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Thermal conductivity in the catalyst layer of hydrogen fuel cells

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Sveučilište u Splitu
Prirodoslovno-matematički fakultet
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Doktorski rad

Toplinska vodljivost katalitičkog sloja vodikovih gorivnih članaka

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Ph.D. thesis

**THERMAL CONDUCTIVITY IN THE CATALYST LAYER OF
HYDROGEN FUEL CELLS**

Anton Kabaši

Thesis performed at:

1. University of Split, Center of excellence for science and technology-Integration of Mediterranean region (STIM),
2. University of Split, Faculty of Science.

Abstract:

Local overheating in catalyst layers can reduce hydrogen fuel cell performance and durability, motivating ionomer films with improved thermal transport.

A deterministic two-dimensional inverse finite element method (FEM) was developed to account for the film–heater–substrate geometry in the 3ω response. Classical asymptotic and differential thermal resistance approximations in the literature do not describe the full response of intermediate thickness films over the investigated frequency range. The method was applied to determine the temperature dependence of thermal conductivity in dry Nafion films relevant to catalyst layers. Solution-cast films were deposited on sensors developed and calibrated in this work, then measured with an automated 3ω platform over a targeted operating range of 25–95 °C.

The thermal conductivity of dry Nafion was approximately $0.25 \text{ W m}^{-1} \text{ K}^{-1}$, with no resolvable temperature trend within the propagated uncertainty. The methodology also provides a theoretical framework for predicting defect effects and assessing their measurability within experimental uncertainty. Gas-phase water redistribution and membrane voids are predicted to be detectable under the modeled conditions, whereas the effect of a surface skin remains near the resolution limit. The combined experimental and numerical methodology provides a reproducible basis for studying modified Nafion and related films.

(154 pages, 102 figures, 24 tables, 76 references, original in English)

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TOPLINSKA VODLJIVOST KATALITIČKOG SLOJA VODIKOVIH GORIVNIH ČLANAKA

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Rad je izrađen u:

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Sažetak:

Lokalno pregrijavanje katalitičkih slojeva može smanjiti učinkovitost i trajnost vodikovih gorivnih članaka, zbog čega su potrebni ionomerni filmovi s boljim prijenosom topline.

Razvijena je deterministička dvodimenzijaska inverzna metoda konačnih elemenata (FEM), koja obuhvaća geometriju film–grijač–podloga i njezin utjecaj na odziv 3ω . Klasične asimp-totske i diferencijalne aproksimacije toplinskog otpora ne opisuju potpuni odziv filmova sred-njih debljina u istraženom frekvencijskom rasponu. Metoda je primijenjena za određivanje temperaturne ovisnosti toplinske vodljivosti suhih filmova Nafiona relevantnih za katalitičke slojeve. Filmovi iz otopine nanoseni su na razvijene i kalibrirane senzore te izmjereni autom-atiziranim platformom 3ω u ciljanom radnom rasponu 25–95 °C.

Toplinska vodljivost suhog Nafiona iznosila je približno $0.25 \text{ W m}^{-1} \text{ K}^{-1}$, bez razlučivoga temperaturnog trenda unutar propagirane mjerne nesigurnosti. Razvijena metodologija pruža i teorijski okvir za predviđanje utjecaja oštećenja te procjenu njihove mjerljivosti un-tar eksperimentalne nesigurnosti. Za preraspodjelu vodene pare u plinovitoj fazi i šupljine u membrani model predviđa mjerljiv odziv, dok je učinak površinskog sloja blizu granice ra-zlučivosti. Kombinirana eksperimentalna i numerička metodologija pruža ponovljivu osnovu za istraživanje modificiranog Nafiona i srodnih filmova.

(154 stranica, 102 slika, 24 tablica, 76 literaturnih navoda, jezik izvornika engleski)

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Ključne riječi: gorivni članci, vodik, nafion, polimerna elektrolitska membrana, 3 omega metoda, toplinska vodljivost

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ABSTRACT

Local overheating in catalyst layers can reduce hydrogen fuel cell performance and durability, motivating ionomer films with improved thermal transport.

A deterministic two-dimensional inverse finite element method (FEM) was developed to account for the film–heater–substrate geometry in the 3ω response. Classical asymptotic and differential thermal resistance approximations in the literature do not describe the full response of intermediate thickness films over the investigated frequency range. The method was applied to determine the temperature dependence of thermal conductivity in dry Nafion films relevant to catalyst layers. Solution-cast films were deposited on sensors developed and calibrated in this work, then measured with an automated 3ω platform over a targeted operating range of 25–95 °C.

The thermal conductivity of dry Nafion was approximately $0.25 \text{ W m}^{-1} \text{ K}^{-1}$, with no resolvable temperature trend within the propagated uncertainty. The methodology also provides a theoretical framework for predicting defect effects and assessing their measurability within experimental uncertainty. Gas-phase water redistribution and membrane voids are predicted to be detectable under the modeled conditions, whereas the effect of a surface skin remains near the resolution limit. The combined experimental and numerical methodology provides a reproducible basis for studying modified Nafion and related films.

List of Symbols and Acronyms

Symbols

The table lists the principal and repeatedly used symbols.

Symbol	Definition (units)
T	Temperature (K)
T_0	Initial equilibrium and linearization temperature (K)
$\vartheta = T - T_0$	Small temperature perturbation (K)
T_{av}	Mean heater temperature over one cycle (K)
ΔT_{DC}	Static heater temperature rise (K)
$\Delta T, \Delta T_{\text{pp}}$	Peak to peak temperature oscillation at 2ω (K)
$\Delta T_{2\omega}$	In phase temperature oscillation at 2ω (K)
$\tilde{T}_{2\omega}(\omega)$	Complex peak temperature response at 2ω (K)
$\bar{T}_{\text{heater}}(t)$	Spatially averaged heater temperature (K)
T_{bottom}	Prescribed bottom boundary temperature (K)
t	Time (s)
Δt	Numerical time step (s)
f	Electrical drive frequency (Hz)
$\omega = 2\pi f$	Angular frequency of the electrical drive (rad s^{-1})
$\Omega = 2\omega$	Angular frequency of Joule heating (rad s^{-1})
f_{min}	Lower frequency of the linear regime (Hz)
f_{max}	Upper frequency of the linear regime (Hz)
f_{linear}	Frequency within the selected linear regime (Hz)
$\phi_{2\omega}$	Thermal response phase ($^\circ$ or rad)
ϕ	Lock in phase used in the bridge balancing criterion ($^\circ$)
$I(t)$	Instantaneous drive current (A)
I_0	Peak drive current (A)
I_{rms}	RMS drive current (A)
ΔI	Change in LED light intensity during bridge balancing (—)
$V(t)$	Instantaneous voltage (V)
V_0	Peak heater voltage (V)
V_{rms}	RMS heater voltage (V)
$V_{1\omega, \text{rms}}$	Fundamental RMS voltage (V)
$V_{3\omega}$	Third harmonic voltage (V)

Continued on next page

Symbol	Definition (units)
$V_{3\omega,\text{rms}}$	RMS third harmonic voltage (V)
$V_{3\omega,\text{peak}}$	Peak third harmonic voltage (V)
$V'_{3\omega}$	In phase third harmonic component, $\text{Re } V_{3\omega}$ (V)
V_{heater}	RMS voltage across the heater (V)
V_{source}	Source voltage (V)
V_A	Voltage at Wheatstone bridge node A relative to ground (V)
V_B	Voltage at Wheatstone bridge node B relative to ground (V)
$V_{3\omega,\text{meas}}$	Measured third harmonic voltage (V)
$V_{3\omega,\text{corr}}$	Corrected third harmonic voltage (V)
$V_{\text{branch,meas}}$	Measured branch voltage (V)
$V_{\text{heater,true}}$	Corrected heater voltage (V)
$ \Delta V_{3\omega}(f) $	Difference between third harmonic amplitudes of two states (V)
X	Lock-in in-phase output (V)
Y	Lock-in quadrature output (V)
V_{mag}	Lock-in magnitude output (V)
R	Heater resistance (Ω)
R_0	Heater resistance at the stated operating point (Ω)
R_{heater}	Heater resistance used in the FEM power mapping (Ω)
R_1	Wheatstone bridge resistor (Ω)
R_2	Wheatstone bridge resistor (Ω)
R_4	Wheatstone bridge resistor (Ω)
R_{ext}	Equivalent external resistance (Ω)
R_p	Parasitic series resistance in the calibration correction (Ω)
β	Temperature coefficient of resistance (K^{-1})
$P(t)$	Instantaneous Joule power (W)
P_{mean}	Mean Joule power (W)
P_{RMS}	Mean Joule power calculated from RMS quantities (W)
P_{line}	Heater power per unit length (W m^{-1})
L	Heater length (m)
L_{heater}	Heater length used in the FEM source mapping (m)
w	Heater width (m)
b	Heater half width, $b = w/2$ (m)
W_{heater}	Heater width in the FEM source mapping (m)
H_{heater}	Heater height in the FEM source mapping (m)
t_{sub}	Substrate thickness (m)
t_{film}	Film thickness (m)
t_{skin}	Surface layer thickness (m)
A	Exposed surface area (m^2)
A_{heater}	Heater domain area (m^2)
A_{cs}	Conductor cross sectional area (m^2)
κ	Thermal conductivity; without a subscript, $\kappa_{\perp}$ ($\text{W m}^{-1} \text{K}^{-1}$)
$\boldsymbol{\kappa}$	Thermal conductivity tensor ($\text{W m}^{-1} \text{K}^{-1}$)
$\kappa_{\parallel}$	In plane thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

Continued on next page

Symbol	Definition (units)
$\kappa_{\perp}$	Through plane thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_m	Matrix thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_f	Filler thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{eff}	Effective thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{sub}	Substrate thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{glass}	Glass thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{film}	Film thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
$\hat{\kappa}_{\text{film}}$	Film thermal conductivity estimate from inversion ($\text{W m}^{-1} \text{K}^{-1}$)
$\hat{\kappa}$	Thermal conductivity estimate ($\text{W m}^{-1} \text{K}^{-1}$)
u_{κ}	Propagated standard uncertainty of the thermal conductivity estimate ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{Nafion}	Nafion thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
$\kappa_{\text{eff,system}}$	Effective thermal conductivity of the complete system ($\text{W m}^{-1} \text{K}^{-1}$)
$\kappa_{\text{eff,FEM}}$	Effective thermal conductivity obtained numerically ($\text{W m}^{-1} \text{K}^{-1}$)
$\kappa_{\text{eff,exp}}$	Effective thermal conductivity obtained experimentally ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{raw}	Thermal conductivity before the stated correction ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{corr}	Thermal conductivity after the stated correction ($\text{W m}^{-1} \text{K}^{-1}$)
$\kappa_{\text{H}_2\text{O}}$	Water thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{air}	Air thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{N_2}	Nitrogen thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{O_2}	Oxygen thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{H_2}	Hydrogen thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{sur}	Thermal conductivity of the numerical vacuum surrogate ($\text{W m}^{-1} \text{K}^{-1}$)
κ_{skin}	Surface layer thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
c_f	Filler volume fraction (—)
$c_{\text{H}_2\text{O}}$	Water volume fraction (—)
c_{gas}	Gas phase volume fraction (—)
$\Delta c_{f,\text{min}}$	Minimum resolvable filler fraction change (—)
$\Delta c_{\text{H}_2\text{O},\text{min}}$	Minimum resolvable water fraction change (—)
$\Delta c_{\text{gas},\text{min}}$	Minimum resolvable gas fraction change (—)
$\Delta t_{\text{skin},\text{min}}$	Minimum resolvable surface layer thickness change (m)
$\Delta \kappa_{\text{skin},\text{min}}$	Minimum resolvable surface layer thermal conductivity change ($\text{W m}^{-1} \text{K}^{-1}$)
p	Generic model parameter (units depend on the parameter)
$\Delta p_{\text{min,mean}}$	Mean minimum resolvable parameter change (units of p)
λ	Nafion hydration number (—)
ρ	Mass density (kg m^{-3})
c_p	Specific heat capacity at constant pressure ($\text{J kg}^{-1} \text{K}^{-1}$)
ρc	Volumetric heat capacity ($\text{J m}^{-3} \text{K}^{-1}$)
ρc_p	Volumetric heat capacity ($\text{J m}^{-3} \text{K}^{-1}$)

Continued on next page

Symbol	Definition (units)
$(\rho c)_{\text{skin}}$	Surface layer volumetric heat capacity ($\text{J m}^{-3} \text{K}^{-1}$)
α	Thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)
$\boldsymbol{\alpha}$	Thermal diffusivity tensor ($\text{m}^2 \text{s}^{-1}$)
α_{Naf}	Nafion thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)
q	Complex thermal wavenumber, $q = \sqrt{i\Omega/\alpha}$ (m^{-1})
q_x	Conductive heat flux component in the x direction (W m^{-2})
$\mathbf{q}$	Conductive heat flux vector (W m^{-2})
$\dot{q}$	Volumetric heat source density (W m^{-3})
q_{heater}	Heater volumetric source amplitude (W m^{-3})
δ	Thermal penetration depth, $\delta = q ^{-1}$ (m)
δ_s	Substrate thermal penetration depth (m)
δ_Ω	Thermal penetration depth at angular frequency Ω (m)
δ_{glass}	Glass thermal penetration depth (m)
δ_{Naf}	Nafion thermal penetration depth (m)
$A_{2\omega}$	Peak fitted temperature amplitude (K)
C	Mean value in the fitted temperature waveform (K)
$\Delta R_{2\omega}(t)$	Oscillatory resistance change at 2ω (Ω)
N_{pp}	Time steps per electrical period (—)
θ	Time integration weight (—)
a_T	Experimental logarithmic fit intercept (K)
b_T	FEM logarithmic fit intercept (K)
s	Signed slope of $\text{Re } V_{3\omega}$ versus $\ln(2\omega)$; $s < 0$ and $ s $ is its positive magnitude (V)
S	Signed slope of $\Delta T_{2\omega}$ with respect to $\ln(2\omega)$ (K)
S_T	Temperature response logarithmic slope (K)
$s_{T,\text{pp}}$	Peak to peak temperature logarithmic slope (K)
s_f	Bridge transfer scaling factor (—)
η	Cahill integration constant, approximately 0.923 (—)
$\eta_j(f)$	Normalized regional harmonic thermal power (%)
e	Thermal effusivity ($\text{J m}^{-2} \text{K}^{-1} \text{s}^{-1/2}$)
e_f	Film thermal effusivity ($\text{J m}^{-2} \text{K}^{-1} \text{s}^{-1/2}$)
e_s	Substrate thermal effusivity ($\text{J m}^{-2} \text{K}^{-1} \text{s}^{-1/2}$)
h	Combined heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
h_{conv}	Convective heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
h_{rad}	Radiative heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
T_s	Surface temperature (K)
T_∞	Bulk gas temperature (K)
T_{sur}	Surroundings temperature (K)
T_{avg}	Mean temperature used to linearize radiation (K)
ε	Emissivity (—)
σ	Stefan Boltzmann constant ($\text{W m}^{-2} \text{K}^{-4}$)
G_{rad}	Linearized radiative thermal conductance (W K^{-1})
G_{eff}	Effective conductive thermal conductance (W K^{-1})

Continued on next page

Symbol	Definition (units)
$\dot{Q}_{\text{conv}}$	Convective heat transfer rate (W)
$\dot{Q}_{\text{rad}}$	Radiative heat transfer rate (W)
$\dot{Q}_{\text{cond}}$	Conductive heat transfer rate (W)
$\dot{Q}_{\text{loss}}$	Total heat loss rate (W)
ρ_e	Electrical resistivity ($\Omega \text{ m}$)
$\mathcal{D}$	Two dimensional FEM computational domain
$\mathbf{M}$	FEM capacity matrix ($\text{J m}^{-1} \text{ K}^{-1}$)
$\mathbf{K}$	FEM thermal conductivity matrix ($\text{W m}^{-1} \text{ K}^{-1}$)
$\mathbf{Q}$	FEM load vector (W m^{-1})
$\mathbf{T}$	FEM nodal temperature vector (K)
$\mathbf{A}_{\text{CN}}$	Crank Nicolson update matrix ($\text{J m}^{-1} \text{ K}^{-1}$)
$\mathbf{B}_{\text{CN}}$	Crank Nicolson update matrix ($\text{J m}^{-1} \text{ K}^{-1}$)
$\mathcal{N}_{\text{heater}}$	Set of unique heater nodes
N_{heater}	Number of unique heater nodes (—)
$\mathbf{y}_{\text{FEM}}$	FEM observable (units of the selected observable)
S_{κ}	Sensitivity of the FEM observable to film thermal conductivity ($[\mathbf{y}]/[\kappa]$)
m	FEM mesh density factor (—)
$\tilde{P}'_{j,2\omega}$	Complex regional harmonic power per unit length (W m^{-1})
$\tilde{P}'_{\text{src},2\omega}$	Complex source harmonic power per unit length (W m^{-1})
S_n	Standard deviation over the most recent electrical period (K)
d_{mean}	Change in the periodic mean temperature metric (K)
d_S	Change in the periodic standard deviation (K)
r_{mean}	Relative tolerance for the mean temperature metric (—)
r_S	Relative tolerance for the periodic standard deviation (—)
ε_{abs}	Absolute convergence tolerance (K)
$\varepsilon_{\text{mean}}$	Dynamic mean temperature tolerance (K)
ε_S	Dynamic standard deviation tolerance (K)
$E(t)$	Thermal energy per unit out of plane length (J m^{-1})
$d_E(t)$	Relative thermal energy drift (—)
σ_x	Standard uncertainty associated with quantity x
ε_{RMS}	RMS relative FEM to Cahill deviation (%)

Note on q : plain q denotes the complex thermal wavenumber, q_x denotes a scalar heat flux component, and $\mathbf{q}$ denotes the heat flux vector.

