Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2018

Supporting Information for:

Sub-μl measurements of the thermal conductivity and heat capacity of liquids

C. López-Bueno, D. Bugallo, V. Leborán, and F. Rivadulla*

Centro de Investigación en Química Biológica y Materiales Moleculares (CIQUS), Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain.

E-mail: f.rivadulla@usc.es

Solution of the Heat Equation

The 3ω method was originally developed by David Cahill[1] for the measurement of the thermal conductivity of solids, particularly of thin-films.[2] In this method, an AC current of frequency ω is driven along a narrow metallic line deposited on top of the sample under study (Fig. S1a)). The temperature distribution in the solid due to Joule heating can be obtained by solving the heat equation, whose expression in cylindrical coordinates is:

$$\frac{1}{D}\frac{\partial T(r,t)}{\partial t} - \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T(r,t)}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 T(r,t)}{\partial \theta^2} + \frac{\partial^2 T(r,t)}{\partial z^2}\right] = \frac{q(t)}{\kappa} \tag{1}$$

where D, and κ are the thermal diffusivity, the heating power and the thermal conductivity respectively. In the limit where the metal strip can be considered to be infinitely long and narrow, at a depth r ($l \gg r \gg \mathrm{w}$) the heat propagation can be considered to be cylindrical (Fig. S1b)). In this case the temperature function should not depend on θ and z:

$$\frac{1}{D}\frac{\partial T(r,t)}{\partial t} - \left(\frac{1}{r}\frac{\partial T(r,t)}{\partial r} + \frac{\partial^2 T(r,t)}{\partial r^2}\right) = \frac{q(t)}{\kappa} \tag{2}$$

The solution of this equation is proportional to the zeroth-order modified Bessel function (K_0)[3]:[4]

$$\Delta T(r) = \frac{P}{\pi l \kappa} K_0\left(\frac{r}{\delta}\right) \tag{3}$$

where δ is the penetration depth of the evanescent temperature wave:

$$\delta = \sqrt{\frac{D}{2i\omega}} \tag{4}$$

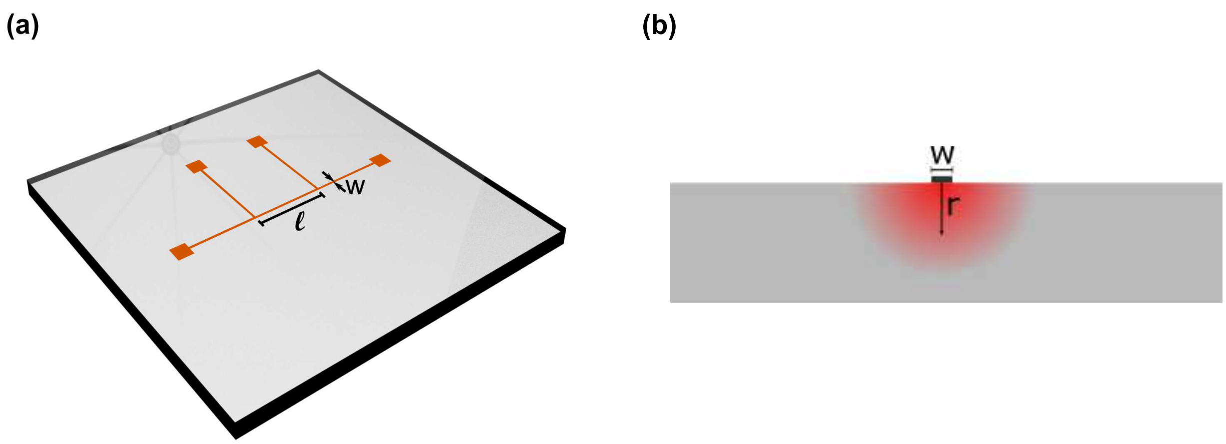

Figure S1: (a) Experimental setup for the measurement of the thermal conductivity of solids. A metallic line of width w and length l is deposited on top of the solid, and it is used as a heater and sensor. (b) Heat propagation through the solid in a perpendicular plane to the metallic strip, due to Joule heating.

