4.3   Analysis Models

4.3.1   Thermal Models

Central to the conversion of raw data into heat capacity numbers is the mathematical model used to describe the temperature response of the sample platform as a function of time.

4.3.1.1   SIMPLE MODEL

The simple model, which is the most basic analysis of the raw measurement data, assumes that the sample and sample platform are in good thermal contact with each other and are at the same temperature during the measurement. In the simple model, the temperature T of the platform as a function of time t obeys the equation

$$C_{\text{total}} \frac{dT}{dt} = -K_w (T - T_b) + P(t),$$

where C_{total} is the total heat capacity of the sample and sample platform; K_w is the thermal conductance of the supporting wires; T_b is the temperature of the thermal bath (puck frame); and $P(t)$ is the power applied by the heater. The heater power $P(t)$ is equal to P_0 during the heating portion of the measurement and equal to zero during the cooling portion. The solution of this equation is given by exponential functions with a characteristic time constant τ equal to C_{total}/K.

The Heat Capacity software uses the simple model to measure the addenda and generally uses the simple model to measure most samples. However, when the thermal contact between the sample and sample platform is poor, the software uses the more sophisticated two-tau model to measure the heat capacity. [1]

4.3.1.2   TWO-TAU MODEL

The Heat Capacity software uses the two-tau model to measure the heat capacity of the sample when poor thermal attachment of the sample to the platform produces a temperature difference between the two. The two-tau model simulates the effect of heat flowing between the sample platform and sample, and the effect of heat flowing between the sample platform and puck. The following equations express the two-tau model:

$$C_{\text{platform}} \frac{dT_p}{dt} = P(t) - K_w \left(T_p(t) - T_b \right) + K_g \left(T_s(t) - T_p(t) \right)$$

$$C_{\text{sample}} \frac{dT_s}{dt} = -K_g \left(T_s(t) - T_p(t) \right),$$

where C_{platform} is the heat capacity of the sample platform, C_{sample} is the heat capacity of the sample, and K_g is the thermal conductance between the two due to the grease. The respective temperatures of the platform and sample are given by $T_p(t)$ and $T_s(t)$.

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[1] Two-tau model™ is a trademark of Quantum Design.

4.3.2   Data Fitting

Using a nonlinear, least-square fitting algorithm, the system compares the solution to the simple model to the actual measurement. The values of the parameter that give the smallest fit deviation determine the heat capacity. The sensitivity of the fit deviation (chi square) to small variations in the fitting parameters is used to estimate the standard errors for the heat capacity.

Except when measuring the addenda (the heat capacity of only the platform), a fit to the solution of the two-tau model is also performed. The heat capacity numbers derived in this way are used only if the fit has a smaller fit deviation than in the first case. Under some circumstances, the fit to the two-tau model does not converge, in which case the simple fit is again used. Such a lack of convergence can occur when the sample is perfectly attached to the platform, in which case the simple model is correct. Fitting difficulties can also arise in other cases where the sample is poorly attached and the heat capacity of the sample is not large compared to the platform. In either case, the sample coupling is shown to be 100%.

4.3.3   Derived Quantities from Model Parameters

4.3.3.1   SIMPLE MODEL: ADDENDA MEASUREMENT

An addenda measurement uses only the simple model (Section 4.3.1.1) for computing heat capacity. In this case, the measurement fields in the Measurement Status Viewer (Section 4.5) are computed as indicated in table 4-2.

Table 4-2. Simple Model Parameters Used for Addenda Measurement

STATUS VIEWER FIELD	EXPRESSION FROM MODEL
Total Heat Cap	C_{total}
Sample Heat Cap	zero
Addenda Heat Cap	C_{total}
Time Const (tau1)	C_{total}/K_w
Time Const (tau2)	Zero
Sample Coupling	100%

4.3.3.2   SIMPLE MODEL: SAMPLE MEASUREMENT

When the analysis of a sample heat capacity measurement fails to find a fit to a two-tau solution, the simple fit (Section 4.3.1.1) is used as in the case of the addenda measurement. The Sample Heat Cap measurement field is computed by subtracting the total heat capacity of the fit from the addenda heat capacity $C_{addenda}$ as retrieved from a previously measured addenda table. In this case, the measurement fields in the Measurement Status Viewer (Section 4.5) are computed as indicated in table 4-3.

Table 4-3. Simple Model Parameters Used for Sample Heat Capacity Measurement

STATUS VIEWER FIELD	EXPRESSION FROM MODEL
Total Heat Cap	C_{total}
Sample Heat Cap	$C_{total} - C_{addenda}$
Addenda Heat Cap	$C_{addenda}$
Time Const (tau1)	C_{total}/K_w
Time Const (tau2)	Zero
Sample Coupling	100%

4.3.3.3   TWO-TAU MODEL: SAMPLE MEASUREMENT

When the two-tau model (Section 4.3.1.2) is fit to the measurement data for a sample heat capacity measurement, the addenda heat capacity $C_{addenda}$ is retrieved from a previously measured addenda table and $C_{platform}$ is treated as a constant equal to $C_{addenda}$ in the fitting routine. In this case, the measurement fields in the Measurement Status Viewer (Section 4.5) are computed as indicated in table 4-4.