Acronyms

Acronym	Meaning
3ω	3 omega thermal conductivity method
AC / DC	Alternating current / direct current
BNC	Bayonet Neill Concelman connector
CN	Crank Nicolson
CPU	Central processing unit
CUDA	Compute Unified Device Architecture
DI	Deionized
FEM	Finite element method
GPU	Graphics processing unit
HDF5	Hierarchical Data Format version 5
JSONC	JavaScript Object Notation with Comments
LED	Light emitting diode
LDR	Light dependent resistor
MEA	Membrane electrode assembly
PCB	Printed circuit board
PEMFC	Polymer electrolyte membrane fuel cell
PFSA	Perfluorosulfonic acid
PID	Proportional integral derivative control
PTFE	Polytetrafluoroethylene
PWM	Pulse width modulation
QCM	Quartz crystal microbalance
RMS	Root mean square
RMSE	Root mean square error
rpm	Revolutions per minute
sccm	Standard cubic centimetres per minute
SAXS	Small angle X ray scattering
SEM	Scanning electron microscopy
TCR	Temperature coefficient of resistance
TPS	Transient plane source
UV	Ultraviolet

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Chapter 1

INTRODUCTION

1.1 THERMAL MANAGEMENT IN FUEL CELLS

Polymer electrolyte membrane fuel cells (PEMFCs) are among the hydrogen technologies relevant to decarbonizing transport under the European Green Deal and the European Union hydrogen strategy [1]. In automotive applications operated under high, rapidly varying loads, heat generation in the membrane electrode assembly (MEA) can be intense and nonuniform [2]. Nafion, a perfluorosulfonic acid (PFSA) proton-conducting ionomer used as the membrane electrolyte in PEMFCs, has low thermal conductivity. The resulting thermal bottlenecks can contribute to local hot spots, dehydration, and long-term ionomer degradation during transient and cyclic operation [3, 4]. PEMFCs typically operate in the range of 60 to 100°C [5].

In addition to transient loads, PEMFC components experience repeated thermal cycling during start-stop operation, which contributes to mechanical and chemical degradation of the membrane and catalyst layers [3, 5]. Figure 1.1 is a qualitative illustration that highlights where low thermal conductivity regions concentrate thermal resistance in the cathode microstructure.

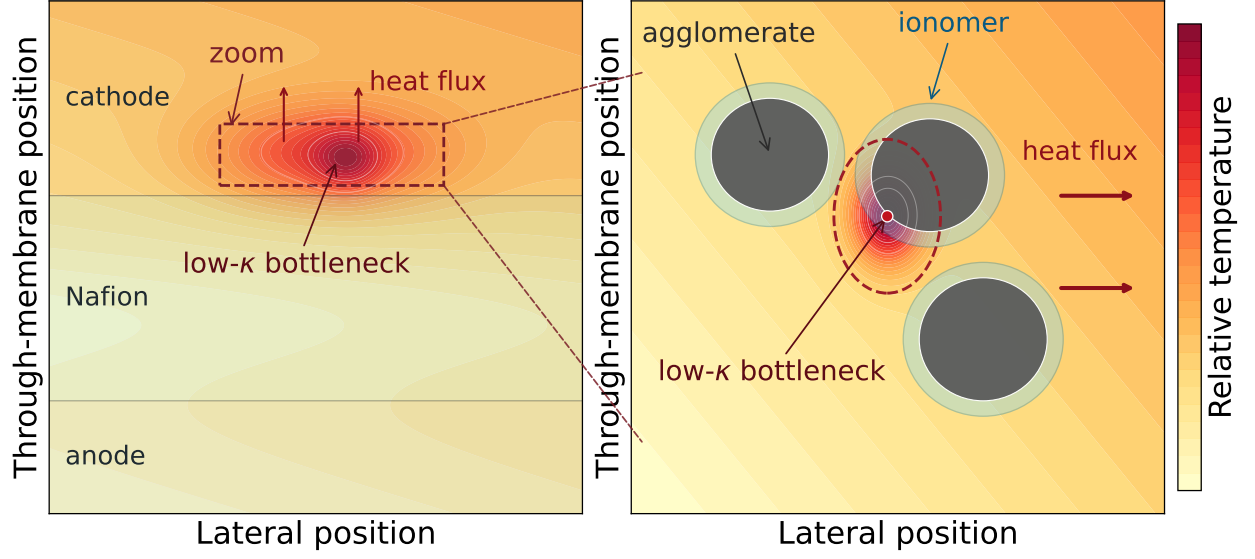


Figure 1.1: Cathode illustration showing low thermal conductivity ionomer regions near catalyst agglomerates that create local thermal bottlenecks and promote hotspot formation.

During operation, protons move through the ionomer matrix and water-rich domains, while heat transport remains limited by the low thermal conductivity of the ionomer. The thermally insulating matrix surrounding these domains forms thermal bottlenecks, illustrated in Figure 1.2 for a hydrated ionomer cross section. Measuring the thermal conductivity, κ , of thin, soft polymer films is difficult. Steady state methods suffer from radiative losses ($\propto T^4$), parasitic convection, and uncertain boundary conditions. Humidity and hydration state strongly affect thermal transport and contact resistances bias results unless explicitly modeled [6, 7]. In low- κ polymers (~ 0.1 to $0.3 \text{ W m}^{-1} \text{ K}^{-1}$), absolute uncertainty becomes critical because an error of 0.05 - $0.1 \text{ W m}^{-1} \text{ K}^{-1}$ can obscure or mimic the full magnitude of a weak temperature trend. For this reason, reliable $\kappa(T)$ requires controlled film state variables, in particular water content and boundary conditions.

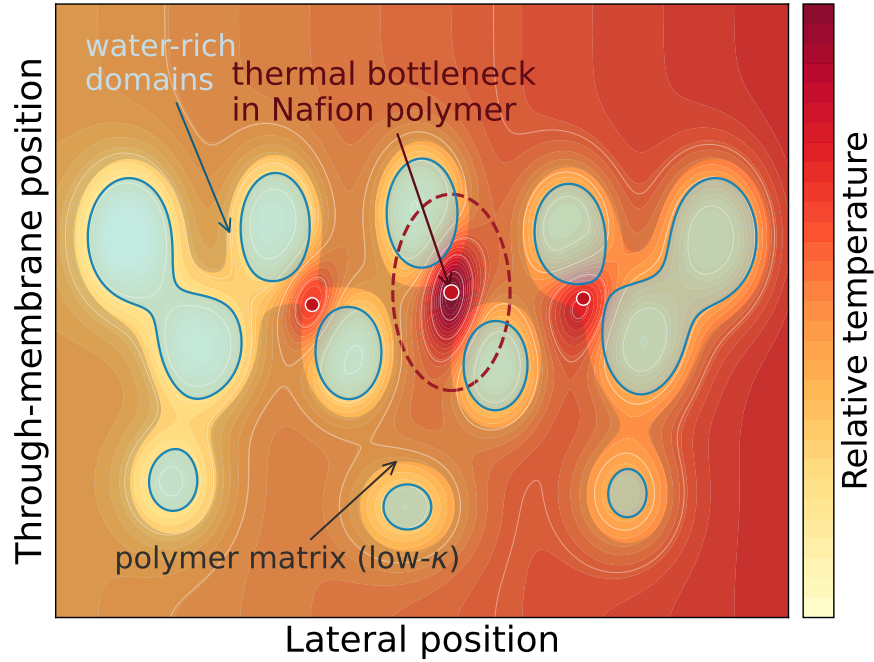


Figure 1.2: Hotspot development and thermal gradient amplification in low thermal conductivity ionomer regions.

The ionomer has a through-plane thermal conductivity of order $0.2 \text{ W m}^{-1} \text{ K}^{-1}$ [8], which is an order of magnitude below that of common glasses ($\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$) and many orders below metallic current collectors. The dry state value is close to that of polytetrafluoroethylene (PTFE), which forms the polymer backbone [9]. Thorough understanding of the thermal transport is lacking in the literature, and reported values vary widely with measurement method, sample state, and boundary conditions. This thermal bottleneck is an important contributor to local temperature gradients in the active area, which in turn drive dehydration and membrane and catalyst degradation.

Effective thermal management requires reliable values of the thermal conductivity κ .

1.2 NAFION

Nafion is a perfluorosulfonic acid (PFSA) polymer with a comb-like molecular architecture in which numerous perfluorinated ether side chains extend from long hydrophobic PTFE backbones and terminate in strongly acidic sulfonic acid groups. In the membrane, the hydrophobic backbone chains become entangled and provide mechanical robustness and chemical stability. Upon hydration, the terminal sulfonic acid groups dissociate, while their affinity for water drives the formation of interconnected, water-rich ionic nanodomains within the fluorinated matrix. These domains provide pathways for proton transport across the membrane [3, 10, 11, 12]. Small-angle X-ray scattering (SAXS) supports this phase-separated description through electron density contrast between the ionic domains and the surrounding fluorinated matrix [3, 10]. Figure 1.3 schematically illustrates a single branch, or “tooth,” of this comb-like architecture: a segment of the hydrophobic PTFE backbone is highlighted in blue, the perfluorinated ether side chain in purple, and its terminal sulfonic acid group in

yellow.

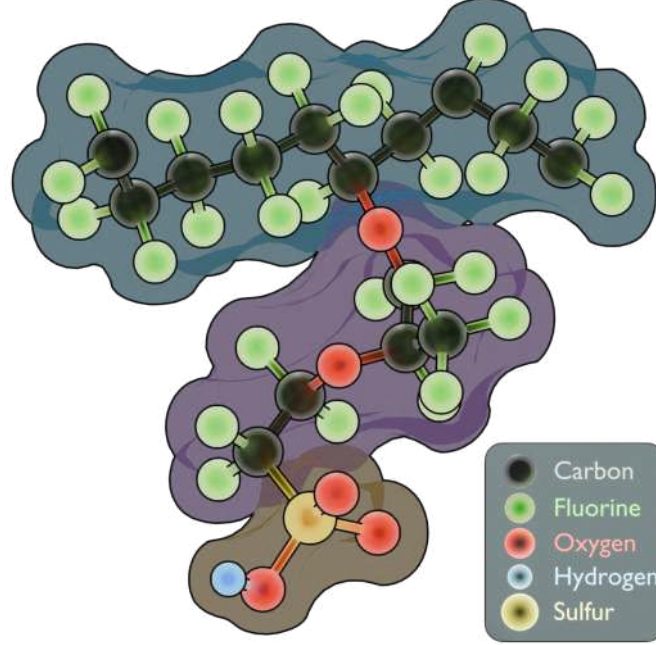


Figure 1.3: Schematic representation of a single branch, or “tooth,” of the comb-like Nafion molecular architecture. The shaded regions identify a segment of the hydrophobic PTFE backbone (blue), a perfluorinated ether side chain (purple), and its terminal sulfonic acid group (yellow).

Nafion has many positive properties that make it ideal for application inside PEMFCs. It combines high proton conductivity, electrical insulation, and thermal and chemical stability, making it the most widely used ionomer for low temperature fuel cells [3, 5]. The membrane efficiently conducts protons from anode to cathode while blocking electrons, thus enforcing electron flow through the external circuit. At the same time, its low thermal conductivity and its transport properties depend strongly on hydration. These properties are coupled, so to determine the thermal conductivity reliably, the film state must be controlled.

Nafion is a phase-separated ionomer whose transport properties depend strongly on water content. Hydration governs the connectivity and volume fraction of hydrophilic domains and therefore alters proton transport. It can also modify heat transport through changes in morphology and local composition. Reported thermal conductivity trends with temperature are difficult to interpret unless hydration is explicitly controlled, because the water uptake itself can vary with temperature and ambient conditions [3, 11, 12, 13]. For this reason, the present work focuses on dry state Nafion films measured in vacuum and treats hydration dependent transport as out of scope. In other words, without controlling water content, an apparent $\kappa(T)$ trend may reflect a changing film state. Nafion hydration is commonly quantified by the hydration number

$$\lambda = \frac{n_{\text{H}_2\text{O}}}{n_{\text{SO}_3\text{H}}}, \quad (1.1)$$

where $n_{\text{H}_2\text{O}}$ is the amount of water and $n_{\text{SO}_3\text{H}}$ is the amount of sulfonic acid sites. Thus, λ

represents the average number of water molecules per sulfonic acid site. Figure 1.4 contrasts an illustrative low-hydration state with a higher hydration state.

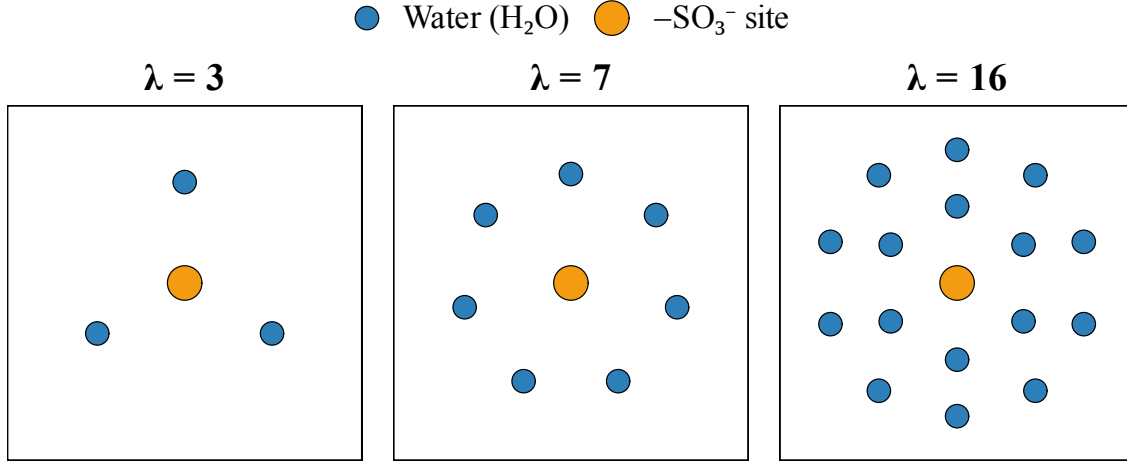


Figure 1.4: Schematic representation of the Nafion hydration number λ . The value $\lambda = 3$ is used here as an illustrative low hydration state, while $\lambda = 16$ represents a higher hydration state. [14].