In the limit where $r \ll \delta$, the Bessel function can be approximated by:

$$K_0\left(\frac{r}{\delta}\right) \simeq -\ln\left(\frac{r}{2\delta}\right) - \gamma \tag{5}$$

where $\gamma \simeq 0.5772$ is the Euler-Mascheroni constant. By introducing this approximation in the equation (3), the temperature oscillation can be expressed as follows:

$$\Delta T(r) \simeq \frac{P}{\pi l \kappa}\left[\ln(2) - \gamma + \frac{1}{2}\ln\left(\frac{D}{r^2}\right) - \frac{1}{2}\ln(2\omega) - \frac{i\pi}{4}\right] \tag{6}$$

This equation is the solution for an infinitely narrow line. However, the solution for a strip with a finite width w can be calculated as the convolution of many infinitely narrow heating lines along the width of the sensor. The spatial heat generation function can be expressed as a normalized rectangle function:

$$f_2(x) = \frac{\mathrm{rect}\left(\frac{x}{\mathrm{w}}\right)}{\mathrm{w}} \tag{7}$$

In order to perform the convolution of this function and the equation (3), it is convenient to move to the Fourier space, where the convolution of two functions is the product of their Fourier transforms. Then, the Fourier cosine transform of the Bessel function along the width direction (x) is:

$$\begin{aligned} f_1(k_x) =& \frac{P}{2\pi l \kappa}\int_0^\infty K_0\left(\frac{|x|}{\delta}\right)\cos(k_x x)dx = \\ =& \frac{P}{2\pi l \kappa}\int_0^\infty \left[\int_0^\infty \frac{\cos\left(\frac{|x|t'}{\delta}\right)}{\sqrt{t'^2+1}}dt'\right]\cos(k_x x)dx = \frac{P}{2\pi l \kappa\sqrt{k_x^2 + \left(\frac{1}{\delta}\right)^2}} \end{aligned} \tag{8}$$

And the transform of the spatial function (7) is:

$$f_2(k_x) = \int_0^\infty f_2(x)\cos(k_x x)dx = \frac{\sin\left(\frac{k_x \mathrm{w}}{2}\right)}{\frac{k_x \mathrm{w}}{2}} = \mathrm{sinc}\left(\frac{k_x \mathrm{w}}{2}\right) \tag{9}$$

Then, applying the convolution theorem and making the inverse Fourier transform, the temperature distribution created by the strip can be expressed as follows:

$$\Delta T(x) = \frac{P}{2\pi l\kappa}\int_0^{\infty} \frac{\text{sinc}\left(\frac{k_x \text{w}}{2}\right)\cos(k_x x)}{\sqrt{k_x^2 + \left(\frac{1}{\delta}\right)^2}} dk_x \tag{10}$$

Whose average provides the mean temperature measured by the strip:

$$\Delta T = \frac{2}{\text{w}}\int_0^{\text{w}/2} \Delta T_{strip}(x)dx = \frac{P}{\pi l\kappa}\int_0^{\infty} \text{sinc}^2\left(\frac{k_x \text{w}}{2}\right)\frac{1}{\sqrt{k_x^2 + \left(\frac{1}{\delta}\right)^2}} dk_x \tag{11}$$

The integral of the equation (11) does not have an analytic solution. However, in the limit where $\delta \gg \text{w}$, the sinc function can be approximated by 1 and the upper limit of the integral can be reduced to the inverse of the half-width of the strip, $1/b = 2/\text{w}$. On this limit, the solution can be rewritten as follows:

$$\begin{aligned} \Delta T &\simeq \frac{P}{\pi l\kappa}\int_0^{1/b} \frac{1}{\sqrt{k_x^2 + \left(\frac{1}{\delta}\right)^2}} dk_x = \frac{P}{\pi l\kappa}\ln\left[\sqrt{1+\left(\frac{\delta}{b}\right)^2} + \frac{\delta}{b}\right] \underbrace{\simeq}_{\delta \gg b} \\ &\simeq \frac{P}{\pi l\kappa}\left[\frac{1}{2}\ln\left(\frac{D}{b^2}\right) - \frac{1}{2}\ln(2\omega) + \ln(2) - \frac{i\pi}{4}\right] \end{aligned} \tag{12}$$

