TRANSIENT AND STEADY STATE EFFECTS OF APPLIED TEMPERATURE ON CYLINDRICAL CALORIMETRY PANS

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ABSTRACT

Liquid heat capacity is measured assuming the liquid has negligible temperature gradients. This assumption was tested by treating the system as a cylinder of known heat capacity exposed to insulated and convective conditions and solved using finite integral transforms. The PDE model shows that this assumption can be correct, but this assumption should be checked with larger calorimeter pans.

NOMENCLATURE

\( C_p \) = heat capacity  \( q \) = heat flow  \( T \) = Temperature
\( L_c \) = characteristic length  \( h \) = convection coefficient
\( \rho \) = density  \( k \) = thermal conductivity
\( r \) = radial dimension  \( z \) = height dimension
\( \theta \) = angular dimension  \( \alpha \) = thermal diffusivity
\( U \) = modified temperature  \( L \) = height of pan
\( r_1 \) = radius of pan  \( t \) = time dimension

INTRODUCTION

Calorimetry is an important science for determining physical properties, reaction heats, heats of fusion and vaporization, and other industrially important data. Calorimetry involves carefully adding heat to an isolated system and measuring the change in state variables. When measuring liquid heat capacity, a small amount of heat is added to a sample of the test fluid. The change in temperature is measured, and the heat capacity is defined as:

\[
C_p = \frac{q}{\Delta T}
\]  

Since heat capacity is reported at a temperature point, measuring this property accurately requires the change in temperature of the test liquid be measured as close to the reported temperature as possible. Often, this will be done by oscillating from just below and above a temperature and reporting the heat capacity of the average temperature.

To allow for accurate measurement as close to the given temperature as possible, it is best to make the heat flux and measured change in temperature as small as can be accurately measured. This requires using small samples and limiting resistance to heat transfer by using aluminum (or another low heat-resistance metal) pans. A typical setup for a modern modulating digital scanning calorimeter (MDSC) is shown in Figure 1. [1] The change in temperature of the sample is measured at the base of the pan (noted as Sample Pan in the figure). This implies an assumption that the fluid sample has a uniform temperature profile.

Generally, the pan used in calorimetry is small, with a characteristic length in the millimeter range. The Biot number is a non-dimensional number that describes the internal heat transfer resistances to the resistance at the surface. The Biot number is defined as:

\[
Bi = \frac{L_c h}{k}
\]
With a characteristic length of less than a centimeter, most liquids will yield a Biot number below 0.1, where we can assume a uniform temperature distribution. \[2\]

Figure 1 also shows that there is a purge gas flow. This is done both to allow modulation around a temperature and for safety reasons. This forced convection around the pans forces us to consider whether the sample in the pan actually does have a uniform temperature, especially as the characteristic length grows beyond the Biot limit for lumped capacitance. It would be difficult to measure this directly without upsetting the system, so a mathematical analysis is useful.

**METHODS**

The energy equation in cylindrical coordinates with no fluid flow and constant physical properties is \[3\]:

\[
\rho C_p \left( \frac{dU(r, \theta, z, t)}{dt} \right) = k \left( \frac{1}{r} \frac{d}{dr} \left( r \frac{dU(r, \theta, z, t)}{dr} \right) \right) + \frac{1}{r^2} \frac{d^2U(r, \theta, z, t)}{d\theta^2} + \frac{1}{z^2} \frac{d^2U(r, \theta, z, t)}{dz^2}
\]

The considered system is shown in Figure 2. As shown in Figure 1, the sample fluid is contained in a sealed aluminum pan. Due to the high thermal conductivity of aluminum, we can assume that the pan itself has a negligible effect on the temperature profile. Above the sample in the sealed pan is a layer of air. This has such a small mass that it is negligible in measuring liquid heat capacity, but in this analysis it produces a useful insulated (Neumann) boundary at the top of the fluid. At the base of the cylinder, a constant temperature is maintained by the DSC (Dirichlet boundary condition). The sides of the cylinder have a convective (Robin) boundary condition with the inlet purge gas.

The cylinder is initially at the temperature of the inlet gas \(T_{\infty}\) and the constant temperature boundary condition \(T_{base}\) is applied at \(t > 0\).

We can make several simplifying assumptions in our analysis. The first assumption is to assume that the temperature profile \(U\) is symmetric about \(\theta\), allowing us to remove the second term from the right side of the energy equation. We can safely make this assumption by using an average convection coefficient for flow around a transverse cylinder.