At the catalyst-layer scale, Figure 1.5 shows a scanning electron microscopy (SEM) image of a small Pt/C–Nafion agglomerate from a catalyst–ionomer mixture prepared in collaboration with Krešimir Dželalija, PhD. The sample represents a carbon-supported Pt catalyst mixed with a Nafion solution. Its highly ramified, porous morphology is qualitatively apparent at the micrometre scale and provides a large accessible surface relative to the volume of the agglomerate. In a catalyst layer, this high surface-to-volume ratio increases the interfacial area available for electrochemical reactions. During operation, protons generated at the anode are transported through the hydrated ionomer and across the Nafion membrane, while electrons are conducted through the interconnected carbon support and into the external circuit. Membrane thickness is a key design parameter because it sets a trade-off between ionic transport and durability - thinner membranes reduce the proton transport length and typically lower ohmic losses, whereas thicker membranes improve mechanical robustness and resistance to degradation [15, 16, 17].

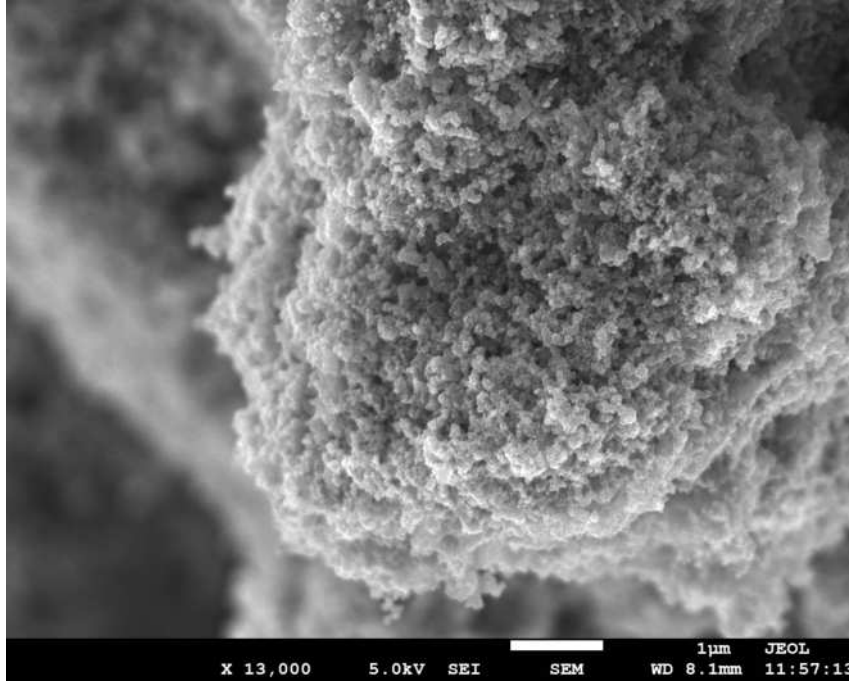


Figure 1.5: Scanning electron micrograph of a small Pt/C–Nafion agglomerate, showing the highly ramified and porous morphology of the catalyst–ionomer mixture.

1.3 THERMAL CONDUCTIVITY OF NAFION

Existing measurements characterize thick commercial Nafion 115 ($\sim 127\mu\text{m}$). Many studies lack controlled humidity, so $\kappa(\lambda)$ is only coarsely estimated [8]. Consequently, weak reported temperature trends remain difficult to separate from hydration-dependent changes.

Beyond direct thermal conductivity extraction, PEMFC literature has repeatedly linked thermal behavior with system efficiency, electrochemical degradation, and lifetime. These results support the need for thermal property measurements with explicit uncertainty control because small thermal conductivity bias can propagate into durability and performance predictions [18, 19, 20].

Studies of flow-field design and water distribution show that channel geometry and spatial variations in local transport influence thermal load distribution across the active area. This is another reason to treat boundary condition control as a primary requirement in low thermal conductivity film measurements [2, 21, 22, 23]. Complementary transport studies in fluoropolymer fuel cell materials and nanoscale heat transport methodology further motivate controlled state metrology for Nafion type systems [24, 25, 26, 27].

Steady state approaches are compromised by radiative losses at elevated T and by uncertain boundary conditions in thin films [7]. A transient, frequency domain method of thermal thermal conductivity measurement of highly insulating films, the 3ω method, is widely used in the literature and offers a route to mitigate these bias channels. Cahill demonstrated the 3ω method for thermal conductivity measurements from 30 to 750 K [28]. Because the method uses small temperature oscillations and frequency dependent slope information, it can reduce radiative and boundary condition bias relative to steady state approaches when the measurement window is properly modeled. Reported values also depend on measure-

ment geometry. Studies variously probe through-plane or in-plane transport, and in thin films apparent κ can depend on thickness because boundary conditions, contact resistances, and lateral heat spreading contribute differently across methods and sample formats [7, 29]. The major contributors for systematic error in thermal conductivity measurements of insulators at high temperature that motivate the methodology choices in later chapters are summarized in Figure 1.6.

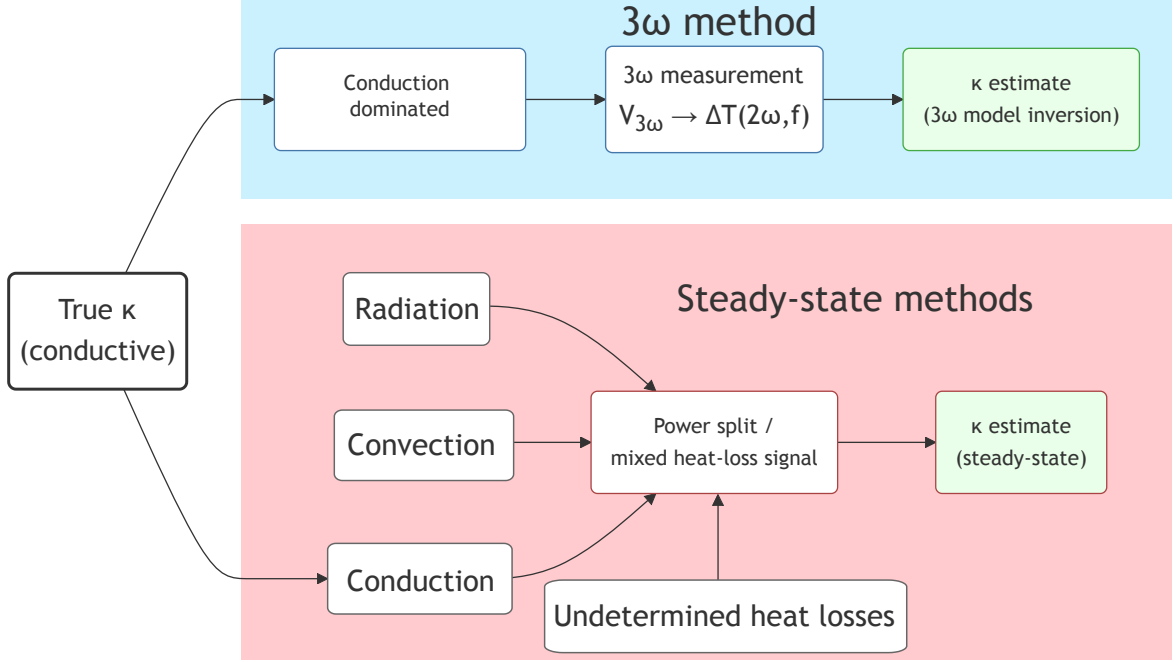


Figure 1.6: Schematic comparison of elevated temperature thermal conductivity measurements.

Steady-state methods may measure a mixed heat signal containing conduction, radiation, convection, and undetermined losses, while the 3ω method estimates κ from the measured third harmonic voltage $V_{3\omega}$ through model inversion described later in the text.

Atomistic and molecular dynamics studies provide a consistent qualitative picture that hydration is the dominant state variable in Nafion nanostructure and transport [3, 11, 30]. At fixed hydration, moderate temperature changes have only a slight effect on morphology, while increasing hydration enlarges and connects hydrophilic domains that define continuous transport pathways [11, 12]. This means that apparent experimental $\kappa(T)$ trends can be biased if hydration is not tightly controlled, because λ can drift with ambient conditions and with temperature during measurement. Hydration focused studies therefore often use gravimetric control by weighing the polymer before and after conditioning or measurement to estimate water uptake. Within the literature surveyed for this thesis, several reports suggest that Nafion thermal conductivity decreases slightly with temperature over the fuel cell operating range, whereas the present 3ω measurements on dry films under vacuum are consistent with a temperature-independent value within experimental uncertainty.

A decreasing trend, if intrinsic and sufficiently strong, would reduce local heat spreading and increase temperature gradients, which could accelerate long-term hot-spot driven degradation. It does not necessarily imply rapid thermal runaway because the thermal response

in an operating cell is also governed by heat removal and by the time evolution of reaction rates and water management. Among the studies reviewed here, no study performs elevated-temperature thermal conductivity sweeps while actively controlling hydration in situ [6, 7, 8]. Gravimetric protocols constrain an average water content, but they do not fully capture hydration changes during acquisition of the thermal signal. For this reason, the scope of the present thesis and immediate follow-up work is restricted to dry-state Nafion films under vacuum, where hydration coupling is suppressed and the working hypothesis is that κ is approximately constant over a moderate temperature interval.

1.4 ON THICKNESSES

For clarity, this thesis adopts the working definitions summarized in Table 1.1. The depositable Nafion layers studied here are referred to as *films*. In this thesis, films thinner than 1 μm are termed thin films, while films of 1 μm or greater are termed microfilms. The Nafion films used here are in the tens of micrometers range, so they are not in the classical ultrathin/thin differential limit regime for the 3ω methodology.

The studied Nafion lies in the thick film range by geometry. For 3ω analysis, the physically relevant classification is set by the film thickness relative to the thermal penetration depth δ , which depends on the material properties and modulation frequency. This relationship and its implications for the Nafion films studied here are discussed in Section 2.3.

The two stack geometries relevant to this thesis are heater-film-substrate and film-heater-substrate. Published analytical and semi-analytical reductions rely on assumptions about layer order, thermal thickness, heater dimensions, and boundary conditions [31, 32, 33, 34, 35]. In the classical heater-film-substrate geometry, reduced interpretations are commonly used in limiting cases, including ultrathin films ($t_{\text{film}} \ll \delta$) and quasi-bulk interlayers ($t_{\text{film}} \gg \delta$). In the film-heater-substrate geometry, reduced approaches can also be practical for thermally thick coatings in the selected band, including bidirectional-style limits [35].

Because Nafion processing is constrained by fabrication chemistry and lithography process compatibility is challenging, this thesis adopts the film-heater-substrate geometry to ensure pristine Nafion films are measured.

The Nafion case considered in this thesis lies in the thermally intermediate regime ($t_{\text{film}} \sim \delta$) over the relevant measurement frequencies. For the present film-heater-substrate geometry and frequency range, the numerical length-scale and forward-response evidence developed in this thesis shows that neither a thermally thin series-resistance reduction nor a thermally thick half-space reduction represents the complete response over the analyzed band. The analysis therefore employs a geometry-aware finite element model (FEM) coupled with inverse parameter extraction. This is the specific methodological gap addressed in this thesis: a calibrated, uncertainty-aware interpretation path for intermediate thickness polymer films in the real deposited stack. The supporting numerical evidence and validation are given in Chapter 2 and Section 3.4. The resulting workflow determines κ without forcing the present geometry into a limiting analytical approximation.

Table 1.2 gives a general classification applicable to any film, provided that the material-dependent thermal penetration depth is evaluated at the measurement frequency. The Nafion films studied in this thesis lie in the thermally intermediate regime. For the present geometry and measurement frequency range, neither limiting closed-form approximation represents the

Table 1.1: Practical Nafion film thickness classification used in this thesis and its implications for 3ω analysis over the measurement frequency range.

Film scale	Thickness range	Implication for 3ω analysis
Ultrathin	1 to 10 nm	Interfacial thermal resistance can strongly affect the result.
Thin	10 nm to 1 μm	Standard thin film approximations are generally suitable.
Microfilm	1 to 10 μm	Film thickness may need to be included in the analysis.
Thick	10 to 100 μm	Film thickness usually needs to be included in the analysis.
Bulk-like	$\geq 100 \mu\text{m}$	Approaches bulk-like behavior over the measurement frequency range.

Table 1.2: General thermal regimes for film analysis based on the ratio of film thickness t_{film} to thermal penetration depth δ .

Regime	Criterion	Typical 3ω approach
Thermally thin film	$t_{\text{film}} \ll \delta$	Differential 3ω analysis, in which the film is treated as an added thermal resistance [32, 36, 37].
Thermally intermediate finite-thickness film	$t_{\text{film}} \sim \delta$	For the geometry studied here, the complete multi-layer response is evaluated with a geometry-aware forward model.
Thermally thick layer	$t_{\text{film}} \gg \delta$	Classical Cahill analysis for a semi-infinite medium, provided that the measurement geometry satisfies its assumptions [28].

complete response. Nafion spans a wide thickness range in practice, from nanometer scale ionomer films in catalyst layer microstructures to commercial membrane products in the tens to hundreds of micrometers range. At nanometer scale, catalyst layer ionomer films are reported in interface sensitive morphology studies [15, 38, 39]. At membrane scale, solution cast PFSA families are commonly in the 25 to 210 μm range [40]. Extrusion cast PFSA families are commonly in the 127 to 254 μm range [41]. PEMFC trade-off studies frequently compare membrane thickness windows between 25 and 183 μm , where reduced ohmic loss, crossover risk, and durability must be balanced [16, 17].

Although bidirectional 3ω approaches are compatible with the film-heater-substrate geometry, their demonstrated applicability is primarily limited to comparatively thick, bulk-like coatings [35]. They are therefore less suitable for the intermediate thickness Nafion films studied here.

1.5 RESEARCH GAP

In this work we develop and validate an *inverted* 3ω approach in which microfabricated metal strip heaters on glass act as sensors while Nafion is deposited *on top* of the heater as a droplet of controlled volume. Operating in vacuum suppresses convection and promotes a controlled dry-state condition [3, 42]. The analysis relies on a narrowly defined frequency

window, and calibration is performed on reference substrates that serve as calibrated thermal conductivity sensors for the Nafion film deposited on top.

In the classical 3ω method, the frequency response provides high sensitivity to κ through the slope of the in-phase temperature rise as a function of $\ln(2\omega)$. Conventional thin film implementations often require lithography directly on the sample [28, 36, 37, 43], which is problematic for chemically sensitive ionomers and motivates an inverted geometry where the polymer is deposited last. Chip-based bidirectional sensing approaches [35] are closely related but are typically designed for laterally large and thermally thick samples. Feuchter et al. investigated an even more closely related bottom-heater geometry using time-domain FEM for bulk-like materials and thin covering layers [34]. Their inverse evaluation used a neural network trained on a database of FEM responses to map measured temperature amplitudes to thermal conductivity. In contrast, the present work treats the complete intermediate thickness multilayer geometry and extracts thermal conductivity by directly matching measurements to deterministic FEM predictions, without machine-learning or surrogate inference.