If we compare the equations (6) and (12), we can observe that they only differ in the Euler-Mascheroni constant. Therefore, we can express the solution of the temperature oscillations as a function of a constant (η) which should depend on the material.

$$\Delta T \simeq \frac{P}{\pi l\kappa}\left[\frac{1}{2}\ln\left(\frac{D}{b^2}\right) - \frac{1}{2}\ln(2\omega) + \eta - \frac{i\pi}{4}\right] \tag{13}$$

The 3ω voltage

For any resistance supporting an AC current at ω, self-heating by Joule effect produces a voltage at three times the input frequency (3ω), related to the temperature oscillations in the resistance. When we drive an AC current through the heater-sensor resistance (R), the dissipated power which develops due to the Joule effect is:

$$Q = I^2 R = I_0^2 \sin^2(\omega t) R = \frac{I_0^2 R}{2} [1 - \cos(2\omega t)] = P [1 - \cos(2\omega t)] \tag{14}$$

where I_0 is the amplitude of the AC current. This heating will produce a variation in the temperature, which has contributions of transient and oscillatory components. When the transient component reaches the equilibrium, the temperature oscillation (ΔT) can be expressed as follows:

$$\Delta T(r,t) = -\Delta T(r) \cos(2\omega t + \phi) \tag{15}$$

where ϕ is the difference of phase between the input current and the temperature wave. The effect of the self-heating in the resistance produces oscillations in its value. Therefore, according to Ohm's law, the voltage drop in the resistance can be expressed as:

$$\begin{aligned} V = I_0 \sin(\omega t) R = I_0 \sin(\omega t) \left(R_0 + \frac{dR}{dT} \Delta T(r) \cos(2\omega t + \phi) \right) = \\ = I_0 R_0 \sin(\omega t) + I_0 \frac{dR}{dT} \frac{\Delta T(r)}{2} \sin(\omega t + \phi) - I_0 \frac{dR}{dT} \frac{\Delta T(r)}{2} \sin(3\omega t + \phi) \end{aligned} \tag{16}$$

This equation shows that the value of ΔT, and consequently the thermal conductance of the sample, can be obtained by measuring the third harmonic of the voltage ($V_{3\omega}$):

$$V_{3\omega} = \frac{I_0 \frac{dR}{dT}}{2} \Delta T(r) \tag{17}$$

Therefore, we can obtain the thermal conductivity of the substrate from the slope of the $V_{3\omega}/V_{1\omega}$ vs $\ln(2\omega)$ plot:

$$\kappa = \frac{I_0^2 \frac{dR}{dT}}{4\pi l m} \tag{18}$$

where m is this slope.

Extension of the 3ω method for liquids

Chen et al.[5] solved the heat diffusion equation for the case where the metallic strip is placed between two semi-infinite media, a solid substrate and a fluid. Similar to equation (11), the solution of the heat equation when a liquid is placed over the heater line (ΔT_{s+l}) can be expressed as follows:

$$\Delta T_{s+l} = \frac{P}{\pi l}\int_0^\infty \text{sinc}^2\left(\frac{k_x \text{w}}{2}\right)\frac{1}{\kappa_s\sqrt{k_x^2+\left(\frac{1}{\delta_s}\right)^2}+\kappa_l\sqrt{k_x^2+\left(\frac{1}{\delta_l}\right)^2}}dk_x \tag{19}$$

where the subscripts s and l refer to the substrate and the liquid respectively. As in equation (11), the integral of this equation does not have an analytic solution. However, we can use the energy conservation principle and obtain an approximate solution of the equation. The power dissipated in the heater (P) must be the sum of the power dissipated both in the solid (P_s) and the liquid (P_l):