Table 4-4. Two-Tau Model Parameters Used for Sample Heat Capacity Measurement

STATUS VIEWER FIELD	EXPRESSION FROM MODEL
Total Heat Cap	$C_{platform} + C_{sample}$
Sample Heat Cap	C_{sample}
Addenda Heat Cap	$C_{platform}$
Time Const (tau1)	$1/(\alpha + \beta)$
Time Const (tau2)	$1/(\alpha - \beta)$
Sample Coupling	$100 \times K_g/(K_g + K_w)$

The expressions for α and β are given by

$$\alpha = \frac{K_w}{2C_{\text{platform}}} + \frac{K_g}{2C_{\text{platform}}} + \frac{K_g}{2C_{\text{sample}}},$$

$$\beta = \frac{\sqrt{K_g^2 C_{\text{sample}}^2 + 2K_g^2 C_{\text{sample}} C_{\text{platform}} + K_g^2 C_{\text{platform}}^2 + K_w^2 C_{\text{sample}}^2 + 2K_w C_{\text{sample}}^2 K_g - K_w C_{\text{sample}} K_g C_{\text{platform}}}}{2C_{\text{platform}} C_{\text{sample}}}.$$

4.3.3.4   EQUIVALENT DEBYE TEMPERATURE

The system can also express sample heat capacity as an equivalent Debye temperature in the event that the sample mass, formula weight, and atoms per formula unit have been entered.

The Debye model successfully describes the heat capacity of phonons (lattice contribution). Phonons, electrons, and magnons all contribute to the heat capacity in solids.

The general expression for lattice heat capacity and temperature T can be stated as

$$C_v = 3rNk \int_0^\infty \left(\frac{hv}{2kT}\right)^2 \csc h^2 \left(\frac{hv}{2kT}\right) g(v) dv,$$

where r is the number of atoms per molecule, N is the number of molecules, and k is the Boltzmann constant. The density of phonon modes in the frequency range from v to $v + dv$ is given by $g(v)dv$. In the Debye model, the mode density function $g(v)$ is derived by assuming that phonon propagation through the crystal lattice is governed by the same dispersion relation as linear waves in a continuous isotropic solid. To account for the lattice spacing in a real solid, Debye's theory specifies a cutoff frequency, v_D, above which the mode density function is zero. That is,

$$g(v) = \frac{3v^2}{v_D^3} \text{ for } v \le v_D$$

$$g(v) = 0 \text{ for } v > v_D.$$

Physically, v_D corresponds to the smallest phonon wavelength that can propagate in a lattice of atoms with a finite spacing. It is related to both the speed of sound and the elastic properties of the solid. The Debye temperature is then defined as θ, where $hv_D = \theta k$. Putting $g(v)$ into the above expression for heat capacity creates the following relation between C_v and θ:

$$C_v = 9rNk \frac{T^3}{\theta^3} \int_0^{\theta/T} \frac{x^4 e^x dx}{\left(e^x - 1\right)^2} .$$

This expression contains the two well-known limits of heat capacity for nonmetallic solids. At high temperatures, $C_v \rightarrow 3rNk$, whereas at sufficiently low temperatures,

$$C_v \longrightarrow \frac{12}{5} rNk \pi^4 \left(\frac{T}{\theta}\right)^3,$$

which is the familiar T^3 law.

Experimentally, you can determine θ by first measuring the heat capacity of a known quantity N of molecules, each molecule having r atoms, at a temperature T. You then numerically solve the above expression for θ. For a perfect Debye solid, θ does not change with temperature. However, in real solids, lattice effects and electronic and other contributions to the heat capacity cause θ to vary with temperature.

It is important to point out that the value for Debye temperature which is computed by the application assumes that the sample heat capacity contains only a lattice contribution. No special accounting is made for electronic, magnetic, or structural terms.

Plots of equivalent Debye temperature as a function of temperature were first suggested by M. Blackman in "The Theory of the Specific Heat of Solids" (Blackman 1942).

4.3.3.5   MEASUREMENT UNITS

Table 4-5 summarizes common measurement units that express heat capacity and specific heat. The default measurement units, μJ/K, express heat capacity. The sample information that is defined in the open data file determines which measurement units, other than μJ/K, are available. You define sample information in the header of the data file you have opened to log the measurement. If you neglect to define all sample information, the application still collects data, but it expresses the data in the units for heat capacity, μJ/K, rather than in the units you have selected.

Table 4-5. Common Units for Heat Capacity and Specific Heat

	UNITS	FORMULA
HEAT CAPACITY	μJ/K	
MASS SPECIFIC HEAT	μJ/mg-K	μJ/K/mass
	μJ/g-K	μJ/K/mass
	J/g-K	$0.001 \times (\mu J/K)/mass$
	cal/g-K	$0.0002390057 \times (\mu J/K)/mass$
MOLAR SPECIFIC HEAT	mJ/mole-K	$(\mu J/K) \times molwght/mass$
	J/mole-K	$0.001 \times (\mu J/K) \times molwght/mass$
	cal/mole-K	$0.0002390057 \times (\mu J/K) \times molwght/mass$
GRAM-ATOM SPECIFIC HEAT	J/gat-K	$0.001 \times (\mu J/K) \times molwght/(mass \times atoms)$
	cal/gat-K	$0.0002390057 \times (\mu J/K) \times molwght/mass \times atoms)$