The principal methodological contribution comprises the deterministic extraction of thermal conductivity and the development of a physics-based predictive framework for the inverted 3ω geometry. The same validated FEM model is used to solve the inverse thermal conductivity problem, quantify uncertainty, and prospectively assess whether changes in Nafion microstructure, composition, or defect state produce experimentally resolvable thermal signatures. This capability extends the method from property extraction to measurement design and feasibility analysis, providing a foundation for future studies of Nafion composites and other heterogeneous dielectric films.

1.6 OBJECTIVES AND CONTRIBUTIONS

The primary objective of this thesis is to establish a complete experimental and numerical framework for determining the through-plane thermal conductivity of dry Nafion films using the inverted 3ω geometry. Particular emphasis is placed on films in the thermally intermediate regime, where neither thin-film nor bulk-limit analytical approximations provide a reliable interpretation. A further objective is to use the validated framework predictively to determine whether changes in Nafion microstructure, composition, and defect state can be resolved experimentally.

The contributions of this thesis, both scientific and methodological, listed in order of appearance in the thesis, are:

1. A reproducible lithographic process was established for fabricating metal microheaters with controlled geometries suitable for inverted 3ω measurements and consistent with the assumptions used in substrate calibration.
2. An automated inverted 3ω measurement system was developed for stable microvolt-level measurements under vacuum. The system incorporates automated bridge balancing, dense frequency sweeps, and calibration and validation on soda-lime glass with an uncertainty below 2%. The experimentally validated frequency range extends beyond the conservative analytical bounds commonly used for the classical method. The corresponding derivation is provided in Appendix B. This contribution has been published in [44], reproduced in Appendix D.

3. A geometry-aware FEM framework and deterministic inverse methodology were developed for extracting thermal conductivity in the film-heater-substrate geometry. Unlike approaches that use machine-learning surrogates to invert FEM-generated databases, the present method directly matches measurements to predictions of the physics-based forward model and includes explicit uncertainty propagation.
4. The methodology extends quantitative 3ω analysis to the thermally intermediate regime $t_{\text{film}} \sim \delta$. This regime lies between the thin-film and bulk-like limits addressed by established analytical reductions and requires the complete multilayer geometry to be represented.
5. The methodology was applied to depositable dry Nafion films, yielding a through-plane thermal conductivity of approximately $0.25 \text{ W m}^{-1} \text{ K}^{-1}$. No statistically resolvable temperature dependence was observed over the available inversion range from 32.60 to 95.19°C within the quantified measurement uncertainty.
6. The validated FEM framework was extended from inverse property extraction to predictive sensitivity and feasibility analysis. Mean-field representations of composite structure, voids, flooding, and degraded surface layers were used to determine the thermal contrasts and defect states that produce resolvable changes in the 3ω response.

These contributions form three connected research outputs: an experimentally validated automated 3ω platform, a deterministic methodology for thermal conductivity extraction from intermediate thickness Nafion films, and a predictive framework for assessing the measurability of Nafion microstructure, composites, and defect states. The first of these outputs has already been published [44] and the latter two provide the basis for subsequent publications.

Chapter 2

THEORY

This chapter establishes the theoretical framework used to interpret 3ω measurements in this thesis. It first introduces heat diffusion in the linear small-signal regime and defines the material properties governing the frequency-domain thermal response. It then develops the classical 3ω formulation for a line heater on a semi-infinite substrate following Cahill [28], including the sequence from electrical heating to the measured voltage and the conditions required for log-linear thermal conductivity extraction. The thermal penetration depth and the frequency range used for substrate calibration are then examined. Finally, the chapter discusses the limitations of analytical reductions in multilayer geometries and introduces the uncertainty propagation used in thermal conductivity extraction.

2.1 HEAT CONDUCTION AND THERMAL DIFFUSION

In practical systems the net heat flux comprises multiple channels. It is useful to think of the total heat flow as a sum of conductive, radiative, and convective contributions, with their relative importance set by temperature, geometry, and environment [32]. Under oscillatory heating, the temperature response penetrates only a finite distance into the material. This confines the thermally active region and makes the response primarily sensitive to conductive heat transport. Radiative and convective losses are treated as surface contributions and their significance is assessed relative to conduction over the selected frequency range [32].

For small temperature changes about an operating point T_0 , material properties may be treated as constant to first order. The temperature field then obeys the transient heat equation [45]

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\boldsymbol{\kappa} \nabla T) + \dot{q}, \quad (2.1)$$

where $\dot{q}$ is the volumetric heat generation rate. In this thesis, heat generation is confined to the metallic strip, and the surrounding solids are treated as passive media that conduct and store heat. Heat conduction is considered classical and diffusive, so non-Fourier effects are neglected. The thermal conductivity $\boldsymbol{\kappa}$ is treated as a constant tensor over the small temperature variations considered in the linear analysis.

The constitutive relation underlying this equation is Fourier's law. In one dimension, the

conductive heat flux is

$$q_x = -\kappa \frac{dT}{dx}, \quad (2.2)$$

where q_x denotes the heat-flux component in the x -direction in watts per square metre, κ denotes the thermal conductivity in watts per metre kelvin, and dT/dx denotes the temperature gradient in kelvin per metre. In vector form the linear relation reads $\mathbf{q} = -\kappa \nabla T$ for isotropic media. In thin polymer films, processing and confinement can make thermal transport direction dependent. Fourier's law is then written as $\mathbf{q} = -\boldsymbol{\kappa} \nabla T$. When the two in-plane directions are equivalent but transport normal to the film differs, the thermal conductivity tensor takes the transversely isotropic form

$$\boldsymbol{\kappa} = \text{diag}(\kappa_{\parallel}, \kappa_{\parallel}, \kappa_{\perp}), \quad (2.3)$$

where $\kappa_{\parallel}$ is the in-plane thermal conductivity and $\kappa_{\perp}$ is the through-plane thermal conductivity. Throughout this thesis, the symbol κ without a subscript denotes the through-plane component $\kappa_{\perp}$, defined as the thermal conductivity normal to the film surface. The inverted 3ω configuration used here yields this through-plane component from the slope of the in-phase 3ω response with respect to $\ln(2\omega)$. Measurement of the in-plane component requires a different heater and sensor arrangement, such as the bridge configuration described by Dames [32], and is outside the scope of this thesis. The through-plane component is of primary interest because heat removal normal to the membrane is the most relevant transport direction in an operating fuel cell.

Polymers are generally electrical insulators, so the dominant thermal carriers are vibrational excitations. In amorphous and semicrystalline polymers, structural disorder, chain conformation, interfaces, and defects limit the propagation of these excitations, which generally produces a lower κ than in highly ordered crystalline solids [26].

For bulk anisotropic materials, the full thermal conductivity tensor need not be transversely isotropic. Principal directions and off-diagonal terms may matter. Extracting the complete tensor generally requires multiple measurement geometries and is outside the scope of the present Nafion film measurements, for which the film is treated as transversely isotropic [32, 46].

The small-signal approximation used throughout the analysis is

$$\kappa(T) \approx \kappa(T_0) \equiv \kappa, \quad R(T) \approx R_0(1 + \beta \vartheta), \quad \vartheta \equiv T - T_0, \quad |\vartheta| \ll T_0. \quad (2.4)$$

Here $R(T)$ is the heater resistance at temperature T , β is the heater temperature coefficient of resistance in K^{-1} , and R_0 is heater resistance at the linearization temperature T_0 . Under these conditions the governing heat conduction relation is the linear scalar form $\mathbf{q} = -\kappa \nabla T$ with κ treated as constant over small temperature variations. The small-signal approximation ensures that the thermal response remains linear in the applied heating power and can be characterized by a single thermal conductivity at the operating temperature.

Thermal diffusivity and penetration depth.

Thermal diffusivity measures how quickly temperature disturbances spread relative to the medium's ability to store heat. In the linear regime it is defined as

$$\alpha = \frac{\kappa}{\rho c_p}, \quad (2.5)$$

which reduces to $\alpha = \kappa/(\rho c_p)$ for isotropic media, where ρ is the mass density and c_p is the specific heat capacity at constant pressure. Periodic heating at angular frequency Ω introduces the thermal length scale

$$\delta_\Omega = \sqrt{\frac{\alpha}{\Omega}}. \quad (2.6)$$

In this thesis, δ_Ω is called the thermal penetration depth. It is a characteristic measure of how far the periodic temperature variation extends from the heat source. Higher heating frequencies confine the response closer to the source, while lower frequencies probe farther into the material. Here Ω denotes the angular frequency of the applied heating. Its relation to the electrical drive frequency is established in the 3ω derivation below.

Thermal conductivity can be measured by steady-state, transient, and frequency-domain methods. Steady-state approaches are conceptually simple but become difficult for thin films because thermal contact resistances and parasitic losses can dominate the signal. Transient and frequency-domain methods operate with smaller temperature fluctuations and provide internal consistency checks through time or frequency scaling. The 3ω method used in this thesis is well matched to thin and intermediate thickness films on substrates because it provides on-chip electrical heating and temperature measurement and can be performed under vacuum with small ΔT . A qualitative method comparison used to motivate this selection is given in Table 2.1.

Steady-state methods determine thermal conductivity from a time-independent heat balance. Frequency-domain methods determine it from the response to periodic heating. In the 3ω method, the substrate thermal conductivity is obtained from the slope of the in-phase response versus $\ln(2\omega)$ over the frequency range in which this relation is linear.

Table 2.1: Comparison of selected thermal property methods for thin films.

Method	Strengths	Limitations for thin films
Transient plane source (TPS)	Measures thermal diffusivity and thermal conductivity in one experiment.	Requires good sensor contact. The substrate response can dominate for thin films.
Laser flash	Rapidly measures through-plane thermal diffusivity.	Requires ρc_p to calculate thermal conductivity. Coatings or multilayer analysis may be needed.
3ω (this work)	Uses one metal strip for heating and temperature measurement. The response is sensitive to thin films.	Requires microfabrication and a model that includes the heater geometry and substrate.

2.2 CLASSICAL 3ω METHOD

This thesis uses the inverted 3ω configuration to measure the through-plane thermal conductivity of Nafion films in the thermally intermediate regime. The metal strip is fabricated on the glass substrate before Nafion is deposited and acts as both the heater and resistance thermometer. This avoids direct lithographic processing of Nafion and permits small temperature oscillations. The vacuum environment used in this thesis suppresses gas-phase heat transfer and establishes the intended dry measurement condition.

The classical solution developed in this section is used for bare substrate calibration and for establishing frequency-domain validity checks. It is not used to extract the Nafion thermal conductivity directly. After coating, the heater–film–substrate stack is interpreted using numerical forward modelling and inverse estimation.

Alternative 3ω extraction strategies are also used in the literature, notably differential amplifier readout without a bridge [46, 47]. The present work focuses on a balanced Wheatstone bridge architecture because it suppresses the fundamental component at the detector input and enables robust automation under vacuum operation. In this implementation the bridge balancing element is driven by pulse-width modulation (PWM) at a carrier frequency far above the analysis band. The control path is optically isolated from the alternating-current (AC) measurement path, and out of band content at the carrier is rejected by narrowband lock-in detection at $3f$ ($\omega = 2\pi f$, where f is the electrical drive frequency) [44]. The 16-bit Arduino Timer1 implementation is provided in Appendix C, while the complete published system description is reproduced in Appendix D.

2.2.1 Signal generation and electrical measurement

Figure 2.1 shows the microheater geometry used in the measurements. A narrow metal strip of length L and width $w = 2b$ is patterned on the substrate and contacted through separate current and voltage leads. The strip acts simultaneously as the heat source and resistance thermometer, so the electrical observable and the local thermal response originate from the same element.

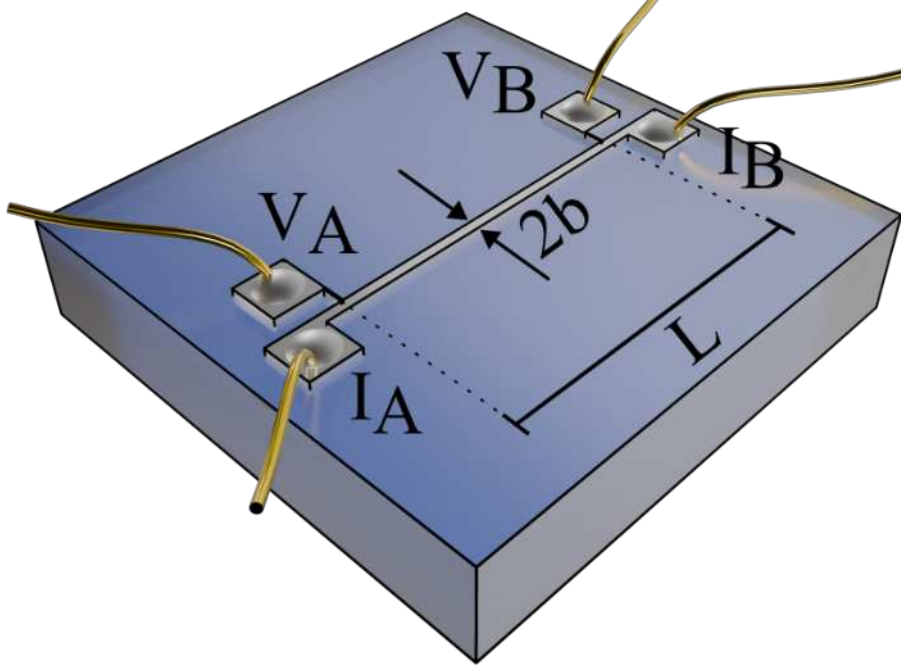


Figure 2.1: Microheater geometry and four-terminal electrical connections. The metal strip of length L and width $w = 2b$ acts as both heater and resistance thermometer.

We denote the electrical drive frequency by f (Hz) and angular frequency by $\omega = 2\pi f$. Joule heating oscillates at the thermal angular frequency $\Omega \equiv 2\omega$.

For sinusoidal electrical excitation, Joule heating contains an oscillatory component at 2ω . The sample does not respond instantaneously throughout its volume. The temperature oscillation decays with distance from the heater and also becomes progressively phase shifted. This thesis uses the complex thermal wavenumber

$$q = \sqrt{\frac{i\Omega}{\alpha}} \quad (2.7)$$

to describe these two features with a single parameter. Its real part sets the spatial attenuation, while its imaginary part sets the phase delay. The thermal penetration depth used throughout this thesis is defined as

$$\delta \equiv |q|^{-1} = \sqrt{\frac{\alpha}{\Omega}} = \sqrt{\frac{\alpha}{2\omega}} = \sqrt{\frac{\alpha}{4\pi f}}. \quad (2.8)$$

Figure 2.2 illustrates the corresponding amplitude decay, and Figure 2.3 shows the accompanying phase lag. In both figures, the heater lies on the top substrate surface at $z = 0$, and positive z denotes depth into the substrate. Heater width is defined as w and half width as b . All instrument readings (lock-in, source measure unit, multimeter) are root-mean-square (RMS) values and are denoted by I_{rms} and V_{rms} . The average electrical power calculated from these RMS quantities is

$$P_{\text{RMS}} = I_{\text{rms}}^2 R = \frac{V_{\text{rms}}^2}{R}.$$

For sinusoidal current excitation, this value is also the peak amplitude of the oscillatory Joule power component at 2ω . The derivation below is written directly in RMS form. In

this thesis, ΔT denotes the AC temperature oscillation at 2ω in peak to peak form. That is, $\Delta T \equiv \Delta T_{AC,pp}$. The corresponding peak amplitude is $A_{2\omega} = \Delta T/2$, and the corresponding RMS thermal amplitude is $\Delta T/(2\sqrt{2})$. At the electrical frequencies used here, skin depth in the metal heater is much larger than the heater thickness, so current crowding through thickness is negligible and uniform Joule heating is a valid approximation. The methodology measures the frequency response of the thermal amplitude, with each excitation frequency treated as a separate measurement point. The result is a set of complex thermal response amplitudes across the selected frequency band.

