Frequency-dependent Specific Heat from Thermal Effusion in Spherical Geometry

Bo Jakobsen, Niels Boye Olsen, and Tage Christensen.

DNRF Centre “Glass and Time”,

Roskilde University, Denmark

arXiv:0809.4617 [cond-mat.soft]

Background

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

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

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:

$$\begin{aligned} M_T \nabla(\nabla \cdot \mathbf{u}) - G\nabla \times (\nabla \times \mathbf{u}) - \beta_V \nabla \delta T &= 0 \\ c_V \frac{\partial \delta T}{\partial t} + T_0 \beta_V \frac{\partial}{\partial t}(\nabla \cdot \mathbf{u}) &= \lambda \nabla^2 \delta T \end{aligned}$$

$$\beta_V = \left(\frac{\partial p}{\partial T}\right)_V$$

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.

$$
\begin{aligned}
c_p &= \frac{K_s}{K_T} c_v \\
c_l &= \frac{M_S}{M_T} c_v = \frac{K_S + 4/3G}{K_T + 4/3G} c_v \\
\frac{c_p - c_l}{c_p} &= \frac{4}{3} \frac{G}{M_T} \frac{c_p - c_v}{c_p}
\end{aligned}
$$

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

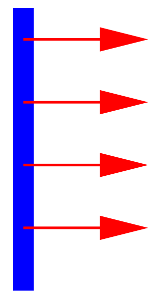
Theoretical results

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

Thermal impedance:

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

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



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

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)

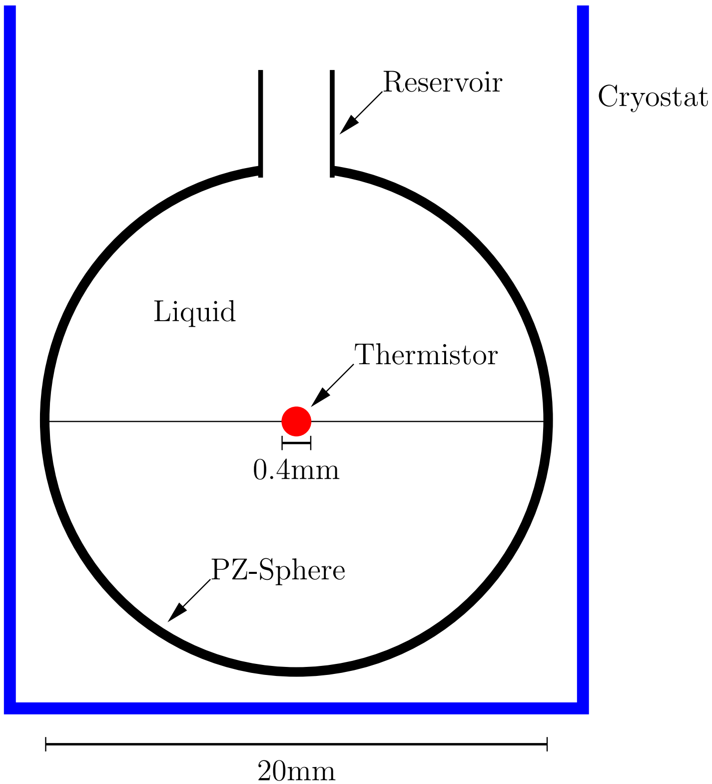
$$Z_{\text{liq,spherical}}(\omega) = \frac{1}{4\pi r_0\lambda\left(1+\sqrt{i\omega r_0^2 c_l(\omega)/\lambda}\right)}$$

Experimental

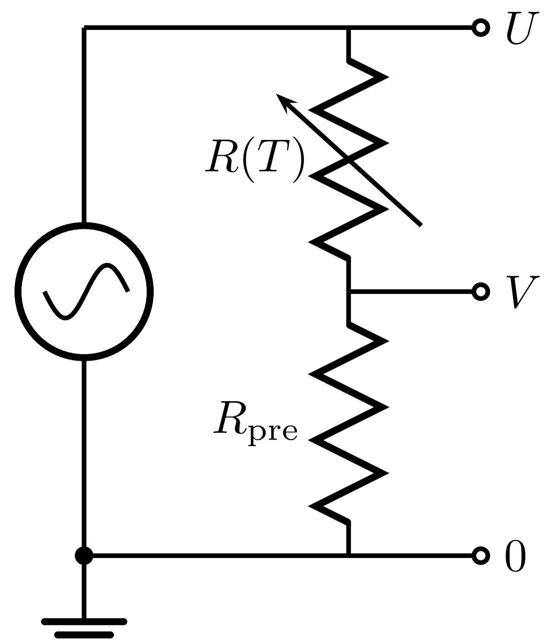
Proof of concept experiment, in spherical geometry

