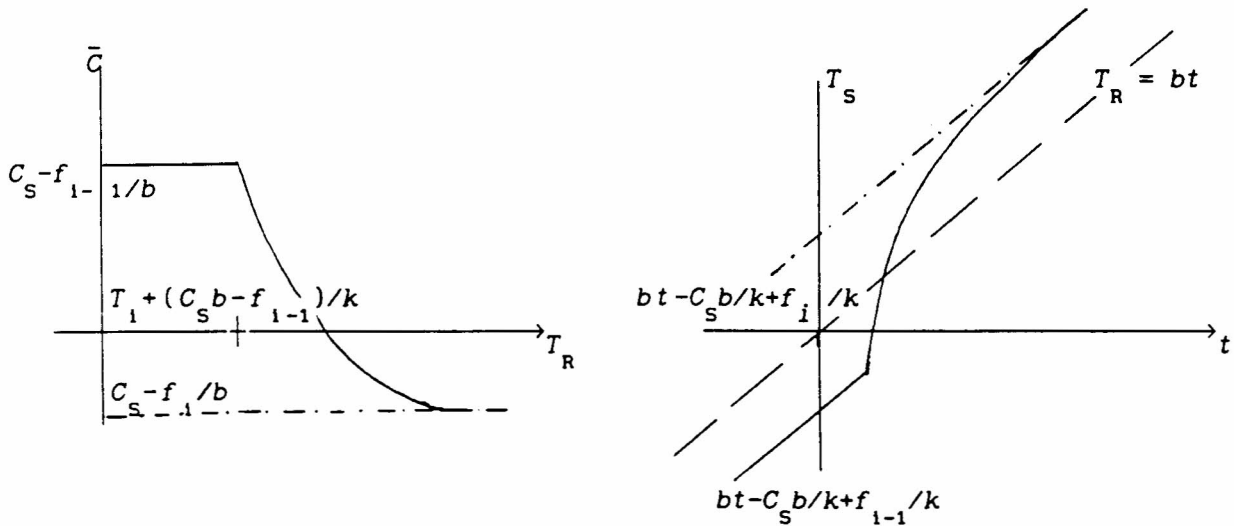
- (1)  $f_1 > f_{i-1}$ , which corresponds to an exothermic reaction switching on ( $f_{i-1} = 0 < f_1$ ) or an endothermic process switching off ( $f_{i-1} < 0 = f_1$ ),

There follows a transient regime, over a time scale of  $O(\lambda)$ , during which  $\dot{Q}$  approaches a new constant value.

$$\dot{Q} = (C_S b - f_1) + (f_1 - f_{i-1}) \exp [-\lambda(T_R - T_1 + C_S b/k - f_{i-1}/k)/b].$$

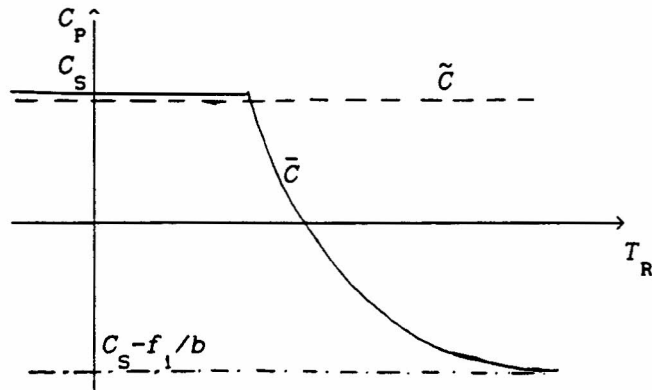
Thus  $\bar{C} = \dot{Q}/b$  decreases from  $C_S - f_{i-1}$  to  $C_S - f_1/b$  with exponential approach at rate  $\lambda/b$ , as a function of temperature ( $T_R$ ). See fig. 3 for a plot of  $\bar{C}$  against  $T_R$  and a plot of sample temperature against time.

Figure 3



Now introducing a small sinusoidal perturbation to  $T_R$ , the problem for  $\dot{Q}$  is linear, except at  $T_S = T_1$ , so, away from  $T_R \approx T_1 + (C_S b - f_{1-1})/k$ , the cyclic response is the same as before and  $\tilde{C} \approx C_S$  (assuming that  $\lambda\omega \ll 1$ ). The two  $C_p$ 's are shown in fig 4 (taking  $f_{1-1} = 0 < f_1$ ).

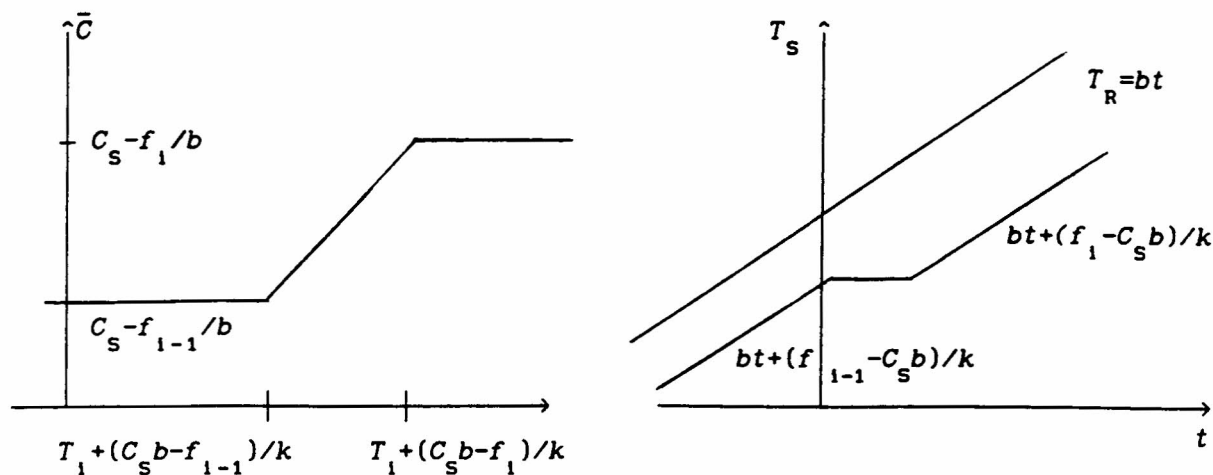
Figure 4. Onset of an exothermic reaction,  $0 = f_{1-1} < f_1$ .