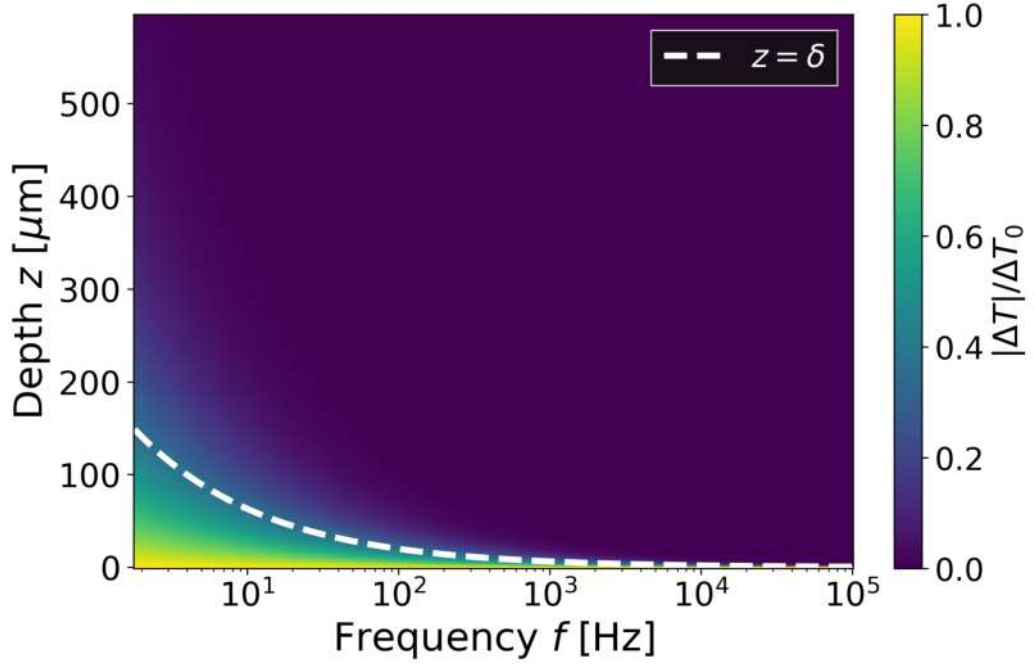


Figure 2.2: Normalized thermal wave amplitude as a function of depth and excitation frequency. The dashed curve marks the thermal penetration depth $z = \delta$.

The phase lag increases with distance from the heater.

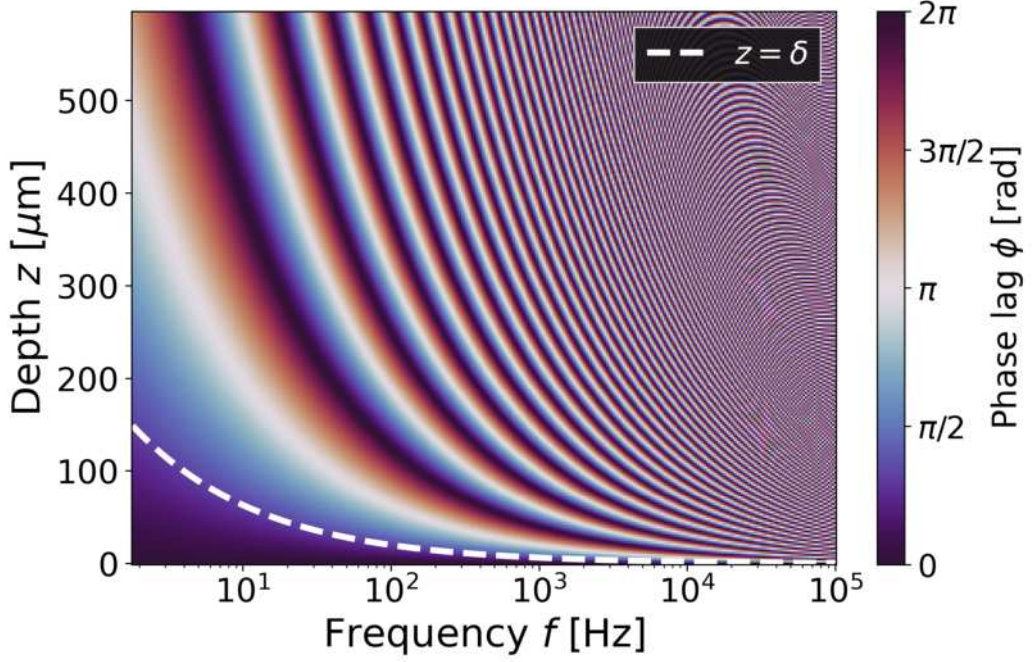


Figure 2.3: Wrapped phase of the oscillatory temperature response as a function of depth and excitation frequency, relative to the heater excitation. Increasing lag with depth visualizes the diffusive delay. The dashed curve marks $z = \delta$. Phase values far beyond this curve correspond to strongly attenuated amplitudes and are shown only to illustrate the mathematical continuation.

Drive at ω and heating at 2ω .

The heater is driven with a sinusoidal current

$$I(t) = \sqrt{2} I_{\text{rms}} \cos(\omega t). \quad (2.9)$$

The dissipated power is quadratic in the current,

$$P(t) = I^2(t)R = 2I_{\text{rms}}^2 R \cos^2(\omega t) = P_{\text{RMS}} [1 + \cos(2\omega t)], \quad (2.10)$$

with

$$P_{\text{mean}} = P_{\text{RMS}} = I_{\text{rms}}^2 R = \frac{V_{\text{rms}}^2}{R}. \quad (2.11)$$

The mean component produces the static temperature rise, while the 2ω component drives the thermal wave that is detected at 3ω . The full signal sequence from electrical drive to thermal response and electrical readout is represented in Figure 2.4.

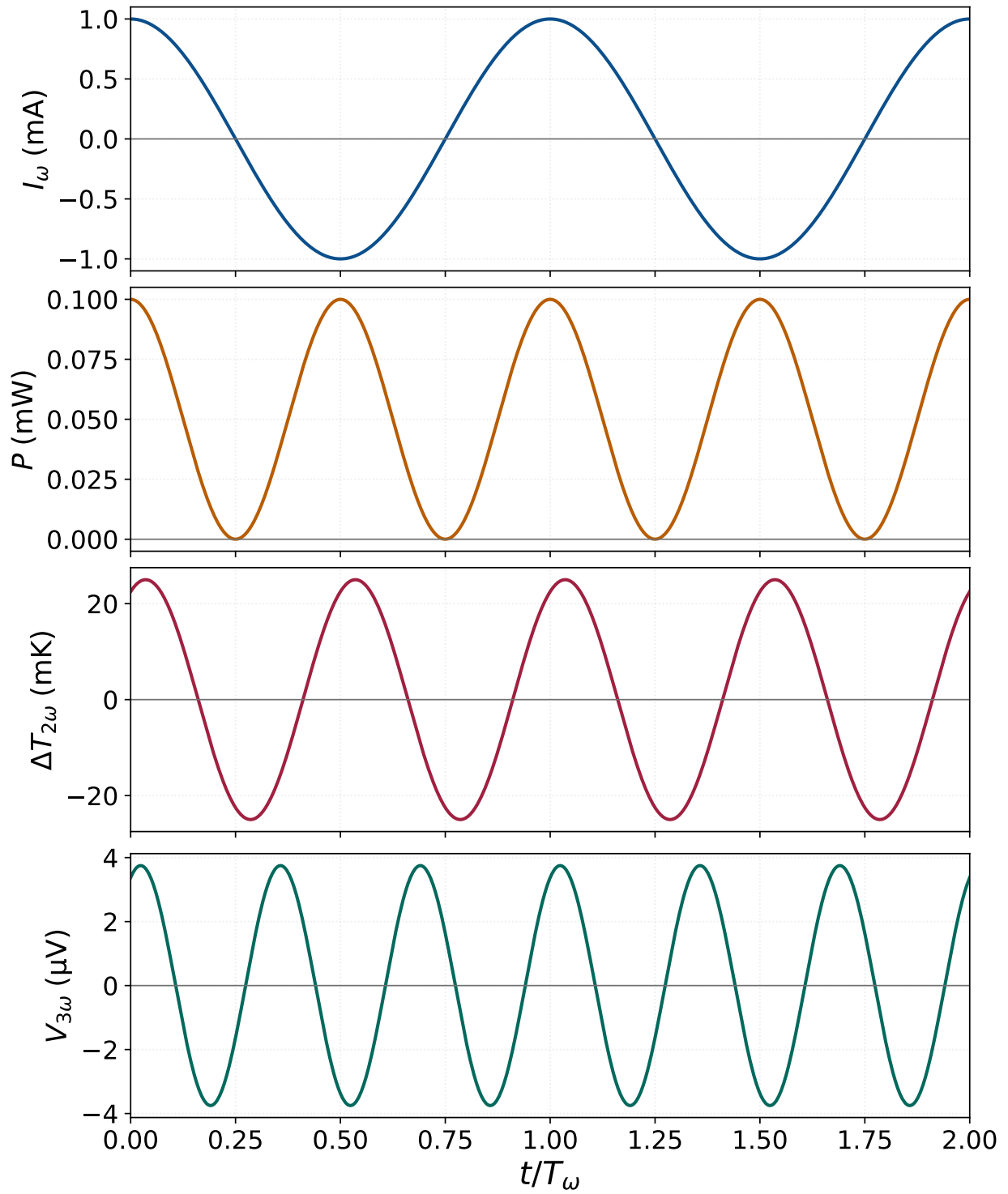


Figure 2.4: Signal generation in the 3ω method: drive at ω , Joule heating at 2ω , thermal oscillation at 2ω , and voltage response at 3ω .

Temperature oscillation and resistance modulation.

In periodic steady state, the heater temperature consists of a time-independent mean temperature and an oscillatory component at 2ω ,

$$T(t) = T_{\text{av}} + \frac{\Delta T}{2} \cos(2\omega t + \phi_{2\omega}), \quad (2.12)$$

where T_{av} is the mean heater temperature over one cycle, ΔT is the peak to peak AC oscillation, and $\phi_{2\omega}$ is the thermal phase.

When the AC current is first applied, Joule heating raises the temperature of the metal strip above that of the surrounding materials. Heat then flows from the strip into the surrounding materials. As the temperature difference increases, the rate of heat transfer away from the strip also increases. The system eventually reaches periodic steady state, where the cycle-averaged Joule power equals the cycle-averaged heat flow away from the heater.

Only the small oscillatory component at 2ω couples to the 3ω signal used in the analysis. The direct-current (DC) component sets the operating point about which the response is linearized. This decomposition into mean and oscillatory parts is illustrated in Figure 2.5. Here T_0 is the initial equilibrium temperature of the heater and its local surroundings before the current is applied and the linearization temperature used for R_0 and β . The periodic operating temperature is $T_{\text{av}} = T_0 + \Delta T_{\text{DC}}$.

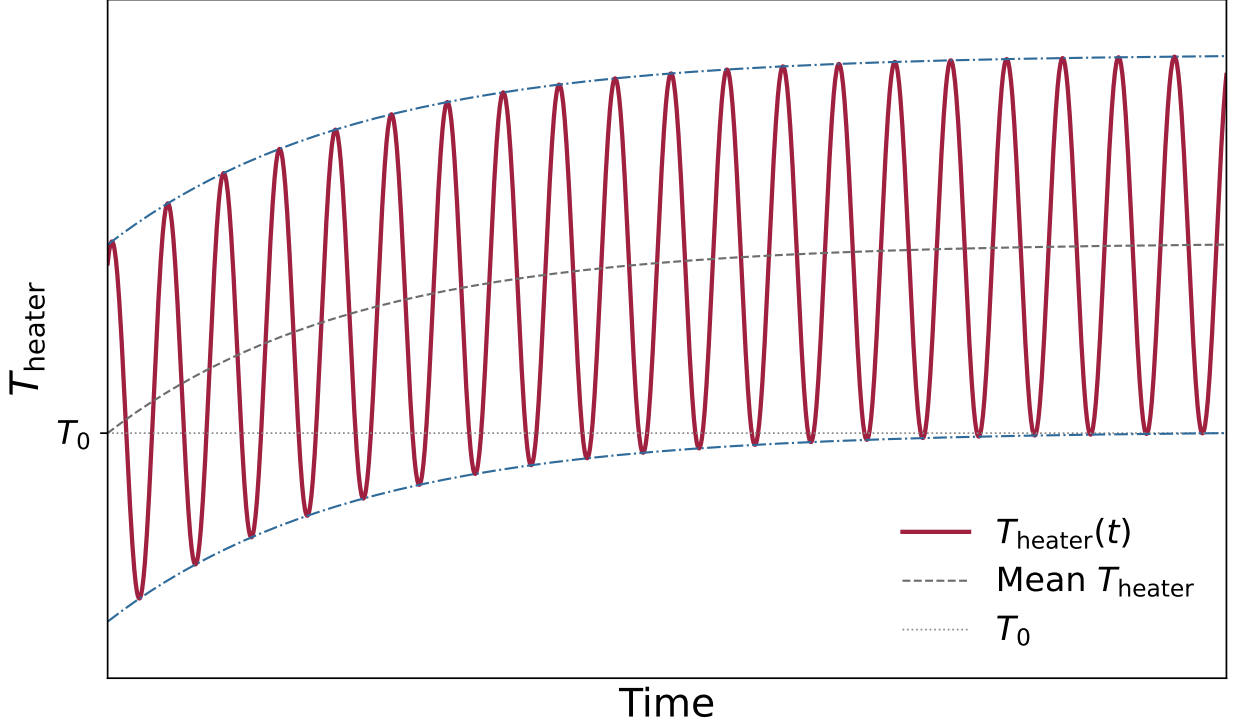


Figure 2.5: Schematic heater temperature during the approach to periodic steady state. The solid curve is the instantaneous heater temperature, the dashed curve is its cycle-averaged value, and the blue dash-dotted curves mark the upper and lower limits of the oscillation. The horizontal dotted line marks the initial equilibrium temperature T_0 of the heater and its local surroundings. The temperature oscillation occurs at 2ω .