- Measurement on 5-polyphenyl-4-ether
  (Santovac 5 vacuum pump fluid)
- Thermistor bead
  Large temperature dependency of resistivity
- 3ω 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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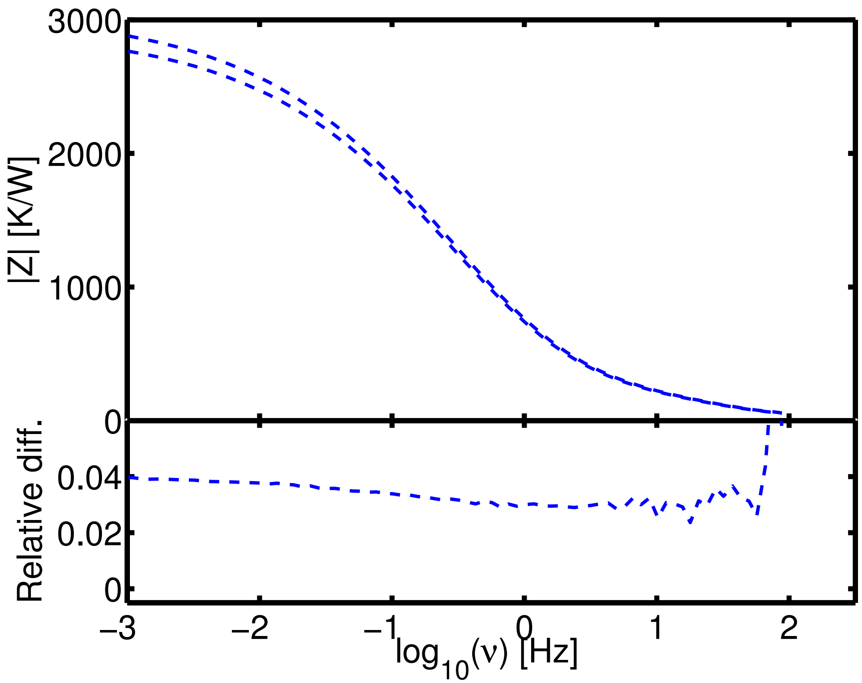
3ω method



$T = 295.6K$ Relative diff:

$|Z_{\text{amp}=4.9\text{V}} - Z_{\text{amp}=2.9\text{V}}| / |Z_{\text{amp}=2.9\text{V}}|$

First order solution

$$T_2 = -2\frac{V_3(A+1)}{aU_1}$$

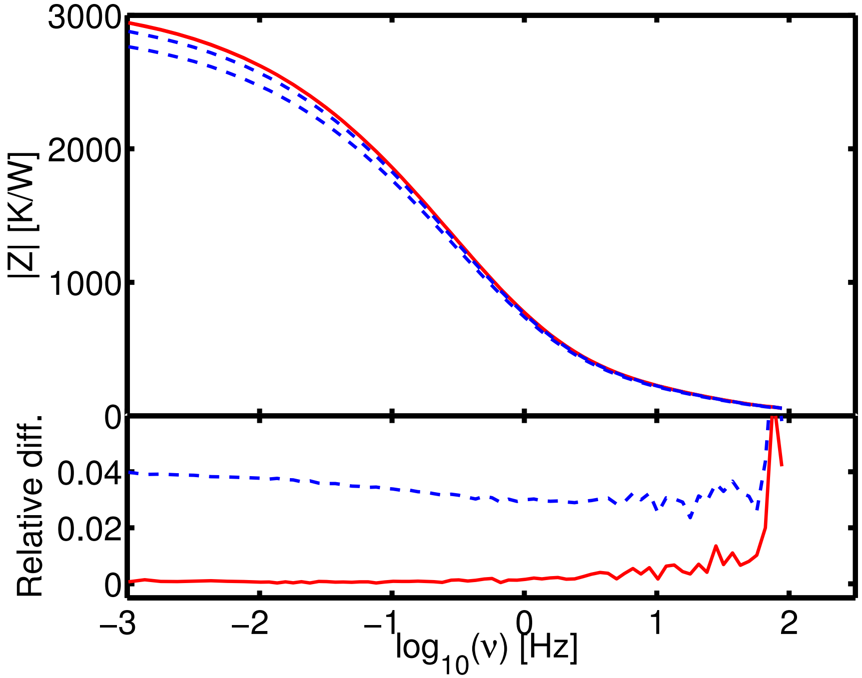
$$T_0 = -\frac{V_1(A+1) - (U_1 - \frac{1}{2}aT_2U_1^*)}{aU_1}$$