(2)  $f_{1-1} > f_1$ , which corresponds to exothermic reaction switching off ( $f_{1-1} > 0 = f_1$ ) or an endothermic reaction switching on ( $f_{1-1} = 0 > f_1$ ).

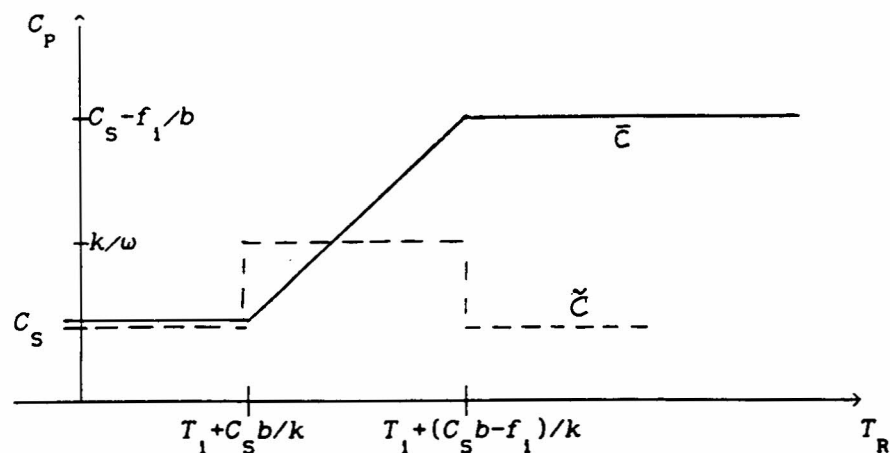
This time  $T_S$  is held fixed at  $T_1$  as the system moves from the first ramp  $T_S = bt - (C_S b - f_{1-1})/k$  to the lower, second one  $T_S = bt - (C_S b - f_1)/k$ , as the rate of heat supply,  $\dot{Q} = k(T_R - T_S)$ , increases from  $C_S b - f_{1-1}$  to  $C_S b - f_1$ . Consequently  $\bar{C}$  increases with slope  $k/b$  from  $C_S - f_{1-1}/b$  to  $C_S - f_1/b$ , see fig. 5.

Figure 5



Where  $\dot{Q}$  (and  $\bar{C}$ ) is constant the problem is linear and putting the oscillation back in again gives  $\tilde{C} \approx C_S$ . For  $T_R$  between  $T_1 + (C_S b - f_{1-1})/k$  and  $T_1 + (C_S b - f_1)/k$ , however,  $T_S$  is fixed at  $T_1$  so  $\tilde{Q} = kB \sin \omega t$  and  $\tilde{C} = k/\omega$ ; see fig. 6 (where we take  $f_{1-1} = 0 > f_1$ ).

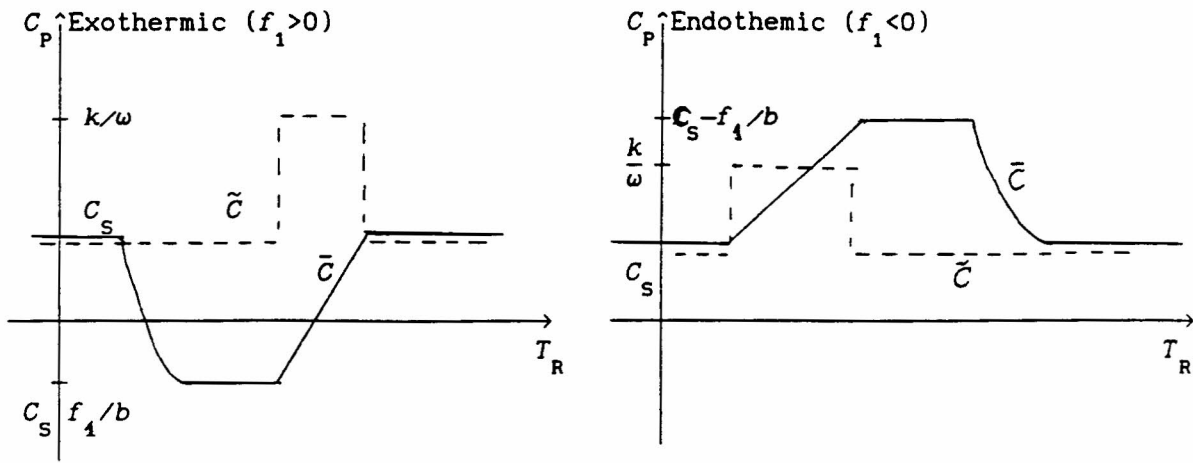
Figure 6. Onset of an endothermic reaction,  $0 = f_{1-1} > f_1$





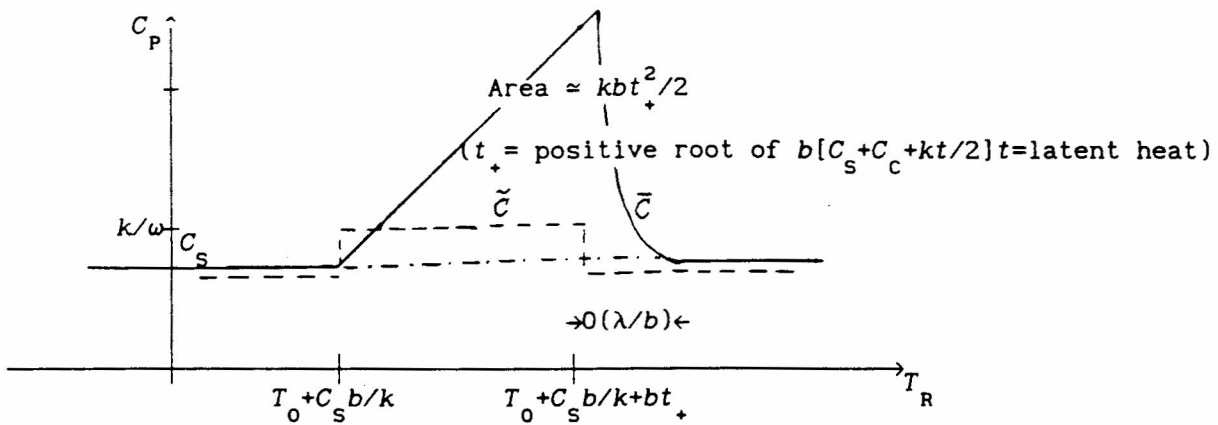
Combining two of these effects we get, for a reaction effective between  $T_1$  and  $T_2$ ,  $C_p$ 's of the form shown in fig. 7.