Because the heater resistance is approximately linear in temperature, the oscillatory resistance term is

$$\Delta R_{2\omega}(t) = R_0 \beta \frac{\Delta T}{2} \cos(2\omega t + \phi_{2\omega}), \quad (2.13)$$

where the total heater resistance is

$$R(t) = R_0(1 + \beta \Delta T_{\text{DC}}) + \Delta R_{2\omega}(t).$$

Applying Ohm's law, $V(t) = I(t)R(t)$, and retaining terms to first order in $\beta \Delta T$ gives

$$V(t) = I(t)R(t) = \sqrt{2} R_0 I_{\text{rms}} \left[(1 + \beta \Delta T_{\text{DC}}) \cos(\omega t) + \frac{\beta}{4} \Delta T (\cos(\omega t + \phi_{2\omega}) + \cos(3\omega t + \phi_{2\omega})) \right]. \quad (2.14)$$

Here ΔT_{DC} is the static temperature rise of the heater above T_0 . Therefore, for the RMS third harmonic magnitude with the peak to peak thermal convention used in this thesis,

$$V_{3\omega, \text{rms}} = \frac{I_{\text{rms}} R_0 \beta}{4} \Delta T. \quad (2.15)$$

This is equivalent to the common peak amplitude form used in many derivations [48],

$$V_{3\omega, \text{peak}} = \frac{1}{2} V_0 \beta \Delta T_{\text{AC, peak}}, \quad V_0 = R_0 I_0, \quad (2.16)$$

with conversions $I_0 = \sqrt{2} I_{\text{rms}}$ and $\Delta T_{\text{AC,peak}} = \Delta T/2$. The 3ω component, i.e. the third harmonic of the measured voltage $V_{3\omega}$, is isolated with a lock-in amplifier and provides a direct measure of the temperature oscillation amplitude. With lock-in reference at 3ω , the measured component can be written as

$$V_{3\omega}(t) = \sqrt{2} V_{3\omega,\text{rms}} \cos(3\omega t + \phi_{2\omega}), \quad (2.17)$$

and the demodulated channels are

$$X = V_{3\omega,\text{rms}} \cos \phi_{2\omega}, \quad Y = V_{3\omega,\text{rms}} \sin \phi_{2\omega}, \quad V_{\text{mag}} = \sqrt{X^2 + Y^2}. \quad (2.18)$$

2.2.2 Line source solution and log linear regime (Cahill)

Consider a metallic strip of resistance R , length L , and half width b on an isotropic semi infinite substrate. With an AC drive, Joule heating produces power at 2ω and drives temperature oscillations of the strip and substrate. These temperature oscillations are complex valued in the frequency domain, and so is the third harmonic voltage. In Fourier space, the temperature rise for a finite width heater is [28]:

$$\tilde{T}_{2\omega}(\omega) = \frac{P_{\text{RMS}}}{\pi L} \int_0^\infty \frac{\sin^2(kb)}{(kb)^2} \frac{1}{\kappa \sqrt{k^2 + q^2}} dk, \quad (2.19)$$

where P_{RMS} is the average electrical power calculated from RMS heater quantities, κ is the substrate thermal conductivity, and k is the spatial Fourier variable. The complex thermal wavenumber is $q = \sqrt{i} 2\omega/\alpha$ with $\alpha = \kappa/(\rho c_p)$. The heater power is calculated from the measured RMS heater voltage as $P_{\text{RMS}} = V_{\text{rms}}^2/R$.

In the line-source limit ($\delta \gg b$), the in-phase temperature response is

$$\Re\{\Delta T(2\omega)\} = -\frac{P_{\text{RMS}}}{2\pi L \kappa} \left[\ln(2\omega) + \ln\left(\frac{b^2}{\alpha}\right) - 2\eta \right] \quad (2.20)$$

with $\eta = 0.923$ the integration constant. Substituting $P_{\text{RMS}} = V_{\text{rms}}^2/R$ and using the linear resistance temperature relation yields the in-phase third harmonic voltage measured by the lock-in:

$$\Re\{V_{3\omega}\} = -\frac{V_{\text{rms}}^3 \beta}{4\pi L \kappa R} \left[\ln(2\omega) + \ln\left(\frac{b^2}{\alpha}\right) - 2\eta \right]. \quad (2.21)$$

The in-phase component $V'_{3\omega} = \Re\{V_{3\omega}\}$ is linear in $\ln(2\omega)$. Its signed logarithmic slope is negative:

$$s = \frac{d \Re\{V_{3\omega}\}}{d \ln(2\omega)} < 0. \quad (2.22)$$

Combining Eqs. (2.21) and (2.22) and solving for κ yields

$$\kappa = -\frac{V_{\text{rms}}^3 \beta}{4\pi L R} \frac{1}{s} = \frac{V_{\text{rms}}^3 \beta}{4\pi L R} \frac{1}{|s|}. \quad (2.23)$$

Equations (2.20)-(2.23) are valid provided the semi infinite and line source assumptions hold over the fitted frequency window. The expected log linear behavior in this asymptotic regime is illustrated in Figure 2.6.

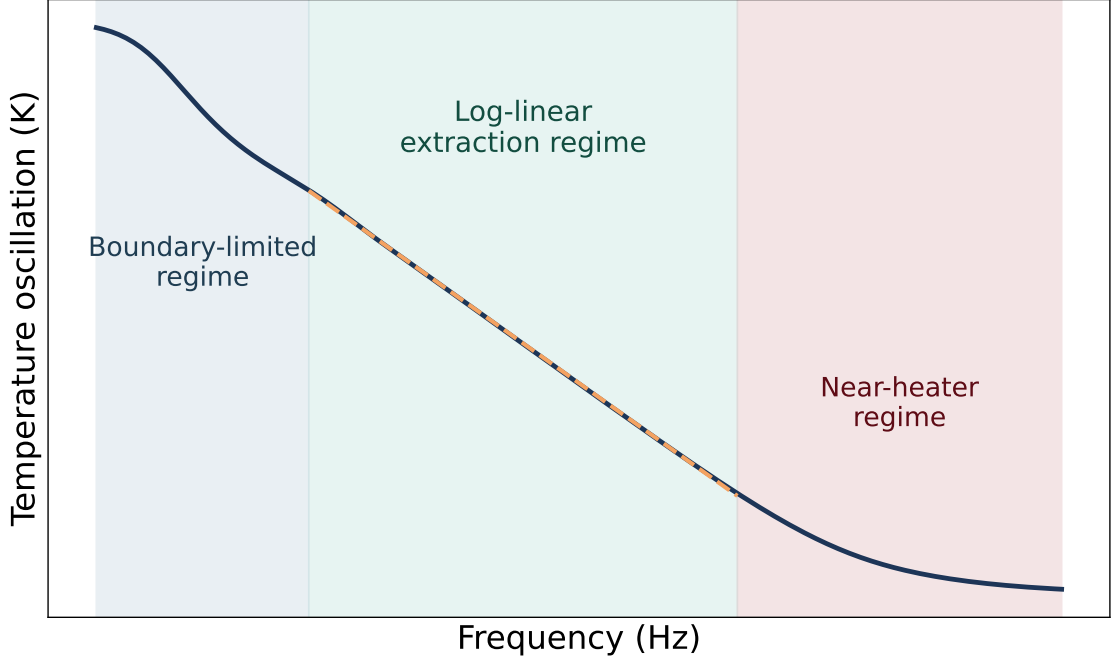


Figure 2.6: Idealized in-phase response versus $\ln(2\omega)$, highlighting the calibrated linear region where slope-based thermal conductivity extraction is valid.

2.3 FREQUENCY RANGE AND VALIDITY

The frequency range used for substrate calibration is determined by the thermal penetration depth and the heater and substrate dimensions. Following the convention in Eq. (2.8), the thermal penetration depth is $\delta = |q|^{-1} = \sqrt{\alpha/(4\pi f)}$ [28, 31]. Linearity of $\Re\{V_{3\omega}\}$ versus $\ln(2\omega)$ holds when the sample is effectively semi infinite ($\delta \ll t_{\text{sub}}$), the heater behaves as a line source ($\delta \gg b$), and the strip heat capacity is negligible.

Radiative and convective surface losses must be small compared with conduction into the substrate. Cahill models the thermally active part of the substrate as a half-cylinder whose radius is set by the thermal penetration depth δ_s [28]. For a heater of length L , the surface-loss rate scales as

$$\dot{Q}_{\text{loss}} \propto h\delta_s L\Delta T,$$

while conduction into the substrate scales as

$$\dot{Q}_{\text{cond}} \propto \kappa_{\text{sub}} L\Delta T.$$

The resulting loss ratio is

$$\frac{\dot{Q}_{\text{loss}}}{\dot{Q}_{\text{cond}}} \simeq \frac{h\delta_s}{2\kappa_{\text{sub}}}, \quad (2.24)$$

where the factor $1/2$ is given by the line-source solution [28, 32]. Since $\delta_s \propto f^{-1/2}$, the relative surface loss decreases as the heating frequency increases.

In his review, Dames groups convection and radiation into the combined surface heat-transfer coefficient

$$h = h_{\text{conv}} + h_{\text{rad}}$$

because their linearized heat rates are both proportional to the temperature difference between the surface and its surroundings [32]. The two contributions are evaluated separately below.

The convective contribution is

$$\dot{Q}_{\text{conv}} = h_{\text{conv}} A (T_s - T_{\infty}), \quad (2.25)$$

where h_{conv} is the convective heat-transfer coefficient, A is exposed area, T_s is surface temperature, and T_{∞} is the bulk-gas temperature. Dames gives $h_{\text{conv}} \approx 2\text{--}25 \text{ W m}^{-2} \text{ K}^{-1}$ for natural convection in atmospheric air and notes that values for microscopic heater strips depend on geometry [32]. Measurements on a suspended $25 \text{ }\mu\text{m}$ platinum wire gave $h_{\text{conv}} \approx 629 \text{ W m}^{-2} \text{ K}^{-1}$ at atmospheric pressure and $14 \text{ W m}^{-2} \text{ K}^{-1}$ at 7 Pa [42]. In the free-molecular regime, the same study found that the gas heat-transfer coefficient scales linearly with pressure. Extrapolation from 7 Pa to the experimental operating pressure of 0.1 Pa used in this work gives

$$h_{\text{conv}}(0.1 \text{ Pa}) \lesssim 14 \frac{0.1}{7} \approx 0.2 \text{ W m}^{-2} \text{ K}^{-1}.$$

This estimate uses a fully exposed suspended wire and therefore provides a conservative comparison for a strip attached to a substrate. With $\delta_s \lesssim 35 \text{ }\mu\text{m}$ and $\kappa_{\text{sub}} \approx 1 \text{ W m}^{-1} \text{ K}^{-1}$, the corresponding convective loss fraction is

$$\frac{\dot{Q}_{\text{conv}}}{\dot{Q}_{\text{cond}}} \lesssim \frac{(0.2 \text{ W m}^{-2} \text{ K}^{-1})(35 \times 10^{-6} \text{ m})}{2(1 \text{ W m}^{-1} \text{ K}^{-1})} \approx 3.5 \times 10^{-6}.$$

The radiative contribution follows the Stefan–Boltzmann law [28]

$$\dot{Q}_{\text{rad}} = \varepsilon \sigma A (T_s^4 - T_{\text{sur}}^4), \quad (2.26)$$

where ε is emissivity, σ is the Stefan Boltzmann constant, and T_{sur} is the surroundings temperature. Factoring the fourth-power difference gives

$$T_s^4 - T_{\text{sur}}^4 = (T_s - T_{\text{sur}}) (T_s + T_{\text{sur}}) (T_s^2 + T_{\text{sur}}^2).$$

For a small temperature difference about T_{avg} , both T_s and T_{sur} are approximated by T_{avg} in the last two factors, giving

$$T_s^4 - T_{\text{sur}}^4 \approx 4T_{\text{avg}}^3 (T_s - T_{\text{sur}}).$$

The radiative heat rate can therefore be written in the linear form

$$\dot{Q}_{\text{rad}} \approx h_{\text{rad}} A (T_s - T_{\text{sur}}), \quad h_{\text{rad}} = 4\varepsilon \sigma T_{\text{avg}}^3.$$

The T_{avg}^3 dependence is the coefficient obtained by linearizing the T^4 Stefan–Boltzmann law [28]. At the highest measurement temperature, $T_{\text{avg}} = 368 \text{ K}$, the limiting case $\varepsilon = 1$ gives

$$h_{\text{rad}} \leq 4\sigma(368 \text{ K})^3 \approx 11.3 \text{ W m}^{-2} \text{ K}^{-1}.$$

For soda-lime glass, $\kappa_{\text{sub}} \approx 1 \text{ W m}^{-1} \text{ K}^{-1}$, and the largest thermal penetration depth in the measurement range is $\delta_s \lesssim 35 \text{ }\mu\text{m}$. The radiative loss fraction is therefore bounded by

$$\frac{\dot{Q}_{\text{rad}}}{\dot{Q}_{\text{cond}}} \lesssim \frac{(11.3 \text{ W m}^{-2} \text{ K}^{-1})(35 \times 10^{-6} \text{ m})}{2(1 \text{ W m}^{-1} \text{ K}^{-1})} \approx 2.0 \times 10^{-4}.$$

The upper bounds are 3.5×10^{-6} for convection and 2.0×10^{-4} for radiation. Their combined contribution is below 0.021% and is neglected in the line-source analysis.

Using the exponential decay of the thermal wave, the conservative Cahill bounds can be extended as derived in Appendix B and reported in [44], reproduced in Appendix D. The expanded linear regime is defined by the following bounds on frequency:

$$\begin{aligned} f_{\min} &= \frac{9\alpha}{4\pi t_{\text{sub}}^2}, \\ f_{\max} &= \frac{\alpha}{36\pi b^2}, \end{aligned} \quad (2.27)$$

where t_{sub} is substrate thickness and b is heater half width, which define the usable linear band

$$\boxed{\frac{9\alpha}{4\pi t_{\text{sub}}^2} \leq f_{\text{linear}} \leq \frac{\alpha}{36\pi b^2}}. \quad (2.28)$$

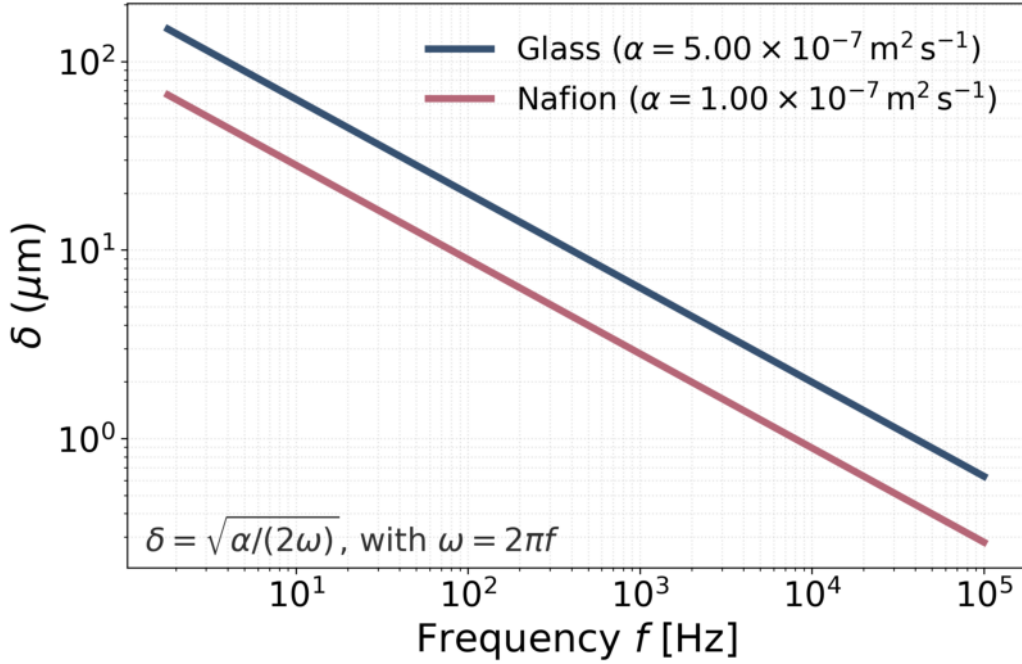


Figure 2.7: Thermal penetration depth as a function of frequency for representative glass and Nafion properties in the thesis range. The curves labeled “Glass” and “Nafion” correspond to the two materials, respectively.

Numerical example 1 (soda-lime glass, $w = 14 \mu\text{m}$). With $c_p = 0.87 \text{ J g}^{-1} \text{ K}^{-1}$, $\rho = 2.5 \text{ g cm}^{-3}$, and $\kappa = 1.06 \text{ W m}^{-1} \text{ K}^{-1}$, the diffusivity is $\alpha = 4.9 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. For $t_{\text{sub}} = 1000 \mu\text{m}$ and $b = 7 \mu\text{m}$, Eq. (2.28) gives $0.351 \text{ Hz} \leq f_{\text{linear}} \leq 88 \text{ Hz}$. Experimentally, $\Re\{V_{3\omega}\}$ was log linear over the full measured sweep $f = 30\text{--}800 \text{ Hz}$ for this heater. The rationale for extending the conservative bounds and the windowing procedure for the $w = 6 \mu\text{m}$ calibration devices are derived in Appendix B and reported in [44]. Over $f = 30\text{--}800 \text{ Hz}$, the penetration depth in glass, $\delta_{\text{glass}} = \sqrt{\alpha/(4\pi f)}$, ranges from about $35 \mu\text{m}$ at 30 Hz down to $6.8 \mu\text{m}$ at 800 Hz . The semi infinite condition $\delta \ll t_{\text{sub}}$ is satisfied throughout, while the line source condition $\delta \gg b$ becomes marginal near the upper end.