**MATHEMATICAL FORMULATION**

With the preceding assumptions, our problem is reduced to the following initial-value boundary problem.

\[
\frac{1}{\alpha} \frac{dU(r, z, t)}{dt} = \frac{1}{r} \frac{d}{dr} \left( r \frac{dU(r, z, t)}{dr} \right) + \frac{d^2U(r, z, t)}{dz^2}
\]

where \(U = T - T_{\infty}\)

subject to boundary conditions:

\[
U(r, L, t) = T_{base} - T_{\infty}
\]

\[
\frac{dU(r, L, t)}{dz} = 0
\]

\[
k \frac{dU(r_1, z, t)}{dr} + h U(r_1, z, t) = 0
\]

and initial condition:

\[
U(r, z, 0) = 0
\]

**Figure 2. Model of Test Liquid**

With the problem formulated, we can use a series of transforms to find a solution. First, a finite Fourier transform was applied to treat the function in the \(z\) dimension. Next, a finite Hankel transform treats the function radially, simplifying the equation substantially. Finally, a Laplace transform is used and the problem can be rearranged and simplified using partial fractions. The three inverse transforms are then applied to derive the following function.

\[
U(r, z, t) = \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \frac{c_{b,n,m}}{b_{n,m}} (1 - e^{-t b_{n,m}}) K_m(z) K_n(r)
\]

(4)

where \(K_m(z)\) and \(K_n(r)\) are kernels of the Finite Fourier and Hankel transforms.

\[
K_n(r) = \frac{J_0(\lambda_n r)}{\int_0^{r_1} J_0(\lambda_n r) r \, dr}
\]

\[
K_m(r) = \sqrt{\frac{2}{L}} \sin \left( m + \frac{1}{2} \frac{\pi}{L} z \right)
\]

Constants are
\[ c_{n,m} = \alpha \left( T_{base} - T_\infty \right) k_m(0) H_0(1) \]

\[ b_{n,m} = \alpha(\lambda_n^2 + \lambda_m^2) \]

This function matches the expected form of the solution. The function can be split into a transient portion with an exponential decay term and a steady state solution. [4] A more detailed derivation can be found in the appendix.

RESULTS

For the solution and graphing shown here, the following values were used.

\[
T_{base} = 50 \quad T_\infty = 20 \quad k = 2 \quad h = 2 \\
\rho = 1000 \quad C_p = 4.2 \quad r_1 = 0.1 \quad L = 0.1
\]

Figure 3. Transient temperature profiles at 1, 5, 10, & 25 seconds. Red lines are at \( z = 0.05L \), green lines at \( L/2 \), and blue curves at \( 0.99L \).

The transient results of the system are shown in Figure 3. As can be observed from the graphs, it doesn’t take long for the system to reach near steady state conditions. The temperature profile is hottest near the heated bottom and decreases as it approaches the edge and near the insulated boundary. Figure 4 shows the temperature profile of a slice of the cylinder at 25 seconds. Unfortunately, due to the setup of the problem, the solution goes to zero at \( z = 0 \). As the number of terms of summation increase, the effect of this numeric issue becomes negligible. The solution shown here sums over 32 eigenvalues in the \( n \) and \( m \) domain of the solution. Additional eigenvalues can be used, but computation becomes very intense because of the double summation term.

Figure 4. Temperature Profile at 25 s for \( 0.025<r<r_1 \) and \( 0<z<L \).

Figure 5 shows the steady state solution found here compared to a different steady state solution found using separation of variables. The solutions are very similar and prove a nice check for the solution found here. The differences in the solutions near the zero height condition can be attributed to the numerical oscillations at low height, which can be seen in Figure 4.

As seen in the steady-state solution, the differences in the temperature profiles are relatively small on an absolute scale. This shows that for this set of parameter values, the assumption of an isothermal liquid phase is justifiable. With the addition on natural convection effects in the liquid, it is likely that the temperature gradient would be even smaller in a real system. For the studied size of pan, the isothermal assumption can be justified. However, depending on the system studied, these effects could be significant and should be checked, especially for larger pan sizes.

Figure 5. This work steady state solution (left,) by separation of variables (right.) Colors the same as Figure 3.
CONCLUSIONS

A transient model for the temperature profile of a calorimetry pan has been derived using integral transform methods. The model was plotted for common values of the parameters. This model shows that the assumption of a uniform temperature distribution can be justified for certain systems, but this assumption must be checked for specific systems.