$$P = P_s + P_l \tag{20}$$

Now, we can assume that the solution for each media can be obtained independently from equation (13):

$$P = \frac{\Delta T_s \pi l \kappa_s}{\mathcal{H}_s(b/\delta_s)} + \frac{\Delta T_l \pi l \kappa_l}{\mathcal{H}_l(b/\delta_l)} \tag{21}$$

where $\mathcal{H}_j(x) = -\ln(x) + \eta_j$. Supposing that the temperature oscillations produced in both media are equal, $\Delta T_{s+l} \simeq \Delta T_s \simeq \Delta T_l$, the equation can be rewritten as:

$$\begin{aligned}\Delta T_{s+l} \approx & \frac{P}{\pi l}\left[\left(\frac{\kappa_s}{\mathcal{H}_s(b/\delta_s)}+\frac{\kappa_l}{\mathcal{H}_l(b/\delta_l)}\right)\right]^{-1} = \\ = & \left[\frac{P}{\pi l(\kappa_s+\kappa_l)}\mathcal{H}_l\left(\frac{b}{\delta_l}\right)\right]\left[1+\frac{\kappa_s}{\kappa_s+\kappa_l}\left(\frac{\mathcal{H}_l(b/\delta_l)}{\mathcal{H}_s(b/\delta_s)}-1\right)\right]^{-1}\end{aligned} \tag{22}$$

This equation shows that in the linear regime, the apparent thermal conductivity calculated from the slope of the $V_{3\omega}/V_{1\omega}$ $vs.$ $\ln(2\omega)$ plot should be the sum of the thermal conductivity of the solid and the liquid:

$$\kappa = \kappa_s + \kappa_l \tag{23}$$

Therefore, if the thermal properties of the substrate are known, the thermal conductivity of the liquid can be obtained.

In order to increase the sensitivity of the method, *i.e.* to increase the 3ω voltage with respect to the 1ω signal as much as possible, the dimensions of the line (particularly its width) must be properly optimized. The effect of line-width over the response of the sensor is shown in Figure S3 below.

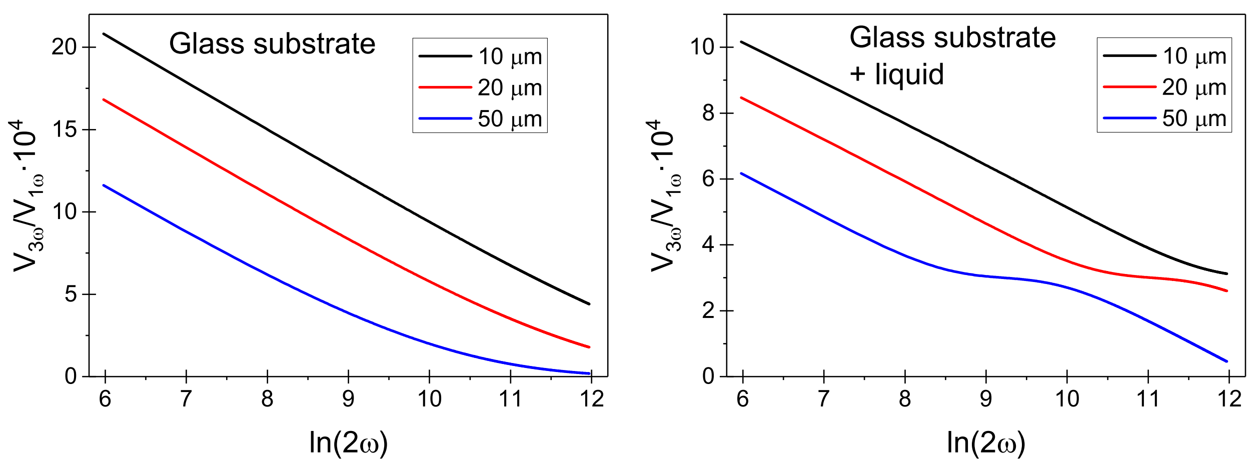

Figure S2: Frequency dependence of the 3ω voltage for different line widths, for a power of 5 mW. Increasing the width of the line produces a departure from the linear regime. This effect is more evident in the presence of liquid (right panel).