Numerical example 2 (Nafion on soda-lime glass, $w = 14 \mu\text{m}$). For the dry-Nafion model, $\kappa_{\text{Nafion}} = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ and the adopted modelling estimate $\rho c_p = 2.94 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ give $\alpha_{\text{Naf}} = 8.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. Over $f = 30\text{-}800 \text{ Hz}$, the penetration depth inside Nafion, $\delta_{\text{Naf}} = \sqrt{\alpha_{\text{Naf}}/(4\pi f)}$, spans about $15 \mu\text{m}$ to $2.9 \mu\text{m}$. For $t_{\text{film}} = 32 \mu\text{m}$, the ratio t_{film}/δ therefore increases from approximately 2.1 to 11 across the sweep. The film response consequently moves from an intermediate regime toward a thermally thick regime as frequency increases. These length scales provide order-of-magnitude checks. For a coated multilayer, log-linear behavior must be verified over the selected frequency window. This frequency-dependent thermal regime crossover motivates the numerical interpretation developed later.

Volumetric heat capacity affects the frequency limits through $\alpha = \kappa/(\rho c_p)$. Variations in volumetric heat capacity shift f_{min} and f_{max} through the diffusion length. Inside the asymptotic log-linear band described by Eq. (2.21), the slope depends on κ and is independent of ρc_p . The FEM sensitivity check discussed in Section 3.3 and shown in Figures A.7 and A.8 indicates that varying volumetric heat capacity shifts the apparent regime edges, with a smaller residual variation in the fitted mid-band slope.

The Cahill bounds in Eq. (2.28) are conservative for the heater-on-substrate calibration geometry. The measured substrate response was log linear over the 30-800 Hz sweep, and the slope was fitted over this full interval. In the coated multilayer geometry, the film introduces additional length scales and boundary conditions that modify the thermal transfer function. Numerical modelling is therefore used to interpret the coated response [44].

Measurements were performed using $w = 6 \mu\text{m}$ and $w = 14 \mu\text{m}$ heaters. The two heater widths initially gave different values of thermal conductivity. This difference was traced to parasitic series resistance in the high temperature coaxial cable and contact path of the insert. The full calibration and uncertainty propagation are given in Section 3.3.

Using two heater widths remains useful as a consistency check on the validity of the chosen frequency window and on the adequacy of the thermal model. If a residual difference persists after electrical correction, it can indicate a real thermal origin such as finite width heat spreading, anisotropy in a film, or boundary condition departures [28, 31, 33]. Numerical forward modelling is used to evaluate these effects. The two heater widths serve as diagnostics, and the multilayer response is interpreted with FEM using the full geometry and boundary conditions.

The 1ω channel carries the fundamental electrical response, including contributions from lead impedances, wiring, and component drift. A balanced Wheatstone bridge or differential amplifier suppresses this component before the 3ω signal is extracted for determining κ [28, 44].

Narrower heaters better satisfy the line source approximation ($w \ll \delta$) and reduce geometric corrections, but increase electrical resistance and fragility. Wider heaters raise signal levels yet can require finite width corrections if w is not small compared with δ . Long aspect ratios ($L \gg w$) suppress end effects but increase lead resistance. Our designs use $L \approx 3 \text{ mm}$ with $w = 6$ and $14 \mu\text{m}$ [28, 31, 32, 33].

The electrical resistance of a metallic line of length L and cross-sectional area A_{cs} is

$$R = \varrho_e \frac{L}{A_{\text{cs}}}, \quad (2.29)$$

where ϱ_e is the electrical resistivity. For fabricated thin film heaters, this relation provides an order-of-magnitude estimate. The value of R used in the analysis is measured directly.

Electrical resistance also depends on the contact path and the microstructure of the metal film, including its polycrystalline grain structure.

2.4 MULTILAYER LIMITATIONS

When a film, encapsulation, or additional layers are present, the heater no longer sits on a single semi infinite substrate. The stack introduces new length scales, including film thickness, interfacial thermal resistances, and possible anisotropy. These features modify the thermal transfer function and can introduce crossovers where neither the line source nor the half space assumptions are valid across a broad band [31, 33].

In multilayers, a log linear region in $\Re\{V_{3\omega}\}$ versus $\ln(2\omega)$ is not guaranteed. A window that is valid for substrate calibration can become inappropriate after coating, even if it remains linear by eye. For reliable film extraction, the interpretation must therefore be tied to a forward model that includes the full geometry and boundary conditions [31, 32, 33, 34].

2.5 UNCERTAINTY ANALYSIS

For a derived quantity $g(x_1, \dots, x_n)$ with independent uncertainties σ_{x_i} ,

$$\sigma_g^2 = \sum_i \left(\frac{\partial g}{\partial x_i} \right)^2 \sigma_{x_i}^2. \quad (2.30)$$

Here g is a derived quantity, x_i are independent input variables, and σ_{x_i} are their standard uncertainties.

Using κ from Eq. (2.23) with independent variables (V_{rms} , β , R , s) gives

$$\sigma_\kappa = \kappa \sqrt{\left(\frac{3\sigma_{V_{\text{rms}}}}{V_{\text{rms}}} \right)^2 + \left(\frac{\sigma_\beta}{\beta} \right)^2 + \left(\frac{\sigma_R}{R} \right)^2 + \left(\frac{\sigma_s}{s} \right)^2}. \quad (2.31)$$

This expression applies directly to datasets where series wiring and contact resistance is negligible.

For the $w = 14 \mu\text{m}$ datasets, a finite parasitic series resistance term must be included in both heater voltage mapping and $V_{3\omega}$ conversion. The detailed correction equations, measured parameter values, and propagated uncertainty treatment are part of the calibration section because they are tied to the specific hardware state of the insert during those measurements. They are presented in Section 3.3 together with the validation plots.

Length tolerances are omitted because L was determined from SEM and its contribution to the total uncertainty was negligible on the scale of the plotted error bars.

Chapter 3

METHODOLOGY

This chapter describes the experimental and numerical methods used to determine the thermal conductivity of dry Nafion. The measurement method is based on a microfabricated 3ω sensor operated in a temperature-controlled vacuum system with automated Wheatstone bridge balancing. The chapter first presents the experimental platform and measurement sequence, followed by the sensor fabrication procedure. It then describes substrate calibration, electrical corrections, and the validation of the measured thermal response. The final section defines the finite element model and inverse procedure used to extract the Nafion thermal conductivity from the coated sensor measurements.

3.1 EXPERIMENTAL SETUP

The experimental setup controls the thermal and electrical conditions required for microvolt-level 3ω measurements. The sensor is mounted on a copper heat sink inside a vacuum tube furnace, with a platinum thermometer positioned at the sample. Electrical excitation and third harmonic detection are performed through a dynamically balanced Wheatstone bridge. At each frequency, the bridge is balanced before $V_{3\omega}$ is recorded.

The first tests identified measurement stability as the main experimental constraint. The nominal instrument sensitivity was sufficient for the expected signal level. The third harmonic voltage is in the microvolt range, so small disturbances in grounding, shielding, and bridge balance directly appear in the readout. Electrical switching events in nearby equipment were visible as step like artifacts in the recorded signal. These artifacts prevented precise slope extraction in the ΔT versus $\ln(2\omega)$ domain. The thermal side was initially limited by weak control of the sample boundary condition at the substrate backside. A well defined heat sink below the substrate was required to shorten thermal stabilization and the dwell time before each frequency sweep. Long acquisitions at elevated temperature also increased the risk of sample drift. For polymer films this drift can appear as non physical thermal conductivity trends. In conventional operation with manual or one point bridge balancing, the first harmonic can drift strongly across frequency and can exceed acceptable levels by orders of magnitude relative to the target third harmonic signal [44]. These observations defined the development targets for the platform. The setup had to enforce a repeatable thermal boundary condition, maintain a controlled atmosphere around the sample, and suppress first harmonic electrical leakage before each third harmonic measurement point. The automation strategy was therefore treated as a metrology requirement.

The measurement assembly was built around a custom insert for a cylindrical tube furnace (Carbolite Gero MTF 12/38/250). The insert positions the sample inside a borosilicate tube and defines a repeatable geometry for thermal and electrical contacts. A Lake Shore PT-103 platinum thermometer is mounted at the sample location, so temperature control is referenced directly to the measurement position.

The four-wire sample contacts use gold wires bonded to the sample with conductive silver paste. The wires are inserted into clamps embedded in the sample-holder head made of fired Grade A Lava, an aluminum-silicate ceramic [49]. The clamps connect to one end of the vacuum-compatible polyimide coaxial leads. The opposite ends of these leads are soldered to vacuum-compatible Fischer connectors, which serve as signal feedthroughs at the chamber boundary. The head was machined before firing, then heated at 40 K h^{-1} to 1030°C and held there for 45 minutes, following the Grade A Lava firing guidance [50]. Pumping is performed with a Pfeiffer DUO 2.5 pump and pressure is monitored with a Pfeiffer PCR 260 gauge. Typical operation is at approximately 0.1 Pa, which suppresses convective heat transfer and stabilizes the environmental contribution to the thermal response [44].

Temperature control is handled by a closed loop proportional integral derivative routine implemented in LabVIEW and interfaced with the furnace controller. The operating protocol uses controlled ramps and a stability gate before data acquisition. Measurements start only after the sample temperature remains within $\pm 0.05 \text{ K}$ over 60 s. This criterion, together with the local thermometer placement, gives reproducible thermal initial conditions for each frequency sweep [44, 51].

In the measured range, the stability criterion is typically reached after about 30 min. A typical frequency sweep then lasts about 2 h and produces one thermal conductivity measurement at the selected temperature. Sample temperature is measured with a calibrated PT-103 platinum thermometer attached to the copper sample holder. The heater remained under AC excitation throughout each change in temperature setpoint, so the 3ω response was generated continuously. During stabilization, the bridge was not balanced and the first-harmonic voltage measured between V_A and V_B was monitored as an indirect indicator of heater resistance and therefore heater temperature stabilization. This signal approached its asymptotic value at approximately the same time as the PT-103 temperature. The PT-103 typically required slightly longer to satisfy the stability criterion, with stabilization taking about 30 min, and was therefore used to determine when the balanced frequency sweep could begin. During reduction, the recorded time-domain temperature history is used to assign each measurement to its actual temperature. The resulting temperature uncertainty is retained through the orthogonal distance regression treatment discussed in the accompanying article [44]. The high temperature coaxial sample leads are rated to approximately 250°C . Routine long duration operation in this setup was limited below 200°C for reliability [44]. The practical operating envelope used in this work is summarized as follows. The pressure setpoint is approximately 0.1 Pa, with pump down to this level in approximately 10 min under normal conditions. The temperature program ramps to each nominal setpoint and starts electrical acquisition only after the sample stability criterion is met. The full measurement at one temperature includes thermal stabilization plus the automated frequency sweep, with an average duration of approximately 2 h [44]. The assembled platform used for these runs is shown in Figure 3.1.

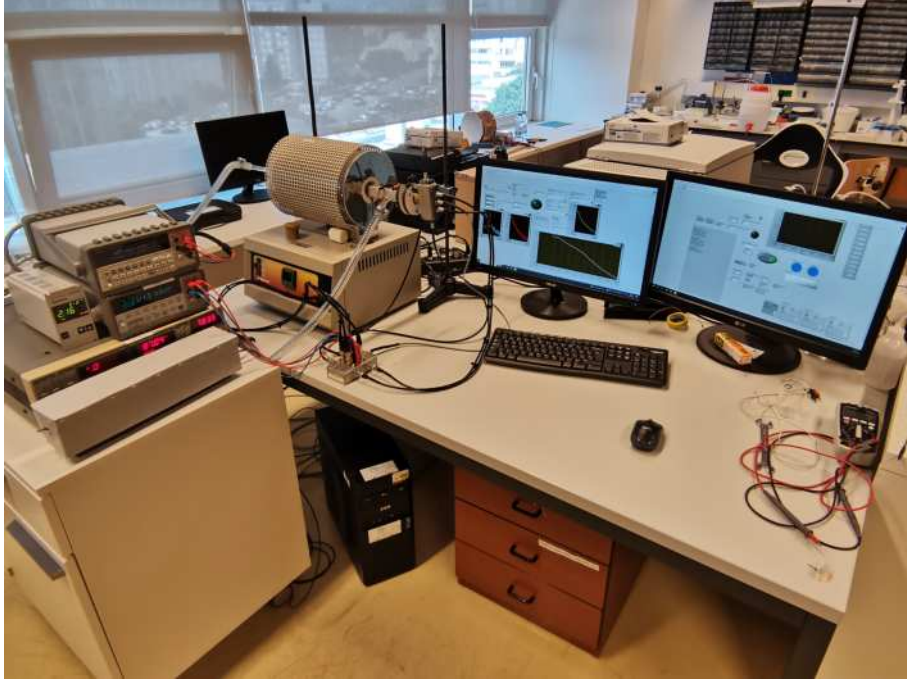


Figure 3.1: Full assembled 3ω platform used in the thesis measurements, including furnace insert, vacuum line, bridge electronics, and control system.

The same platform details are condensed into a configuration summary in Table 3.1, which lists the specific hardware elements and operating limits used in all reported runs. This table is used as the hardware settings for all later chapters.

Table 3.1 summarizes the equipment and operating limits. Measurement quality is monitored through instrument level checks at each point in a sweep. Those checks are organized in Table 3.2, which lists the check applied to each instrument during measurement.

The sample is mounted on a polished copper heat mass. The glass substrate is attached to this copper block using a thin and reproducible layer of two-component electrically conductive epoxy EPOTEK EJ2312 [52], which is later used to make electrical contacts from the heater to the high temperature insert using $75\ \mu\text{m}$ diameter gold wires. The copper block acts as a stable thermal reservoir and defines the thermal boundary condition at the back of the substrate. In practice, the copper coupling reduced stabilization time from the order of hours to tens of minutes. This reduction made the full temperature dependent measurements feasible and limited the exposure of polymer films to elevated temperature for prolonged periods. It also improved repeatability because each sweep started from a better defined thermal state. A stable sample temperature is essential because the material properties measured in the experiment can depend on temperature.

The electrical methodology is based on an automated, dynamically balanced Wheatstone bridge. The balancing branch contains two CdS resistive optoisolators connected in series and an external precision potentiometer [44]. One optoisolator is adjusted automatically at each frequency by changing the PWM duty cycle applied to its light-emitting diode (LED). The second can be controlled remotely when the resistance range of the automatic element is insufficient. During normal operation, its LED is driven at maximum intensity to keep its resistance at the minimum value. The external potentiometer provides coarse manual adjustment to bring the bridge within the automatic balancing range during on-

Table 3.1: Key platform elements and operating limits used in this chapter.

Element	Model or implementation	Application
Tube furnace	Carbolite Gero MTF 12/38/250	High temperature chamber
Temperature controller	Eurotherm 3216 with LabVIEW control	Closed-loop proportional–integral–derivative (PID) operation
Sample thermometer	Lake Shore PT-103	At sample location, < 0.003 K uncertainty
Vacuum pump	Pfeiffer DUO 2.5	Pump down to ~ 0.1 Pa
Vacuum gauge	Pfeiffer PCR 260	Pressure readout at measurement chamber
Sample coax	Allectra 311-KAP50S-RAD	Rated to ~ 250 °C
Routine temperature limit	Methodological choice for reliability	Below 200 °C
Electrical matching	Bridge and lines	50 Ω matching
Lock-in detection	SR830, differential mode	Harmonics at $1f$ and $3f$
Bridge balancing element	Two series CdS resistive optoisolators, external precision potentiometer, and Arduino pulse-width modulation (PWM)	Automatic balancing with remote and manual range adjustment

Table 3.2: Instrumentation checks used during measurements.

