Frequency-dependent Specific Heat from Thermal Effusion in Spherical Geometry

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arXiv:0809.4617 [cond-mat.soft]
Close to $T_g$ the specific heat becomes complex and frequency dependent.

$$C(\omega) = \frac{Q_\omega}{\delta T_\omega}$$

for heat and temperature varying harmonically

$$Q(t) = \Re \left\{ Q_\omega e^{i\omega t} \right\}$$
$$\delta T(t) = \Re \left\{ \delta T_\omega e^{i\omega t} \right\}$$
Background

Thermoviscoelastic coupling is normally not taken into account!
Background

Thermomechanical coupling

Normally it is assumed that:

\[ \frac{\partial \delta T}{\partial t} = \frac{\lambda}{c_p} \nabla^2 \delta T \]

Close to \( T_g \) the full thermomechanical problem has to be addressed:

\[
M_T \nabla (\nabla \cdot u) - G \nabla \times (\nabla \times u) - \beta_V \nabla \delta T = 0
\]

\[
c_V \frac{\partial \delta T}{\partial t} + T_0 \beta_V \frac{\partial}{\partial t} (\nabla \cdot u) = \lambda \nabla^2 \delta T
\]

\[
\beta_V = \left( \frac{\partial p}{\partial T} \right)_V
\]
Theoretical results

Longitudinal specific heat

It is the longitudinal specific heat that enters the solutions and not $c_p$ even though we have free outer boundaries.

\[
c_p = \frac{K_S}{K_T} c_v \\
c_l = \frac{M_S}{M_T} c_v = \frac{K_S + 4/3G}{K_T + 4/3G} c_v \\
\frac{c_p - c_l}{c_p} = \frac{4}{3} \frac{G}{M_T} \frac{c_p - c_v}{c_p} \\
\]

Longitudinal moduli $M_s = K_S + 4/3G$ and $M_T = K_T + 4/3G$
Theoretical results

Thermal effusion in thermally thick ($L \gg |l_D|$) limit

Thermal impedance:

\[ Z_{\text{liq}}(\omega) = \frac{\delta T_\omega}{P_\omega} \]

\[ \delta T(t) = \Re \left\{ \delta T_\omega e^{i\omega t} \right\} \]

\[ P(t) = \Re \left\{ P_\omega e^{i\omega t} \right\} \]

Planar 1D geometry: (Christensen et al., PRE 75, 041502, 2007)

\[ Z_{\text{liq,1D}}(\omega) = \frac{1}{A \sqrt{i\omega c_l(\omega)\lambda}} \]

Spherical geometry: (Christensen and Dyre, PRE 78, 021501, 2008)

\[ Z_{\text{liq,spherical}}(\omega) = \frac{1}{4\pi r_0 \lambda \left( 1 + \sqrt{i\omega r_0^2 c_l(\omega)/\lambda} \right)} \]
Experimental

Proof of concept experiment, in spherical geometry

- Measurement on 5-polyphenyl-4-ether
  (Santovac 5 vacuum pump fluid)
- Thermistor bead
  Large temperature dependency of resistivity
- $3\omega$ detection technique
- Temperature amplitude $< 2.3K$
- Measurements from room temperature down to 10K above $T_g$
Experimental setup

Bead in sphere

\[ V(t) = \frac{R_{\text{pre}}}{R_{\text{pre}} + R(T(t))} U(t) \]

(Igarashi et al., Rev. Sci. Instrum. 79, 045105, 2008)

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3ω method

First order solution

\[ T_2 = -2 \frac{V_3 (A + 1)}{a U_1} \]
\[ T_0 = - \frac{V_1 (A + 1) - (U_1 - \frac{1}{2} a T_2 U_1^*)}{a U_1} \]
\[ T_0 = Z_0 P_0, \quad T_2 = Z_2 P_2 \]

With

\[ A = \frac{R_0}{R_{\text{pre}}}, \quad a = \frac{A \alpha_1}{1 + A} \]

\[ T = 295.6 K \]

Relative diff:
\[ |Z_{\text{amp}=4.9V} - Z_{\text{amp}=2.9V}| / |Z_{\text{amp}=2.9V}| \]
3\omega method

Higher order solution

\[ T_2 = -2 \frac{V_3(A + 1) - (U_3 + X_3)}{a U_1} \]
\[ T_0 = - \frac{V_1(A + 1) - (U_1 - \frac{1}{2} a T_2 U_1^* + X_1)}{a U_1} \]
\[ T_0 = Z_0 P_0, \; T_2 = Z_2 P_2 \]