Figure 7



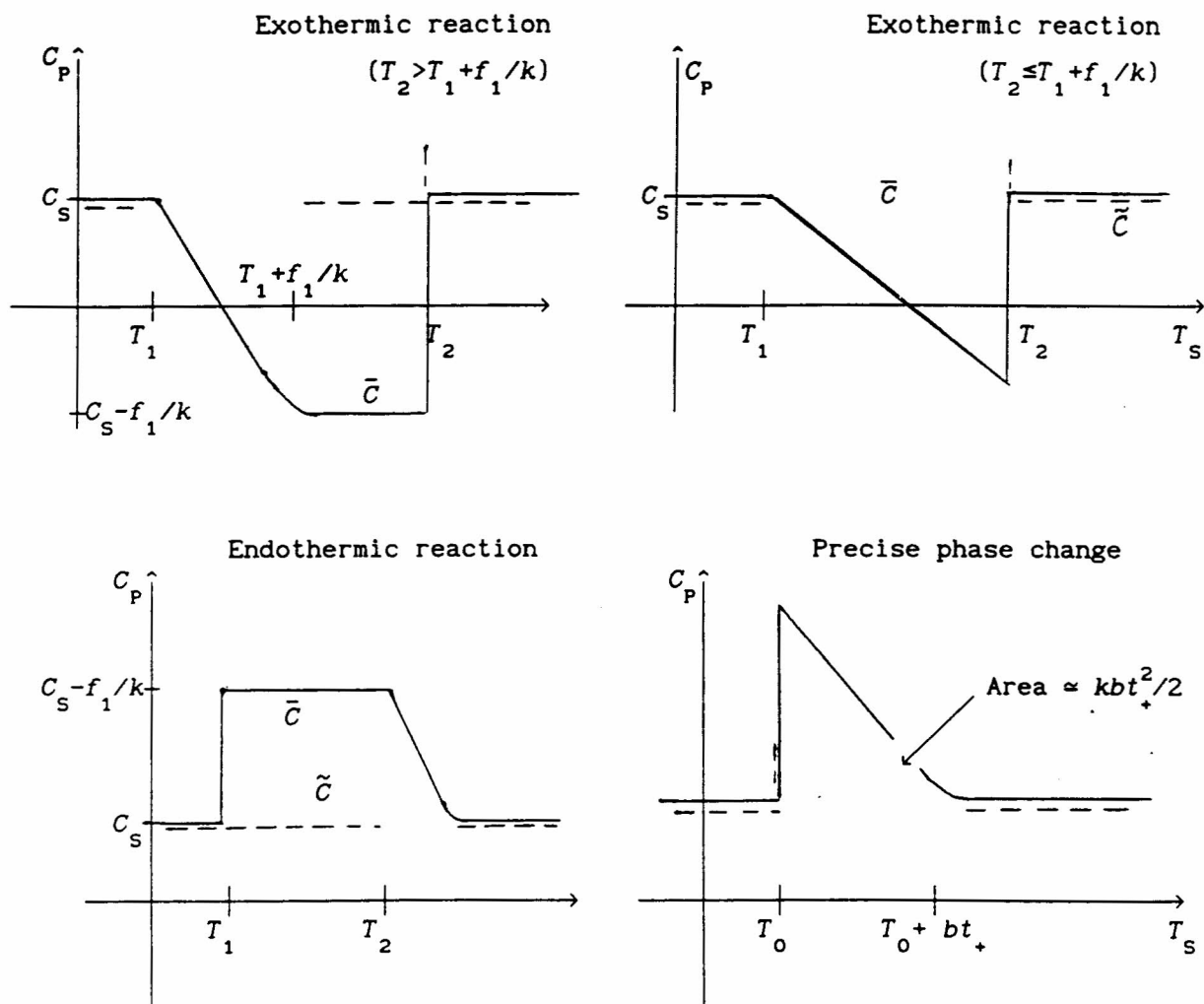
We also note that while an endothermic reaction is taking effect  $T_s$  is held fixed. This is precisely the effect of a phase change taking place at a precise temperature  $T_0$ : a phase change may be regarded as equivalent to an endothermic reaction taking place only at  $T_0$ . Thus a simple phase change could be envisaged as a limiting endothermic process and the  $C_p$ 's then appear as in fig. 8.

Figure 8.  $C_p$ 's for phase changes at  $T_s = T_0$  (taking  $\lambda$  to be small)



The results may be also presented by plotting  $C_p$  against  $T_s$ , which can be recovered from  $T_s = T_R - \dot{Q}/k$ , see fig. 9.

Figure 9. Plots of  $C_p$ 's against sample temperature.



Note that where an exothermic reaction switches off or an exothermic reaction switches on  $T_s$  changes rapidly, over a time scale of  $O(\lambda)$ , during which time  $T_R$  changes little (if  $b\lambda$  is "small") and so  $\bar{C}$  decreases with slope  $k/b$ . If  $\lambda\omega \ll 1$  this takes place over a small part of a cycle so the value of  $\bar{C}$  is unclear.

The case of no reaction ( $f \equiv 0$ ) but with varying  $C_S$  can be approached analytically for some limiting cases as in the next section.

### 3. Results from specified $T_s$

From now on attention is mainly focussed on the case of having  $T_s = T = bt + B\sin\omega t$  with  $\dot{Q}$  the power input to the sample.

To start with consider a material with variable specific heat,  $C_s = C_s(T)$ , which undergoes no reaction, phase changes etc. Then  $\dot{Q} = C_s(T)\dot{T}$  and  $\dot{T} = b + B\omega\cos\omega t$ .

Taking  $B$  to be small (in the sense that any important quantity changes by a relatively small amount during a period of the cycles; regarding specific heat:  $BC'_s \ll C_s$ ),  $C_s(bt + B\sin\omega t) = C_s(bt) + BC'_s(bt)\sin\omega t + \dots$ ,  
 $\dot{Q} = bC_s + B(C'_s\omega\cos\omega t + C'_sb\sin\omega t) + \dots$  giving  $\bar{Q} \approx bC_s$ ,  $\tilde{Q} \approx B\sqrt{C_s^2\omega^2 + b^2C_s^2}$   
 $\cos[\omega t - \tan^{-1}(C'_sb/C_s\omega)]$  and  $\bar{C} \approx C_s$ ,  $\tilde{C} \approx C_s\sqrt{1 + (bC'_s/C_s\omega)^2}$ . For a large  $\omega$   
 $(|bC'_s/C_s\omega| \ll 1$  so that there are no significant changes between the start and end of a period)  $\tilde{C} \approx C_s$ . (The frequency  $\omega$  should not be too great otherwise there might be difficulty regarding non-uniform temperatures through the sample or its crucible.) Note that full expressions for  $\bar{Q}$  and  $\tilde{Q}$  (determining Fourier coefficients) indicate that  $\bar{C}$  and  $\tilde{C}$  depend upon even powers of  $B$  and  $\omega$  only.