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REFERENCES

Appendix: Derivation of Analytical Solution

*All derivatives are partial derivatives.

Reduced Energy Equation:

\[
\frac{1}{\alpha} \frac{d}{dt} (U(r, z, t)) = \frac{1}{r} \frac{d}{dr} \left[ r \left( \frac{d}{dr} U(r, z, t) \right) \right] + \frac{d^2}{dz^2} U(r, z, t)
\]

Where: \( U(r, z, t) = T - T_{\text{inf}} \)

Boundary Conditions:

\[
U(r, 0, t) = T_{\text{base}} - T_{\text{inf}} = f_0 \quad k \frac{d}{dr} U(r_1, z, t) + h \cdot U(r_1, z, t) = 0 \quad \frac{d}{dz} U(r, L, t) = 0
\]

\( U(0, z, t) < \infty \)

Initial Condition:

\( U(r, z, 0) = 0 \)

Apply Finite Fourier Transform:

Kernel of transform is:

\[
K_m(z) = \frac{1}{\sqrt{L}} \cdot \sin \left( \left( m + \frac{1}{2} \right) \frac{\pi}{L} z \right)
\]

Eigenvalues of transform are:

\[
\lambda_m = \left( m + \frac{1}{2} \right) \frac{\pi}{L} \quad m = 0, 1, 2, \ldots \infty
\]

Transformed Energy Equation:

\[
\frac{1}{\alpha} \frac{d}{dt} U_F = \frac{1}{r} \frac{d}{dr} \left[ r \left( \frac{d}{dr} U_F \right) \right] + f_0 \frac{d}{dz} K_m(0) - \lambda_m^2 U_F
\]

Apply Hankel Transform:

Kernel of transform is:

\[
K_n(r) = \frac{J_0(\lambda_n r)}{\int_0^{r_1} r J_0(\lambda_n r) \, dr}
\]

Eigenvalues of transform are roots of:

\[
0 = k \frac{d}{dr} J_0(\lambda_n r_1) + h \cdot J_0(\lambda_n r_1)
\]
Transformed Energy Equation:

\[ \frac{1}{\alpha} \frac{d}{dt} U_{F.H} = -\lambda_n^2 U_{F.H}^2 + \text{Hankel}(1) f_0 \frac{d}{dz} K_m(0) - \lambda_m^2 U_{F.H} \]

Where \( \text{Hankel}(1) = \int_0^1 \frac{J_0(\lambda_n r)}{r} r \, dr \)

Apply Laplace Transform:

Transformed Energy Equation:

\[ \frac{1}{\alpha} U_{F.H}^s = -\lambda_n^2 U_{F.H}^s + \text{Hankel}(1) f_0 \frac{d}{dz} K_m(0) \cdot \frac{1}{s} - \lambda_m^2 U_{F.H}^s \]

Solve for function:

\[ U_{F.H}^s = \frac{\alpha f_0}{\alpha (\lambda_m^2 + \lambda_n^2)} \cdot \text{Hankel}(1) \cdot \frac{1}{s + \alpha (\lambda_m^2 + \lambda_n^2)} \]

Partial Fractionation:

\[ U_{F.H}^s = \frac{\alpha f_0}{\alpha (\lambda_m^2 + \lambda_n^2)} \cdot \text{Hankel}(1) \cdot \left[ \frac{1}{s} - \frac{1}{s + \alpha (\lambda_m^2 + \lambda_n^2)} \right] \]

let \( c_{nm} = \alpha f_0 \frac{d}{dz} K_m(0) \cdot \text{Hankel}(1) \) and \( \beta_{nm} = \alpha (\lambda_m^2 + \lambda_n^2) \)

\[ U_{F.H}^s = \frac{c_{nm}}{\beta_{nm}} \left( \frac{1}{s} - \frac{1}{s + \beta_{nm}} \right) \]

Inverse Laplace Transform:

\[ U_{F.H}^t = \frac{c_{nm}}{\beta_{nm}} \left( 1 - e^{-\beta_{nm} t} \right) \]

Inverse Hankel Transform:

\[ U_F(r, t) = \sum_{n=1}^{\infty} \frac{c_{nm}}{\lambda_n} \left( 1 - e^{-\beta_{nm} t} \right) K_n(r) \]
Inverse Finite Fourier Transform:

\[ U(r, z, t) = \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} \left[ \frac{c_{nm}}{\beta_{nm}} \left( 1 - e^{-\beta_{nm}t} \right) K_n(r) K_m(z) \right] \]