With

\[ X_1 = -a T_1 U_0 + b T_0^2 U_1 + \frac{1}{2} b T_2 T_1^* U_1 + b T_0 T_2 U_1^* \]
\[ X_3 = -\frac{1}{2} a T_4 U_1^* + \frac{1}{4} b T_2^2 U_1^* + b T_0 T_2 U_1 \]
\[ a = \frac{A \alpha_1}{1 + A}, \; b = \left( \frac{A \alpha_1}{1 + A} \right)^2 - \frac{A \alpha_2}{1 + A} \]

\[ T = 295.6 K \] Relative diff:
\[ |Z_{\text{amp}=4.9 V} - Z_{\text{amp}=2.9 V}| / |Z_{\text{amp}=2.9 V}| \]
Measured thermal impedance

Small difference due to frequency dependent $c_i$

Dots: $T = 252.7 \, K$, Lines: $T = 256.7 \, K$
Thermal structure of the bead

Connection between: Measured impedance, $Z$, and Liquid impedance, $Z_{\text{liq}}$.

\[
Z_{\text{liq}} = \frac{1}{i\omega} \frac{T_{11}^\text{th}(r_1, r_0)i\omega Z + T_{12}^\text{th}(r_1, r_0)}{T_{21}^\text{th}(r_1, r_0)i\omega Z + T_{22}^\text{th}(r_1, r_0)}.
\]

\[
Z = \frac{1}{i\omega} \frac{T_{11}^\text{th}(r_0, r_1)i\omega Z_{\text{liq}} + T_{12}^\text{th}(r_0, r_1)}{T_{21}^\text{th}(r_0, r_1)i\omega Z_{\text{liq}} + T_{22}^\text{th}(r_0, r_1)}.
\]

\[
Z_{\text{liq}}(\omega) = \frac{1}{4\pi r_1 \lambda \left(1 + \sqrt{i\omega r_0^2 c_l(\omega)/\lambda}\right)}
\]

Thermal transfer matrix description

\[
\begin{pmatrix}
\delta T(r_1) \\
P(r_1)/(i\omega)
\end{pmatrix}
= T^\text{th}(r_1, r_0)
\begin{pmatrix}
\delta T(r_0) \\
P(r_0)/(i\omega)
\end{pmatrix}
\]

Depends on $\lambda_b, c_b, r_0, r_1$.

(Christensen and Dyre, PRE 78, 021501, 2008)
Thermal impedance of the liquid

Full model compared to measured data

6 parameter fit:
Bead: $\lambda_b, c_b, r_0, r_1$
Liquid: $\lambda, c_l$

$log_{10}(Z')$ and $log_{10}(-Z'')$ [K/W]

$log_{10}((\nu))$ [Hz]

$T = 295.6K$
Characterization of the bead

Calibration using temperatures where liquid is non-relaxing

6 parameter fit:
Bead: $\lambda_b$, $c_b$, $r_0$, $r_1$
Liquid: $\lambda$, $c_l$

4 parameter fit:
Bead: $\lambda_b$, $c_b$
Liquid: $\lambda$, $c_l$
Thermal conductivity of the liquid

Thermal admittance:

\[ Y_{\text{liq}} = 1/Z_{\text{liq}} \]

\[ = 4\pi\lambda r_1 \left( 1 + \sqrt{i\omega r_1^2 c_l / \lambda} \right) \]

For \( c_l \) frequency independent

\[ \lambda = \frac{Y_{\text{liq}}' - Y_{\text{liq}}''}{4\pi r_1} \]

Generally

\[ \frac{Y_{\text{liq}}' - Y_{\text{liq}}''}{4\pi r_1} \xrightarrow{\omega \to 0} \lambda \]
Longitudinal specific heat

Temperatures: 295.6K, 270.8K, 260.8K, 256.7K, 254.7K, 253.7K, and 252.7K.

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DC specific heat

\[ c_0 \left[ 10^6 \text{ J/(m}^3\cdot\text{K}) \right] \]

\( T \text{ [K]} \)

- 260
- 270
- 280
- 290
- 300

- 1.8
- 1.82
- 1.84
- 1.86
- 1.88

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Conclusions

Effusion in spherical geometry

- Thermomechanical coupling and boundary problems can be treated analytically
- Allows for determining both heat conductivity and specific heat
- Has limited frequency range
- Might also be interesting for determining DC specific heat

$3\omega$ technique

- $3\omega$ technique has been generalized to include higher order terms.
Outlook

- Smaller bead: allow for higher frequencies
- Larger bead: allow for lower frequencies
- Better modeling of inner structure of bead: allows for higher frequencies

Conjecture:
if sample size is big enough, geometry does not matter:

\[ Z_{\text{liq, finite sphere}} = Z_{\text{liq, infinite medium}} \]


- Easy to incorporate in other experiments
- Allows for measuring \( c_l \) under pressure