Now include a reaction term of the simple form  $f(T)$ ,  $\dot{Q} = C_0\dot{T} - f(T)$ . Here  $f > 0$  for an exothermic reaction. The procedure above gives

$$\bar{C} = C_s - f/b, \quad \tilde{C} = C_s\sqrt{1 + [(bC'_s - f')/\omega C_s]^2}$$

with  $\omega$  "large" it is observed that here, as in the previous section,  $\tilde{C}$  gives a good approximation to  $C_s$  during an exothermic process where  $\bar{C}$  deviates significantly (see fig. 1). However the difference between  $\bar{C}$  and  $\tilde{C}$  is the wrong sign for a simple change in  $C_s$  as with the glass transition (again see fig. 1).

The requirement that reaction rate is purely a function of temperature is of course generally unrealistic. It would be more accurate to include at least one state variable, say a concentration  $y$ , in which case, taking first order forward and reverse reactions we get instead:

$$\dot{Q} = C_s \dot{T} + \alpha K [y f_1(T) - (1 - y) f_2(T)], \quad \dot{y} = K [(1 - y) f_2(T) - y f_1(T)].$$

Such a reaction was discussed briefly during the meeting but we only note here that in the limiting case of fast reactions,  $K \gg 1$ ,  $y \approx F(T) \equiv f_2 / (f_1 + f_2)$  and so  $\dot{Q} \approx (C_s + \alpha F') \dot{T}$ , i.e. an effective change of specific heat. (If a second reaction depends upon product concentration  $1 - y$  and  $T$  and proceeds only forwards then we do get an additional term dependent only upon temperature:  $\beta(1 - F(T))f_2(T)$ .)

A major difficulty with these theories is that, so far, nothing accounts for the behaviour  $(v) : \bar{C} \approx \text{constant}$ ,  $\tilde{C}$  lies significantly above (see fig. 1). Including a single variable of state  $y$  does not help as any heat released through change of  $y$  would exhibit itself through a change in  $\bar{C}$  as well as  $\tilde{C}$ . Generalizing to any finite number of variables also seems unlikely to help in this respect - assuming rates depend upon  $T$  and the variables of state. An alternative approach was to consider some type of continuum. For example we may envisage a range of crystals of size (or quality)  $y$  with mass fraction  $c(y, t)$  together with a melt, mass fraction  $1 - s$ ,  $s(t) = \int c(y, t) dy$ . Again trying a simple (and unrealistic) law for conversion between crystal and melt we can propose something of the form :  $c_t = -cf(y, T) + (1 - s)g(y, T)$ , where the first term on the right represents rate of melting of crystals, and the second the rate of their formation. Both are taken to depend upon temperature and type of crystal (and to be independent of amounts of other sizes of crystal). This equation can be "reduced" to the integral equation for the single variable  $s$  on the assumption that  $T(t)$  is specified:

$$s(t) = \int A(y) \exp \left\{ - \int_0^t f(y, T(\tau)) d\tau \right\} dy \\ + \int \left[ \int_0^t \exp \left\{ - \int_{\tau}^t f(y, T(\sigma)) d\sigma \right\} (1 - s(\tau)) g(y, T(\tau)) d\tau dy \right]$$

Here  $A(y)$  is the initial crystal distribution function. The integral equation can be rewritten as

$$s(t) = \Phi_T + \int_0^t K_T(t, \tau)(1 - s(\tau))d\tau,$$

the subscript denoting the importance of the temperature history.

Rather than taking this involved approach further two simpler ideas were considered. One was to suppose that the crystal distribution takes some standard form depending on a few parameters which satisfy some differential equations; this is done in the next section. The other is to introduce a direct memory effect, which the integral equation for  $s$  certainly exhibits, only for  $Q$  or  $T$ ; this is done now.

For an autonomous problem with a linear material (constant physical properties) we propose a model of the form

$$\dot{Q}(t) = C\dot{T} + \lambda \int^t K(t - \tau) \dot{T}(\tau)d\tau$$

(Similar equations appear as models of visco-elastic materials. To determine the kernel  $K(\tau)$  for such materials it is standard practice to compare stress and strain with a sample being forced at different frequencies. This gives the kernel's Fourier transform, from which  $K$  is found.)

Taking the simple form of a decaying exponential for the kernel  $\dot{Q}$  and  $T$  are related by  $\dot{Q}(t) = C\dot{T}(t) + \lambda K \int^t e^{-\lambda(t-\tau)} \dot{T}(\tau)d\tau$  which can be written as

$$C\dot{T} + \lambda(K + C)T = \dot{Q} + \lambda Q$$

where  $Q$  is a measure of the heat content of the sample.

For the ramp plus oscillation of temperature  $T = bt + B\sin\omega t$ ,  $Q \approx Q_0 + at + A\sin(\omega t)$  with

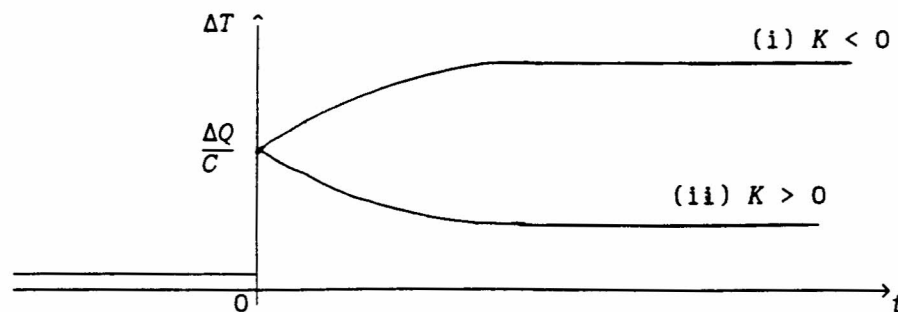
$$a = (K + C)b, \quad A \sqrt{\omega^2 + \lambda^2} = B \sqrt{\omega^2 C^2 + \lambda^2 (K + C)^2}. \quad \text{Then } \bar{C} = a/b = K + C \text{ and}$$

$$\tilde{C} = A/B = \sqrt{[\omega^2 C^2 + \lambda^2 (K + C)^2] / (\omega^2 + \lambda^2)}.$$

The cyclic  $C_p$ ,  $\tilde{C}$ , is a monotonic function of frequency  $\omega$ , for small  $\omega$   $\tilde{C} \approx \bar{C}$ , and  $\tilde{C}$  approaches  $C = \bar{C} - K$  as  $\omega$  gets large.  $\tilde{C}$  is increasing for  $K < 0$  and decreasing for  $K > 0$ .