Heat Capacity of Liquids

The intercept of the $V_{3\omega}$ $vs.$ $\ln(2\omega)$ plot contains information about the thermal conductivity and heat capacity of the liquid and substrate. For obtaining the heat capacity of the liquid, accurate values of C and κ of the substrate must be derived from an independent measurement. The $\kappa(\mathrm{T})$ was obtained directly by the 3ω method in our setup. For the C we have used a PPMS from Quantum Design; see Fig. S3.

The experimental value of η was derived as the only fitting parameter of experimental $V_{3\omega}$ data of different substrates to equation (22). We observed an increase of η with thermal diffusivity $D = \kappa/(\rho C)$; see Fig. S3d).

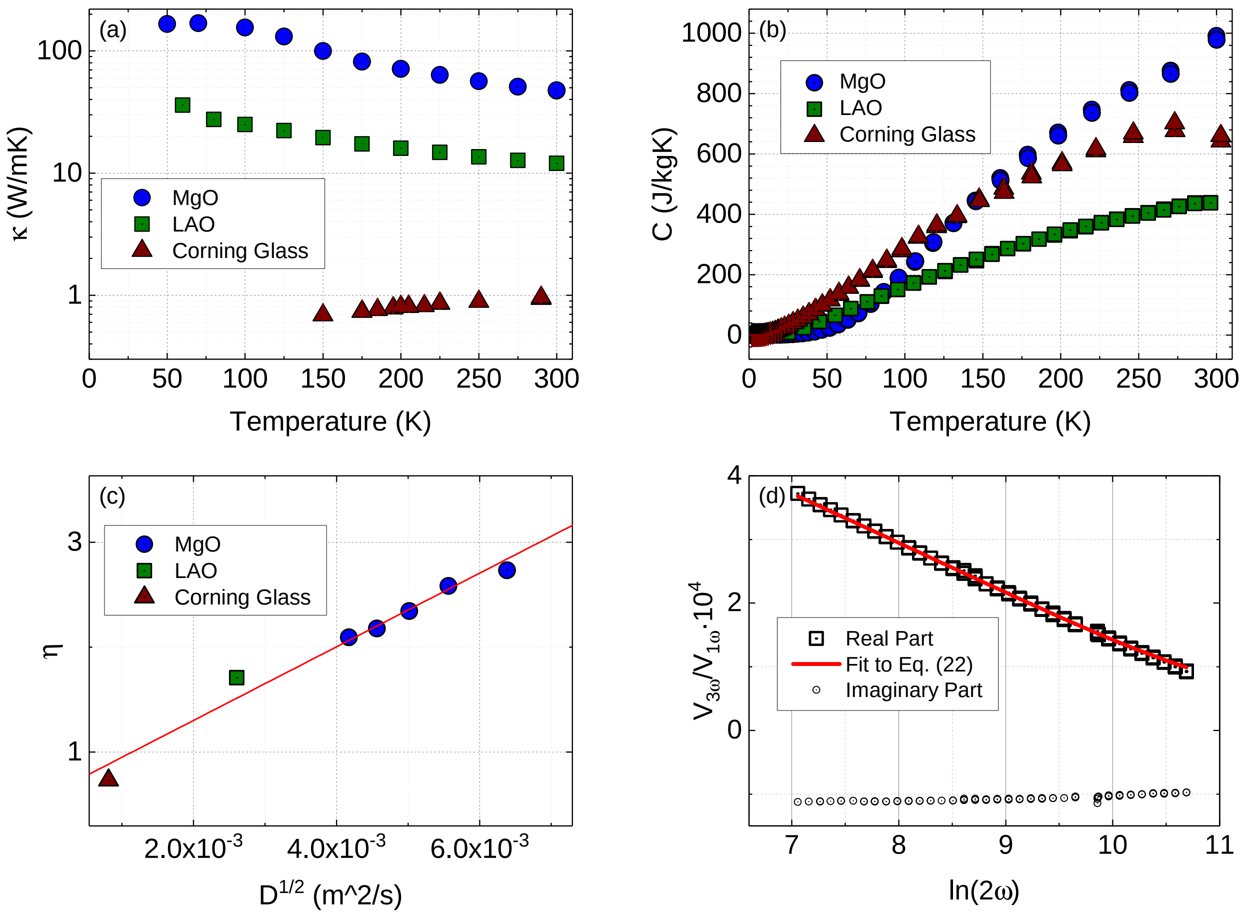

Figure S3: (a) Thermal conductivity of MgO, $LaAlO_3$ (LAO), and Corning® Glass in the temperature range 50-300K. (b) Heat Capacity of MgO, $LaAlO_3$, and Corning® Glass from 2K to 300K. (c) Dependence of the η on the square root of the thermal diffusivity: $\eta = a + bD^{1/2}$, where $a = 0.599 \pm 0.12$ and $b = 351 \pm 27\ s^{1/2}m^{-1}$. (d) Fit of the experimental data to equation (22) for $[MOIM][PF_6]$ on Corning® glass at 295K, from 56 to 2120 Hz.

This dependence of η must be the result of the difference between the solution of the equation (11):

$$\Delta T \propto \int_0^\infty \frac{\mathrm{sinc}(bx)}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} dx \tag{24}$$

and the approximation for a finite (but narrow) line:

$$\Delta T \propto \int_0^\infty \frac{1}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} dx \tag{25}$$

Therefore, the parameter η must be proportional to the difference between these two solutions:

$$\begin{aligned} \eta \propto \Delta &= \int_0^\infty \frac{1}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} dx - \int_0^\infty \frac{\mathrm{sinc}(bx)}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} dx = \\ &= \int_0^\infty \left[\frac{1}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} - \frac{\mathrm{sinc}(bx)}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} \right] dx \end{aligned} \tag{26}$$

and expanding the argument of the integral to first order:

$$\begin{aligned} \eta \propto \frac{1}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} - \frac{\mathrm{sinc}(bx)}{\sqrt{x^2 + \left(\frac{1}{\delta}\right)^2}} &= \cancel{\delta} - \frac{1}{2}\delta^3 x^2 + O(x^4) - \cancel{\delta} + \frac{(3\delta^2 + b^2)\delta}{6} x^2 + O(x^4) \simeq \\ \simeq \frac{\cancel{-3\delta^3} + \cancel{3\delta^3} + b^2\delta}{6} x^2 &= \frac{1}{6} b^2 \delta x^2 \propto \delta \propto D^{1/2} \Longrightarrow \eta \propto D^{1/2} \end{aligned} \tag{27}$$

This gives support to the dependence of η with $D^{1/2}$ found experimentally for different materials over a wide range of D (Fig. S3c)). The values of η also contain any instrumental contribution to this parameter in our setup.

Finally, once κ, C and η are determined for Corning® Glass, we can obtain the values of the heat capacity of the liquid from the intercept of the $V_{3\omega}$ *vs.* $\ln(2\omega)$.

References

(1) Cahill, D. G. *Review of Scientific Instruments* **1990**, *61*, 802–808.

(2) Lee, S.-M.; Cahill, D. G. *Journal of Applied Physics* **1997**, *81*, 2590–2595.

(3) Carslaw, H. S.; Jaeger, J. C. *Conduction of Heat in Solids*, 2nd ed.; Oxford University Press, USA, 1959.

(4) Villalba, F. In *Ph.D. Thesis*; de Barcelona, U., Ed.; Universitat de Barcelona, 2016; p 189.

(5) Chen, F.; Shulman, J.; Xue, Y.; Chu, C. W.; Nolas, G. S. *Review of Scientific Instruments* **2004**, *75*, 4578–4584.