$$T_0 = Z_0P_0, \quad T_2 = Z_2P_2$$

With

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

3ω method



$T = 295.6K$ Relative diff:

$|Z_{\text{amp=4.9V}} - Z_{\text{amp=2.9V}}|/|Z_{\text{amp=2.9V}}|$

Higher order solution

$$T_2 = -2\frac{V_3(A+1) - (U_3 + X_3)}{aU_1}$$

$$T_0 = -\frac{V_1(A+1) - (U_1 - \frac{1}{2}aT_2U_1^* + X_1)}{aU_1}$$

$$T_0 = Z_0P_0, \quad T_2 = Z_2P_2$$

With

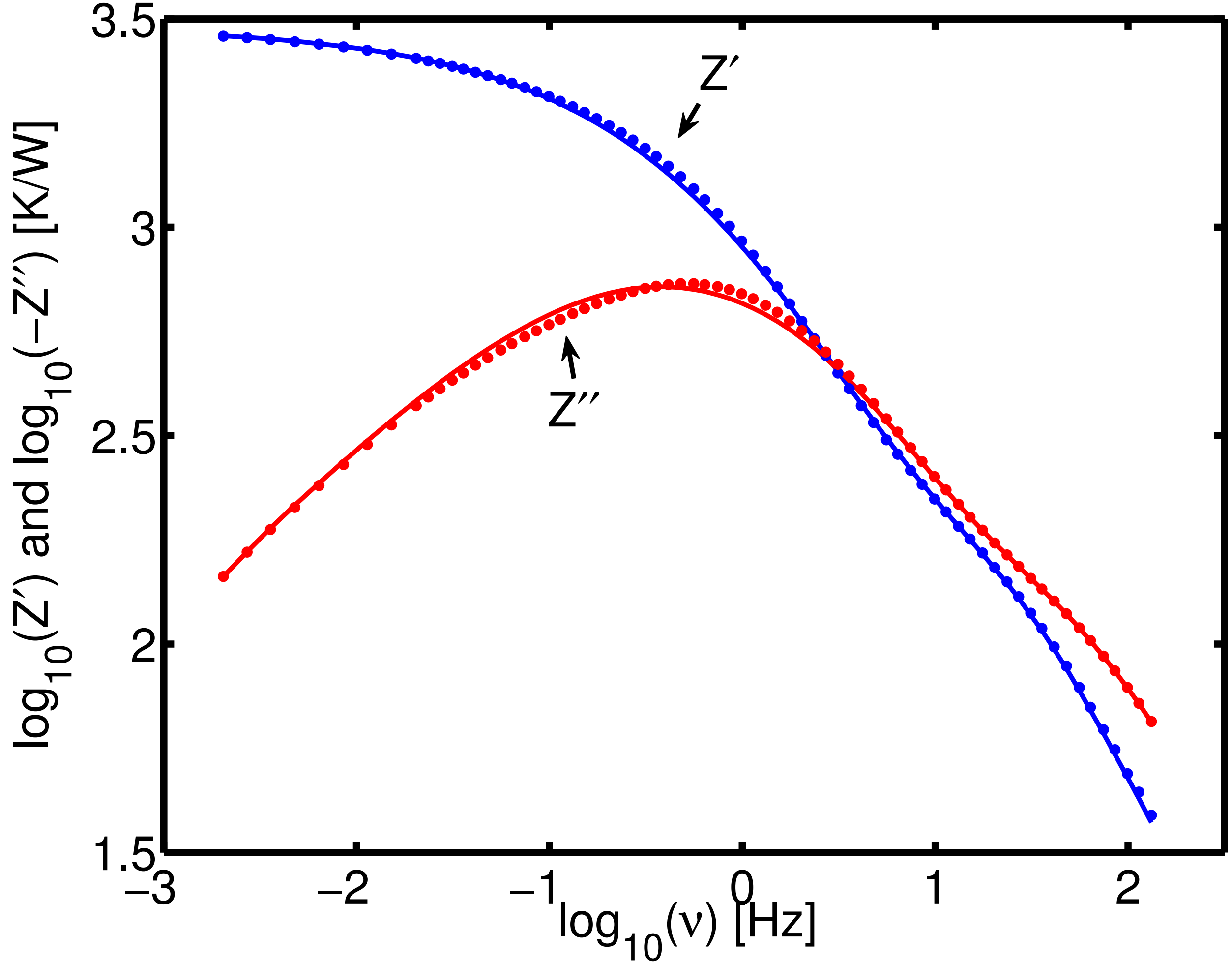
$$X_1 = -aT_1U_0 + bT_0^2U_1 + \frac{1}{2}bT_2T_2^*U_1 + bT_0T_2U_1^*$$