To try to find a possible interpretation of the differential equation relating  $T$  and  $Q$  we might imagine what happens if an amount of heat  $\Delta Q$  is suddenly, and uniformly, added to the sample, previously in equilibrium. The temperature immediately jumps  $\Delta Q/C$  :  $C$  is the "specific heat" for rapid variations -  $\omega$  is large. The temperature difference then relaxes to  $\Delta Q/(K + C)$  :  $K + C$  is the "specific heat" for relatively slow process -  $\omega$  is small; see fig. 10.

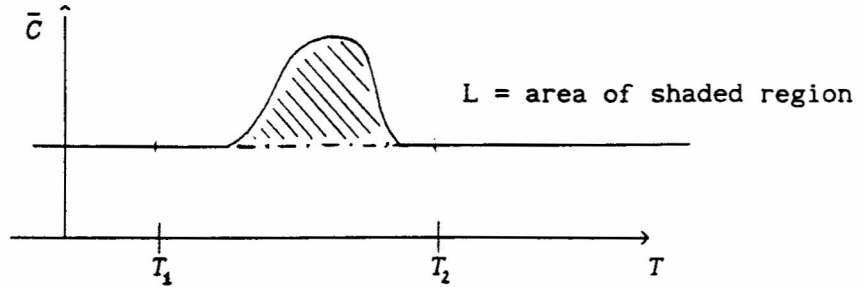
Figure 10. Temperature variation due to an impulsive increase of heat content.



We may interpret this as having a mixture of crystals and melt. Initially melt and crystals are both warmed by  $\Delta Q/C$  :  $C$  would be thought of as a "true" specific heat of the material. As the temperature has changed but the crystal structure of the sample is unaltered it is now out of equilibrium and it gradually changes its structure over a time scale of  $O(1/\lambda)$  to get back into thermal equilibrium. This (i) further increases temperature if  $K < 0$ , but (ii) decreases temperature if  $K > 0$ . These two cases might conceivably correspond to dominance of (i) heat released by change in surface energy as large crystals form at the expense of small crystals (i) heat used in forming melt from crystals. A problem with this scenario is that it would seem likely that the "fast" specific heat,  $C$ , should then stay approximately constant while the "slow" specific heat,  $C + K$  (or  $\bar{C}$ ) should change with temperature. In the experiment (see fig.1) in the region (v) it is the underlying  $C_p, \bar{C}$  (corresponding to small  $\omega$ ), that stays near its earlier (and final) value while the cyclic  $C_p, \tilde{C}$  (corresponding to larger  $\omega$ ) changes.

On a more positive note we can easily obtain the latent heat of melting,  $L$ , from the graph of  $\bar{C}$  against  $T$  (whatever the internal process is) as it is simply the area of the associated "bump", see figure 11.

Figure 11 Bump in the graph of the underlying  $C_p$  due to a phase change.



The total heat added between times  $t_1$  and  $t_2$ , when the sample has temperature  $T_1$ , below first melting point, and  $T_2$ , above final melting point, respectively is

$$\begin{aligned}
 L + C_S(T_2 - T_1) &= \int_{t_1}^{t_2} \dot{Q} dt = \int_{t_1}^{t_2} \bar{Q} dt \quad (\text{since } \bar{Q} \text{ is } \dot{Q} \text{ averaged}) \\
 &= \int_{T_1}^{T_2} \bar{Q} d\bar{T} / \dot{T} \quad (\text{with } \bar{T} \text{ being temperature averaged over a} \\
 \text{period : } \dot{T} &= \text{average of } \dot{T} = b) = \int_{T_1}^{T_2} \bar{C} d\bar{T}.
 \end{aligned}$$

For other ways of controlling the operation of the calorimeter we can again try to obtain results with key assumptions such as  $B$  being "small". This applies to the control of the reference temperature, as in the previous section, but for simplicity we here just briefly look at  $k_c = 0$  so we can assume that the furnace temperature is controlled. Then  $\dot{Q} = k(bt + B\sin\omega t - T) = C_S(T)\dot{T} - f$  ( $T = \text{sample temperature} = T_S$ ,  $k = k_F$ ).

A relatively simple case is again  $f \equiv 0$ . With  $B$  small we can expand  $T$  as a power series in  $B$ :  $T \sim T_0 + BT_1 + \dots$ , then  $C_S(T) \sim C_S(T_0) + BC'_S(T_0)T_1 + \dots$ , giving

$$C_S(T_0)\dot{T}_0 + kT_0 = kbt, \quad C_S(T_0)\dot{T}_1 + (k + C'_S(T_0)\dot{T}_0)T_1 = k\sin\omega t, \dots$$

It is seen that the leading order (underlying) problem is fully nonlinear. However we still have  $\bar{C} = \bar{Q}/\dot{T}_0 = \dot{Q}_0/\dot{T}_0 = k(bt - T_b)/\dot{T}_0 = C_s$ . With suitably large  $\omega$  the first order problem gives the cyclic part:

$$T_1 \sim k[(k + C'_s \dot{T}_0) \sin \omega t - C_s \omega \cos \omega t] / [C_s^2 \omega^2 + (k + C'_s \dot{T}_0)^2],$$

$$\dot{Q}_1 \sim k\{[C_s^2 \omega^2 + (k + C'_s \dot{T}_0)^2] \sin \omega t + k C_s \omega \cos \omega t\} / [C_s^2 \omega^2 + (k + C'_s \dot{T}_0)^2],$$

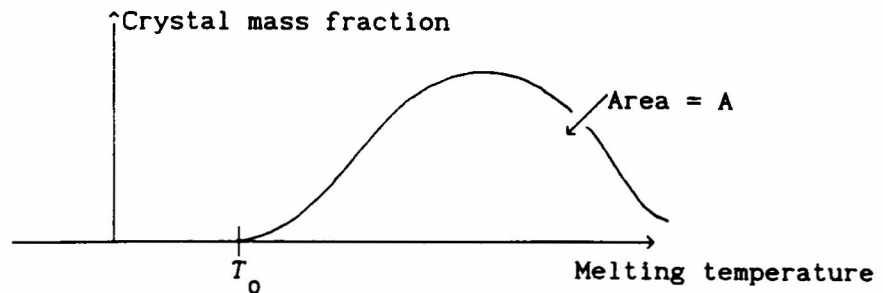
$$\text{and } \tilde{C} \sim \sqrt{\{[C_s^2 \omega^2 + (k + C'_s \dot{T}_0) C'_s \dot{T}_0]^2 + C_s^2 \omega^2 k^2\}} / \sqrt{[(k + C'_s \dot{T}_0)^2 + C_s^2 \omega^2]}.$$

Different values are of course given if we use instead the variation of the controlled (furnace) temperature in the manner of the previous section; e.g.  $\bar{C}(bt) = C_s (T_0) \dot{T}_0 / b$ .

#### 4. Distribution of crystals

Here we make the assumption that the sample contains crystals with a spread of melting temperatures, and that the mass distribution depends upon a small number of parameters. The parameters will include :  $A$  = total mass fraction of crystals;  $T_0$  = lowest melting temperature (see fig. 12); as well as some parameters, say  $\alpha$ , giving for example, the spread of the distribution.

Figure 12 Crystal distribution



As the temperature of the sample increases there is melting but simultaneously more stable (higher melting point) crystals form. This will result in  $T_0$  increasing,  $A$  decreasing and  $\alpha$  changing. These variations should depend upon the rate of temperature change, as well as temperature, to model change in crystal distribution as melting and recrystallization occurs in the presence of an oscillating temperature. There was insufficient time to do



simulations including all the desired effects and terms so we only present here the results from numerically computing pure melting. The equation allows for melting below some critical temperature (last melting temperature)  $T_m$ :

$$\dot{A} = -\gamma A / (T_m - T) \quad T < T_m, \quad A \equiv 0 \quad T \geq T_m.$$

It was again assumed that  $T = bt + B\sin\omega t$  so

$$A = A_0 \exp\{-\gamma \int dt / (T_m - bt - B\sin\omega t)\}.$$

With  $B$  small and  $\omega$  large and rescaling so that  $\gamma / (T_m - bt)$  becomes  $\Gamma / (1 - t)$ ,

$$A \sim A_0 (1 - t)^\Gamma \exp\{-\Gamma B \cos\omega t / \omega (1 - t)^2\},$$

giving an underlying crystal mass fraction  $\bar{A} = A_0 (1 - t)^\Gamma$  with factor due to the cyclic variation  $\exp\{-\Gamma B \cos\omega t / \omega (1 - t)^2\}$ , see fig. 13

The  $C_p$ 's are then given by  $\bar{C} \approx -L\dot{\bar{A}}/b$  and  $\tilde{C} \approx \frac{L}{\omega B}$  x magnitude of the oscillation of  $\dot{A}$ , if we can neglect the contribution from the actual specific heat in comparison with the latent heat. The terms giving the qualitative behaviour of the  $C_p$ 's are

$$\begin{aligned} -\dot{\bar{A}} &= A_0 \Gamma (1 - t)^{\Gamma-1} \quad \text{and} \quad \frac{1}{\omega B} \times \text{maximum over a cycle of } \dot{A} \sim \frac{A_0 (1 - t)^\Gamma}{\omega B} \cdot \frac{\Gamma B}{(1 - t)^2} \\ &= \frac{\Gamma}{\omega} (1 - t)^{\Gamma-2} \quad (\text{for large } \omega), \end{aligned}$$

see fig. 14.

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Figure 13 (a) Full, (b) underlying, and (c) cyclic, mass fraction for  $A_0 = 1$ ,  $\Gamma = 1/20$ ; (i)  $\omega = 200$ ,  $B = 1/200$ ; (ii)  $\omega = 250$ ,  $B = 1/10$ .