$$X_3 = -\frac{1}{2}aT_4U_1^* + \frac{1}{4}bT_2^2U_1^* + bT_0T_2U_1$$

$$a = \frac{A\alpha_1}{1+A}, \quad b = \left(\frac{A\alpha_1}{1+A}\right)^2 - \frac{A\alpha_2}{1+A}$$

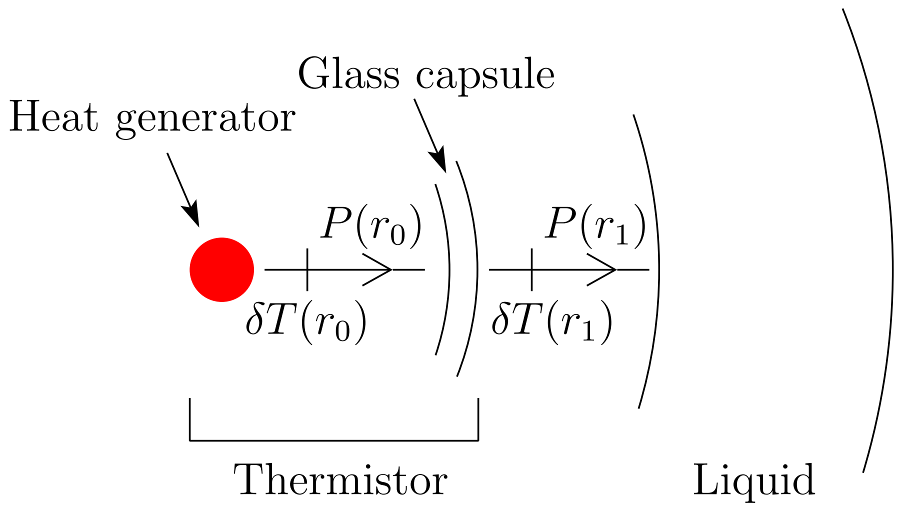
Measured thermal impedance

Small difference due to frequency dependent c_l



Dots: $T = 252.7K$, **Lines:** $T = 256.7K$

Thermal structure of the bead



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

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