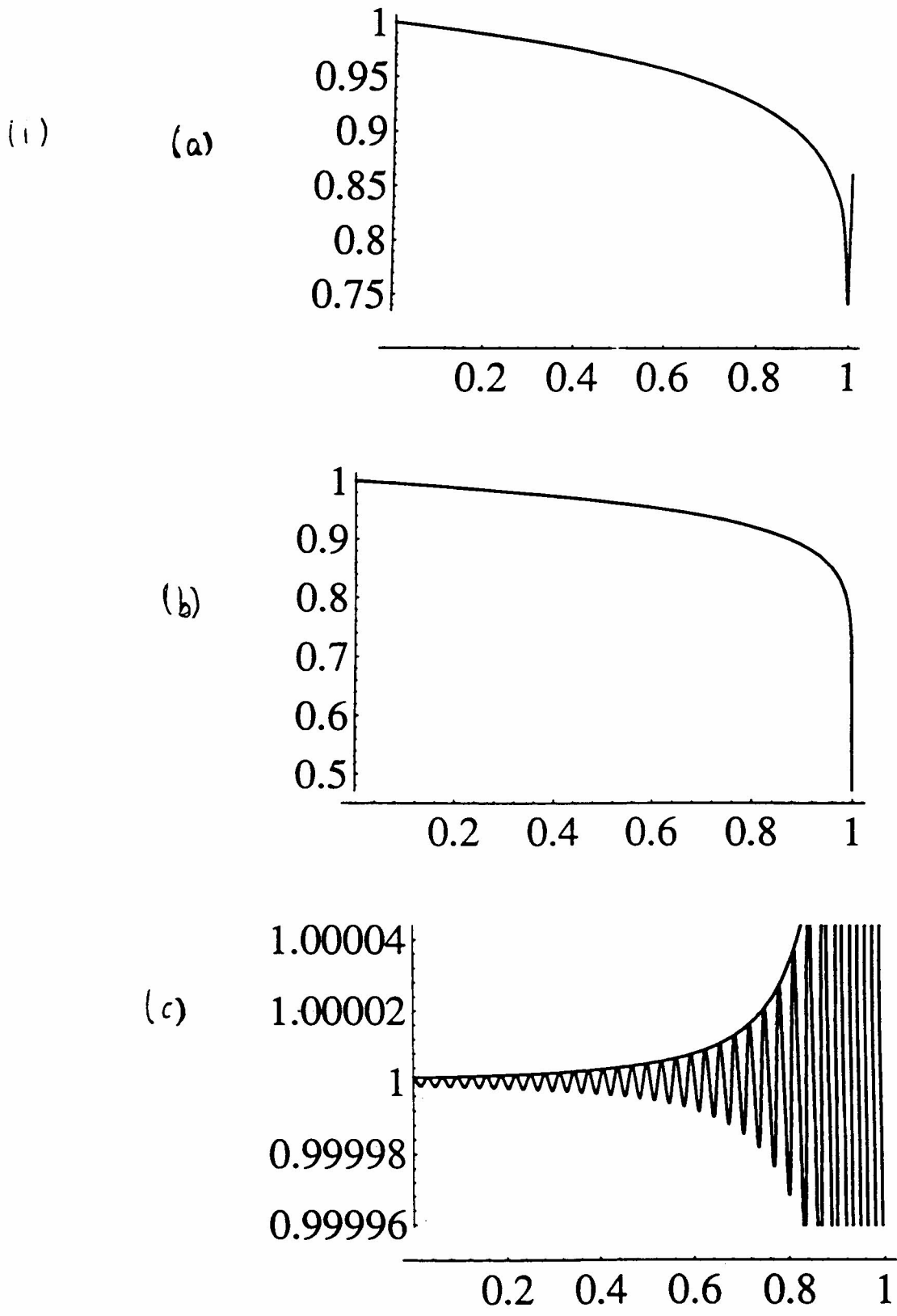


Figure 13 (a) Full, (b) underlying, and (c) cyclic, mass fraction for  $A_0 = 1$ ,  $\Gamma = 1/20$ ; (i)  $\omega = 200$ ,  $B = 1/200$ ; (ii)  $\omega = 250$ ,  $B = 1/10$ .

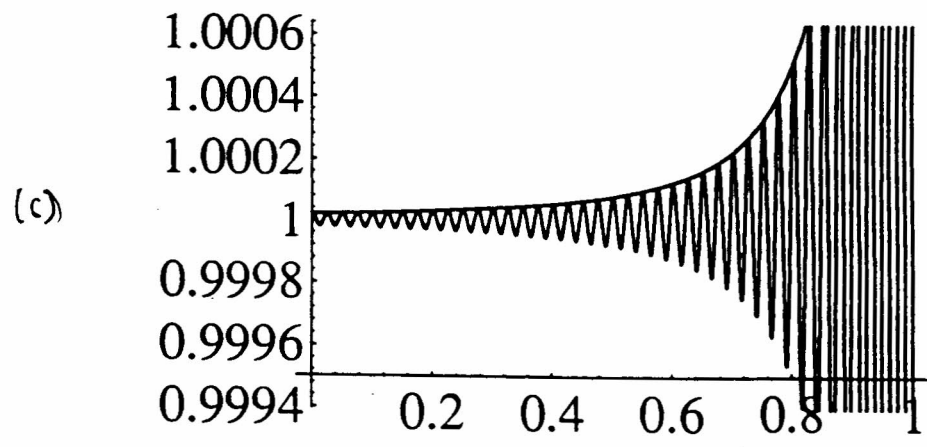
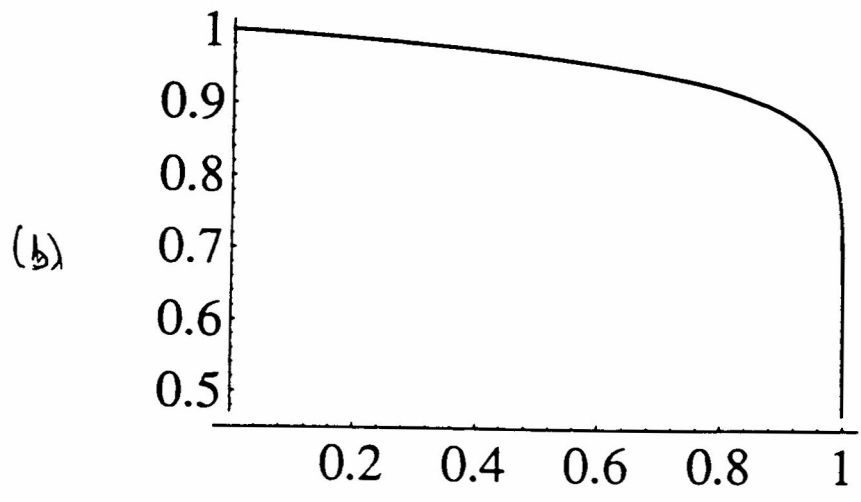
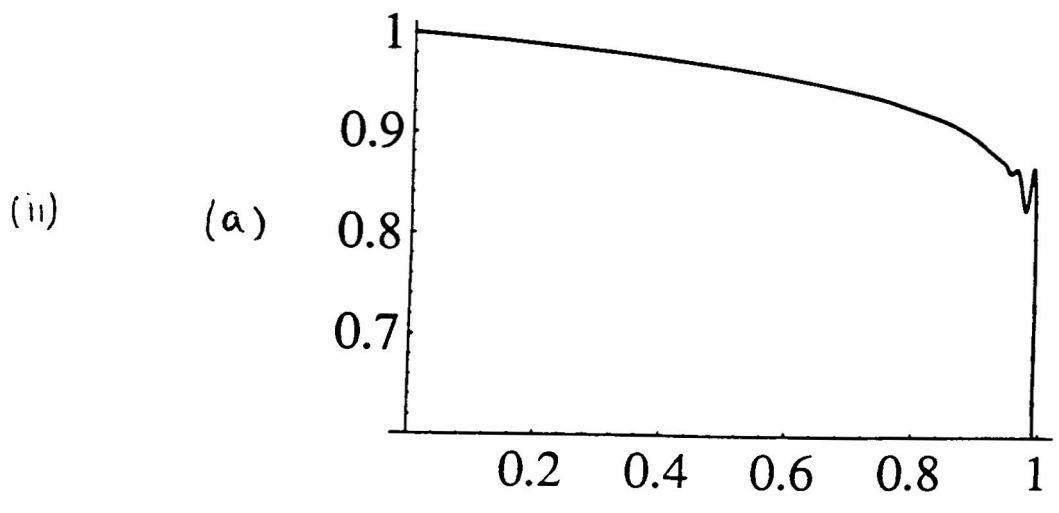


Figure 14. Underlying, (a), and cyclic, (b),  $C_p$ 's for  $A_0 = 1$ ,  $\Gamma = 1/20$ ;

(i)  $\omega = 200$ ,  $B = 1/200$ ; (ii)  $\omega = 250$ ,  $B = 1/10$ .

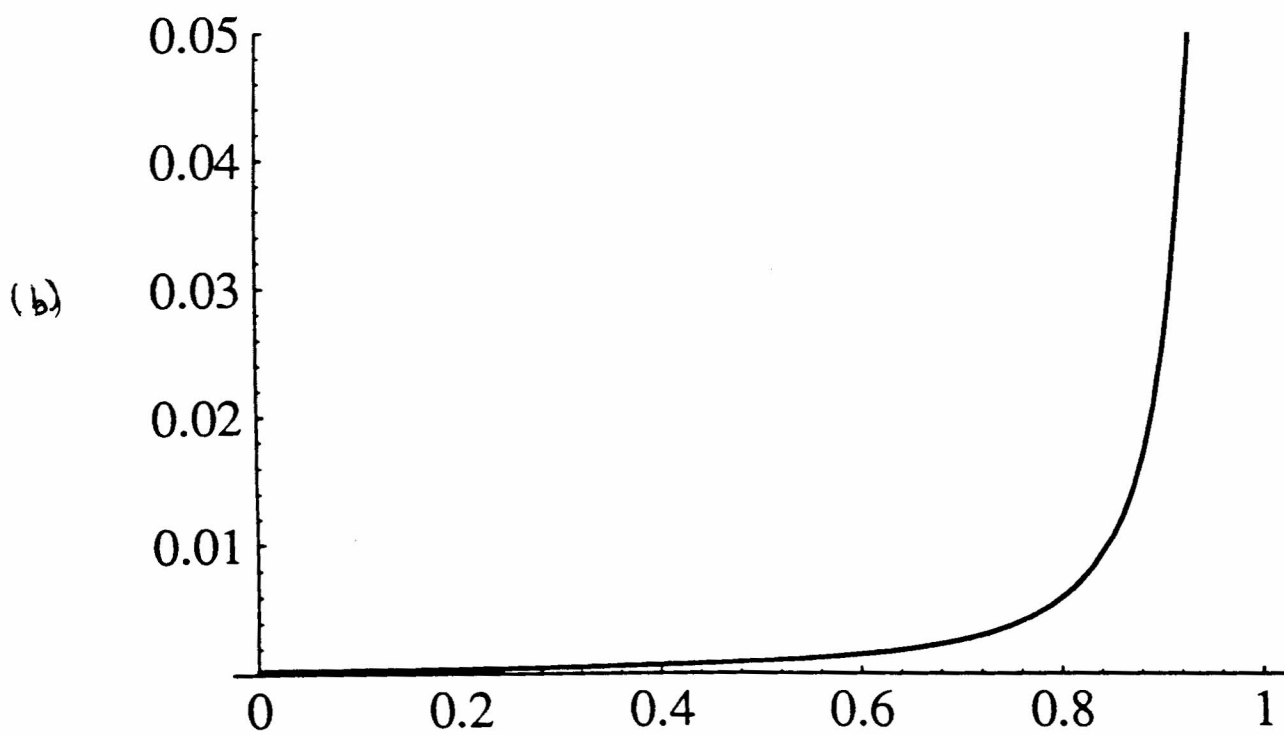
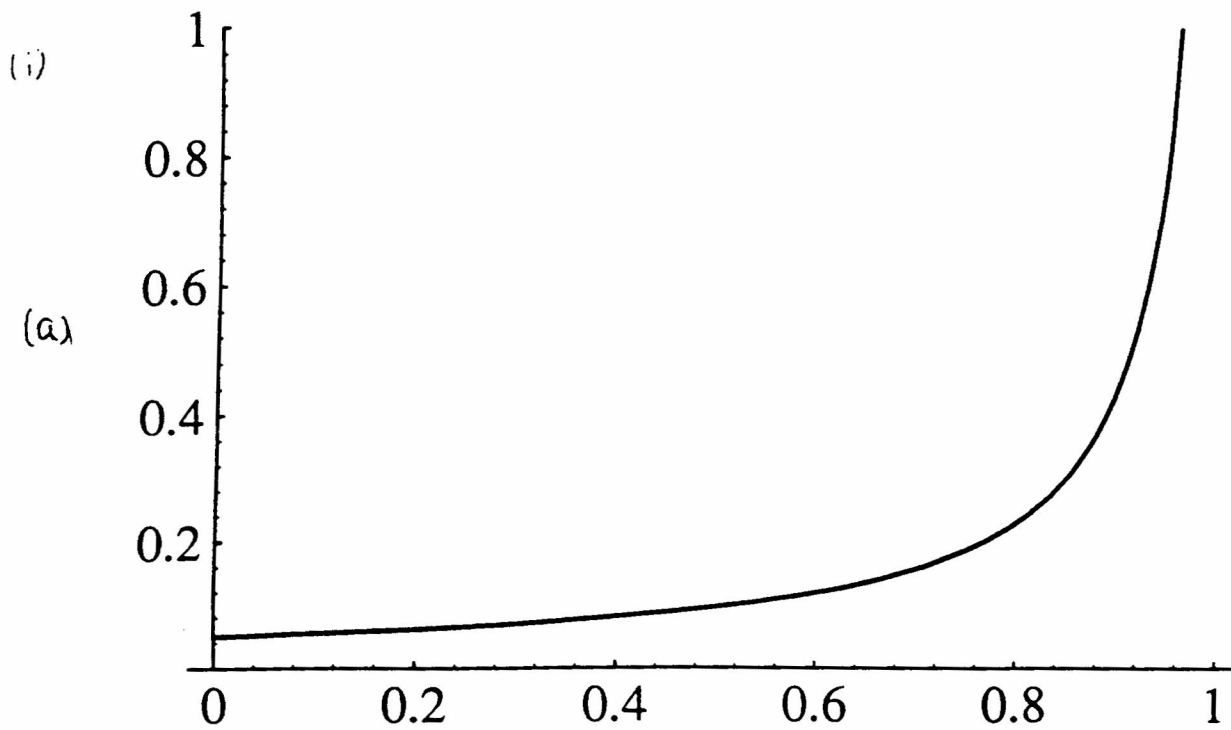


Figure 14. Underlying, (a), and cyclic, (b),  $C_p$ 's for  $A_0 = 1$ ,  $\Gamma = 1/20$ ;  
(i)  $\omega = 200$ ,  $B = 1/200$ ; (ii)  $\omega = 250$ ,  $B = 1/10$ .