Thermal transfer matrix description

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

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

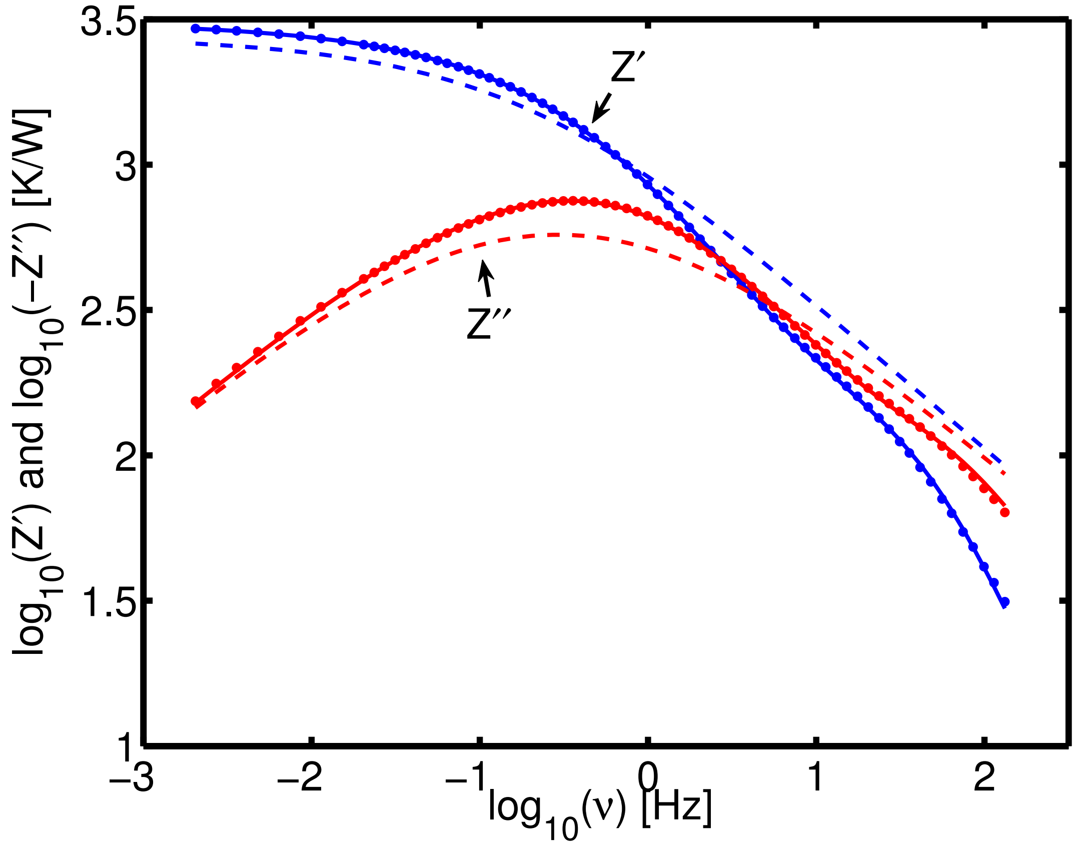
$$Z_{\text{liq}}(\omega) = \frac{1}{4\pi r_1\lambda\left(1+\sqrt{i\omega r_0^2 c_l(\omega)/\lambda}\right)}$$

Depends on λ_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



$T = 295.6K$

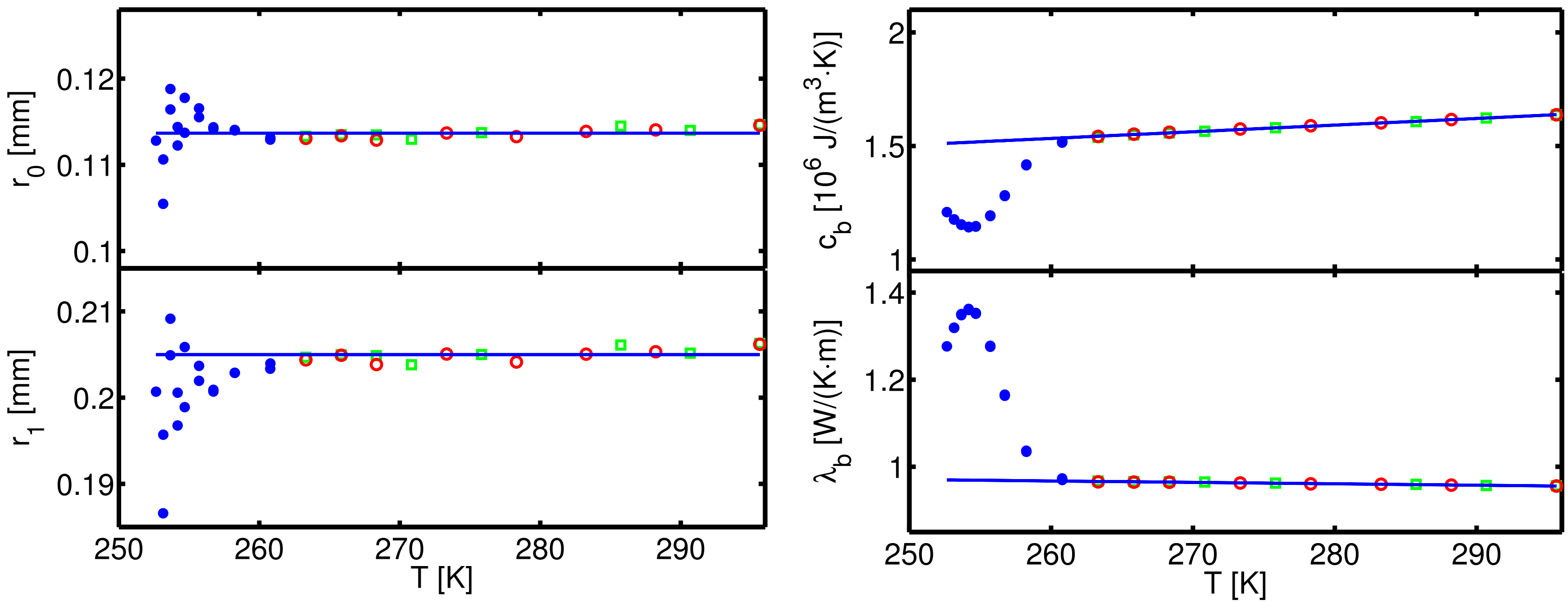
6 parameter fit:

Bead: λ_b, c_b, r_0, r_1

Liquid: λ, c_l

Characterization of the bead

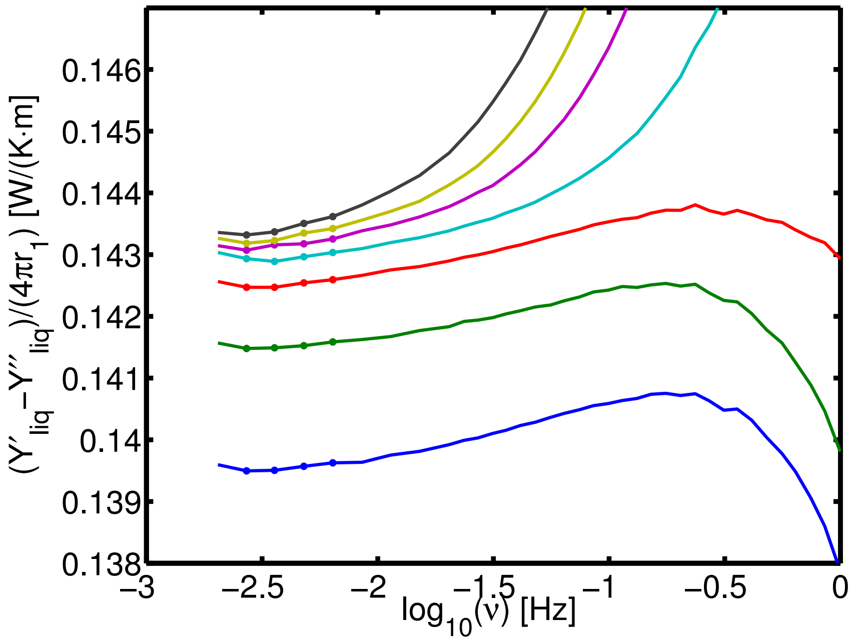
Calibration using temperatures where liquid is non-relaxing

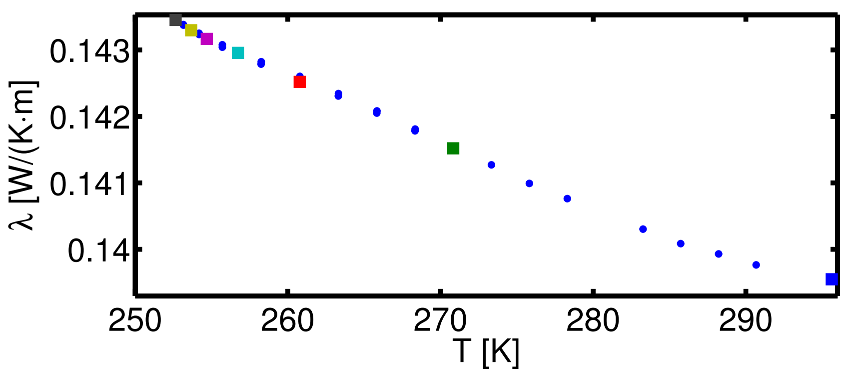


6 parameter fit:
Bead: λ_b, c_b, r_0, r_1
Liquid: λ, c_l

4 parameter fit:
Bead: λ_b, c_b
Liquid: λ, c_l

Thermal conductivity of the liquid





Thermal admittance:

$$Y_{\text{liq}} = 1/Z_{\text{liq}}$$

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

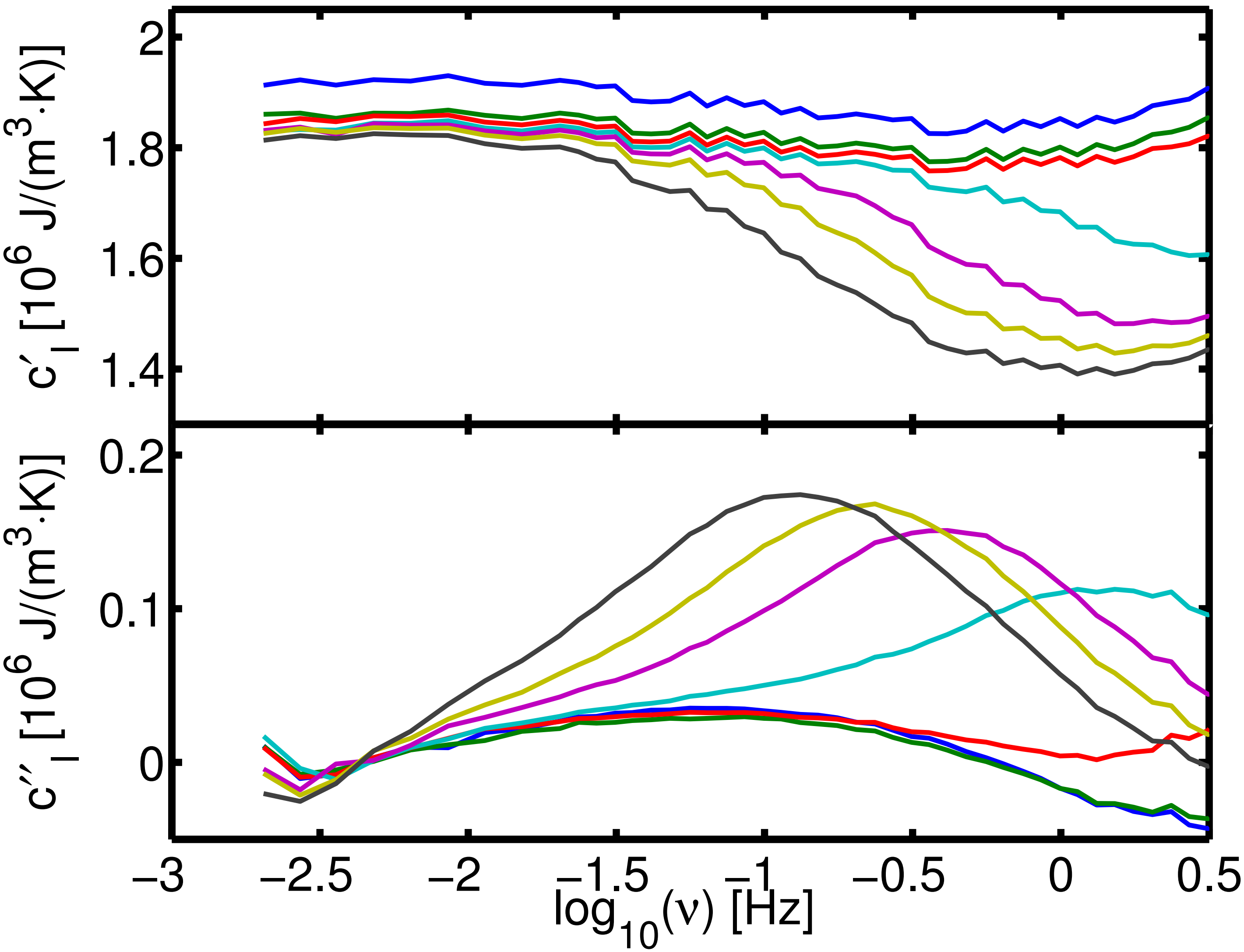
For c_l frequency independent

$$\lambda = \frac{Y'_{\text{liq}} - Y''_{\text{liq}}}{4\pi r_1}$$

Generally

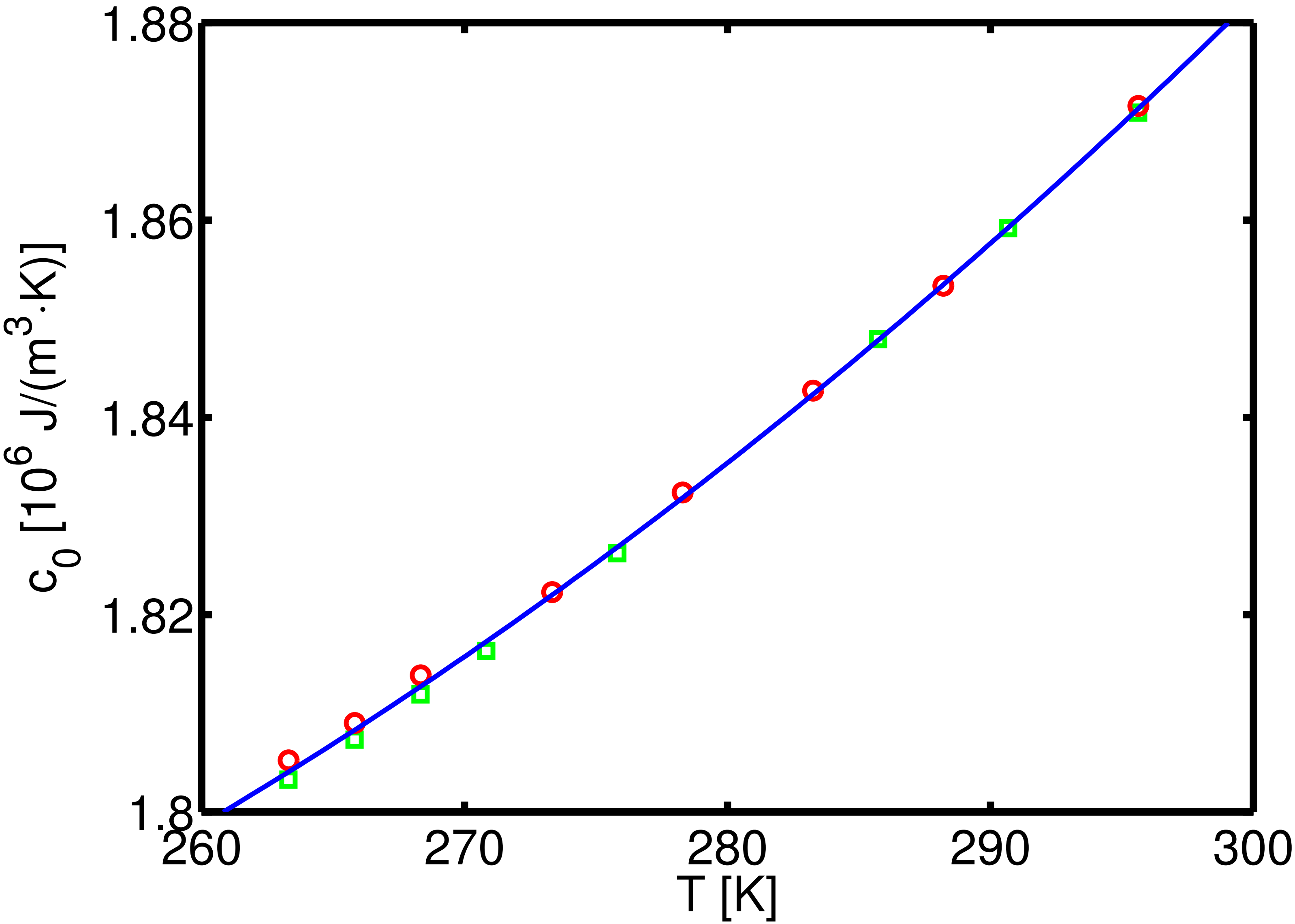
$$\frac{Y'_{\text{liq}} - Y''_{\text{liq}}}{4\pi r_1} \xrightarrow[\omega \to 0]{} \lambda$$

Longitudinal specific heat



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

DC specific heat



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

3ω technique

- 3ω 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:

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

(AIP Conf. Proc. 982, 139 (2008). arXiv:0710.5059v1)

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