Instrument or signal	Primary role	Check during measurement
PT-103 thermometer	Sample temperature reference	Stability gate and repeated hold checks
SR830 lock-in	Harmonic detection at $1f$ and $3f$	Phase gate and residual $V_{1\omega}$ checks at every frequency
Unbalanced 1ω bridge signal	Indirect check of heater temperature stabilization	Approach to a constant value compared with the PT-103 temperature during stabilization
Bridge balancing branch	First harmonic suppression	Logged PWM duty and convergence status
Source and drive branch	Heater excitation	Run-level current and voltage consistency logs
Digital multimeter	Independent resistance measurement	Heater and wiring resistance measurements used for electrical characterization
Vacuum gauge	Environmental state variable	Pressure logging at each temperature hold

site setup. Optical coupling controls the CdS resistances without an electrical connection between the controller and the bridge. The implemented bridge topology and printed circuit

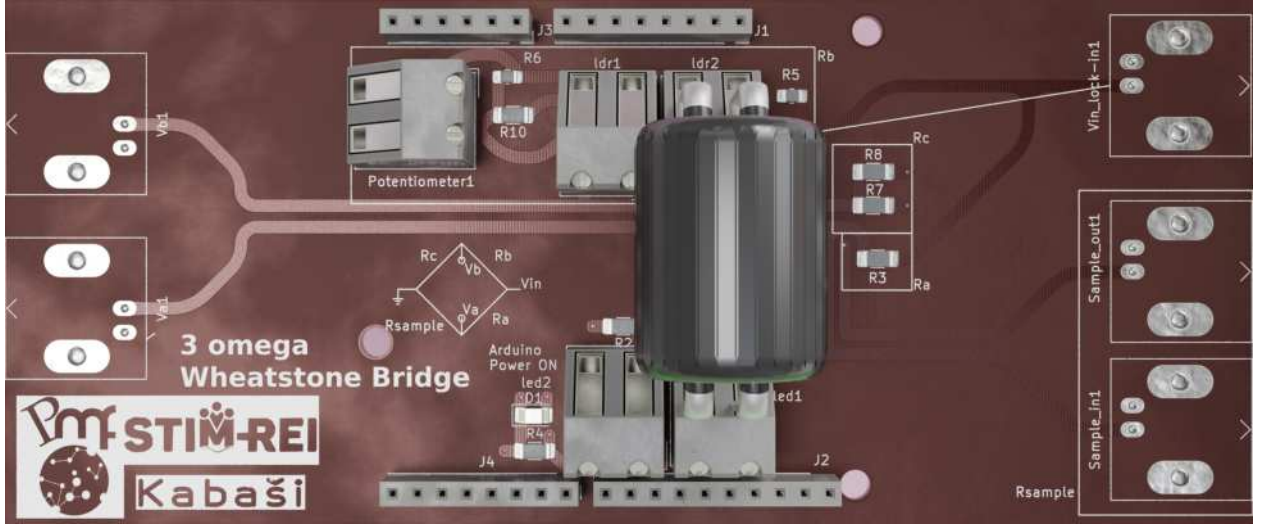


Figure 3.3: PCB model used to verify connector placement and analog digital separation in the bridge electronics.

Figure 3.4 shows the fabricated board used in the measurements. The board attaches directly to an Arduino Uno Rev 3 as a shield. Coaxial connectors carry the source input, heater branch, and bridge output voltages V_A and V_B . The 16-bit PWM firmware used to control the two CdS optoisolators is given in Appendix C. The complete instrument and automation method are reported in [44], reproduced in Appendix D.



Figure 3.4: Fabricated bridge PCB front view used in the measurements. The balancing branch includes the two series photoresistors marked $Ldr1$ and $Ldr2$ and the connection for the external precision potentiometer.

The excitation source applies the drive voltage to the input arm of the Wheatstone bridge. The microheater is the sample resistance arm and is in series with a $10\ \Omega$ precision film resistor. The remaining arm is defined by precision resistors, precision potentiometer and the two series CdS resistive optoisolators. The lock-in amplifier reads the differential voltage between bridge nodes V_A and V_B . Inside the vacuum chamber are the sample, heater,

platinum thermometer attached by platinum wires in a four-wire geometry, and coaxial leads connected to the Fischer signal feedthroughs. Outside the vacuum chamber are the bridge board, Arduino, multimeters, source, lock-in amplifier, and control computer, all attached to an isolation transformer.

The balancing algorithm is executed at every frequency point. After thermal stabilization at the selected temperature, the sequence starts from the highest frequency in the predefined sweep list. The lock-in amplifier measures phase and first harmonic voltage. The balanced condition is a phase of 90° , within 1%. If the phase deviation from 90° exceeds 1% or if the first harmonic amplitude exceeds $10 \mu\text{V}$, the pulse width modulation duty cycle is adjusted in progressively finer steps until both criteria are satisfied [44]. The Timer1 implementation that applies the resulting 16-bit duty-cycle command is provided in Appendix C. The acceptance criteria are therefore

$$\frac{|\phi - 90^\circ|}{90^\circ} \leq 0.01 \quad (3.1)$$

and

$$|V_{1\omega}| \leq 10 \mu\text{V}. \quad (3.2)$$

The typical time to stabilization at a single frequency is around 10 seconds and up to 15 seconds including the allowed settling times for the electronics. Points that take longer than 60 seconds to stabilize are skipped and discarded. Here ϕ is the measured lock-in phase at the balancing step, and $V_{1\omega}$ is the residual first harmonic differential bridge voltage at the lock-in input. The PWM control signal for this loop is shown in Figure 3.5.

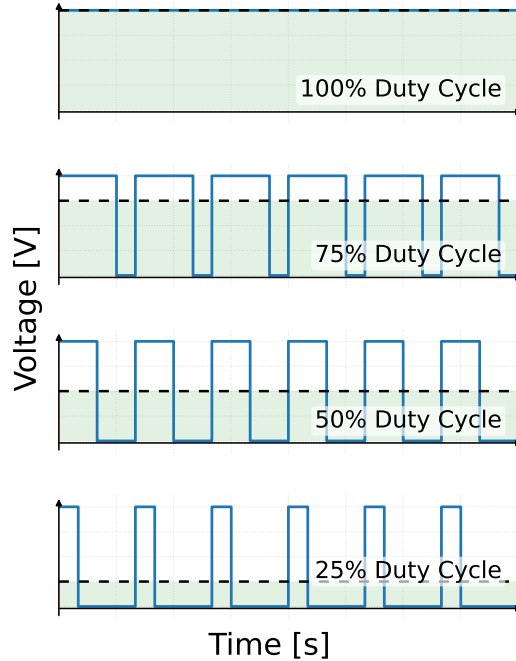


Figure 3.5: PWM duty cycle control behavior used for CdS balancing element tuning during automated bridge nulling.

Once these criteria are met, the system records the first harmonic, switches to third harmonic acquisition at $3f$, logs the data, and returns to first harmonic before moving to the next frequency. The lock-in is operated in differential mode, measuring bridge node

voltage difference. Conversion to heater third harmonic voltage uses the bridge correction factor and is valid only under balanced conditions [44].

The lock-in is used as a narrowband synchronous detector referenced at $3f$. Data quality is established through bridge suppression of the first harmonic, the phase and amplitude gates, and fixed averaging windows in the acquisition sequence. The reported quantity is the steady periodic component after the stability criteria are satisfied. The timing metrics reported in the accepted manuscript are as follows [44]. Bridge stabilization required less than 15 s per frequency point. A single frequency point required up to 40 s including rebalancing. After each frequency change, 3 s were allowed for lock-in settling. First harmonic and third harmonic were each sampled for 10 s. A full sweep at a single temperature required on average 2 h including thermal stabilization.

Automation enabled dense logarithmic frequency sampling and remote unattended sweeps with repeatable balancing criteria at every point. The key outcome is lower uncertainty in slope extraction because operator-dependent variability is removed from the measurement [44].

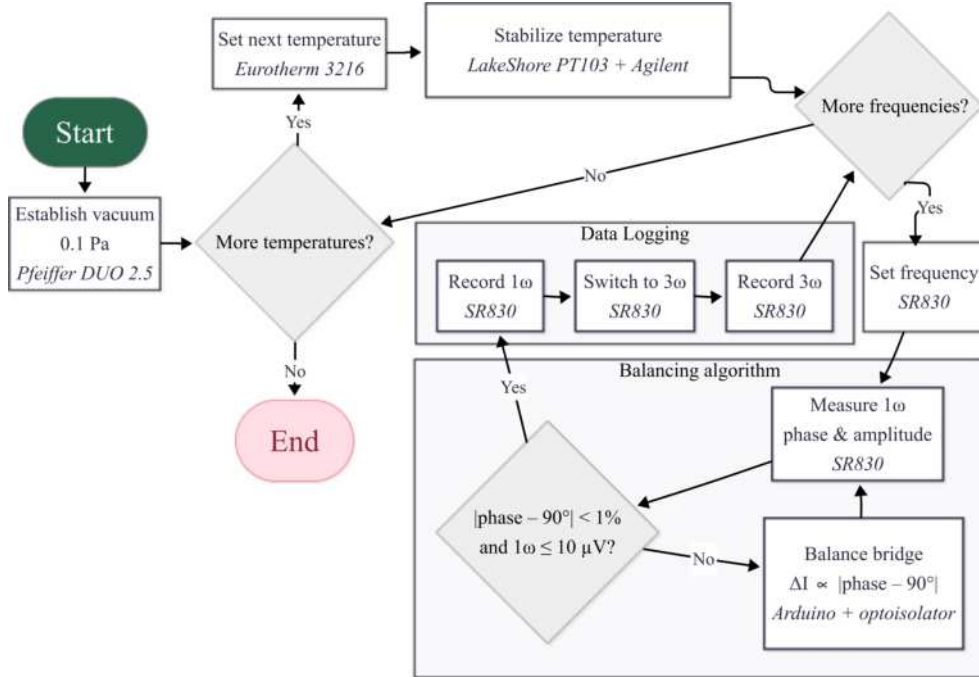


Figure 3.6: Automated measurement sequence with frequency by frequency rebalance criteria for phase and first harmonic suppression, adapted from the accepted manuscript [44]. In the diagram, ΔI denotes the change in LED light intensity, controlled through the PWM duty cycle, that changes the photoresistor resistance during bridge balancing. The adjustment step is proportional to the absolute phase error, $\Delta I \propto |\phi - 90^\circ|$, so the change in light intensity becomes progressively smaller as the measured phase approaches 90° .

Figure 3.6 shows the complete automated measurement sequence. After vacuum is established, the sample is brought to the selected temperature and allowed to stabilize. At each frequency, the bridge is balanced using the measured 1ω amplitude and phase. The system then records $V_{1\omega}$, switches the lock-in amplifier to 3ω , and records $V_{3\omega}$. This sequence is

repeated for every frequency and temperature. Figure 3.7 shows the physical arrangement of the vacuum pump, furnace, high-temperature insert, Wheatstone bridge, thermometer, and lock-in amplifier.

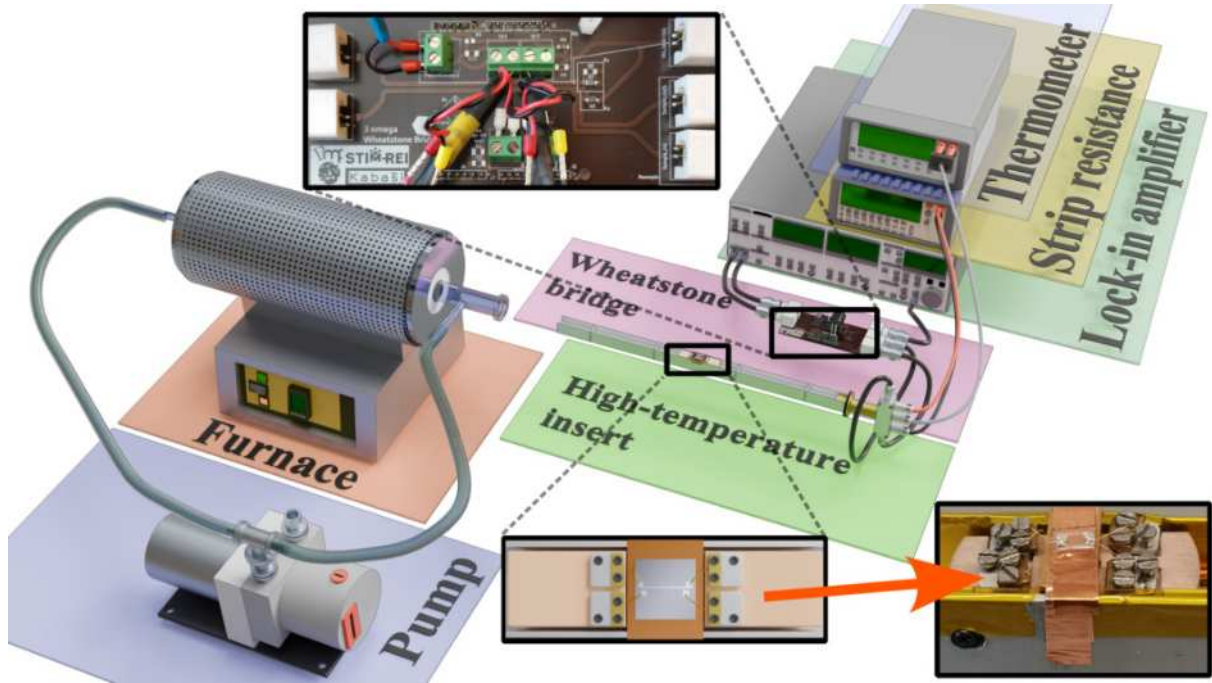


Figure 3.7: Measurement setup layout.

The sample and thermometer are located on the insert inside the furnace. The bridge and measurement instruments remain outside the vacuum chamber and connect to the sample through the insert wiring.

3.2 SENSOR FABRICATION

This section presents the fabrication process used to produce reproducible 3ω sensor chiplets for calibration and coated film measurements. Fabrication and Nafion deposition are performed as separate stages. The fabrication route used for the $6\ \mu\text{m}$ validation dataset reported in the accepted article is the same route used in this thesis [44]. The fabrication and screening procedure uses the materials and instruments summarized in this section. Soda-lime glass microscope slides (Marienfeld Superior) were used as the base substrate, with nominal dimensions $25 \times 75 \times 1\ \text{mm}$ and thickness tolerance $\pm 0.05\ \text{mm}$. Representative vendor composition by mass fraction is SiO_2 72.6%, Na_2O 13.0%, CaO 8.8%, MgO 4.3%, Al_2O_3 0.6%, K_2O 0.3%, SO_3 0.2%, and Fe_2O_3 0.1% [53].

At these thicknesses, the Cahill slope extraction of κ is independent of the exact metallization thickness. Direct electrical resistance is the primary measured quantity for each fabricated heater [33].

Fabrication starts from soda-lime glass slides [53]. Substrates are stored in a 1:1 acetone:isopropanol cleaning mixture until they are needed for processing. For rapid preparation before a fabrication run, slides are cleaned in the same 1:1 mixture with sonication and heating for about 10 minutes. The sonicator bath was kept below boiling. The slides were transferred directly from the cleaning mixture to the sputter chamber. This procedure minimized ambient exposure and contamination. A nominal chromium adhesion interlayer with 0.3 nm equivalent thickness is deposited first. At this nominal level the chromium layer is discontinuous, which improves silver adhesion. Silver is the dominant contribution to the electrical and thermal response. The nominal chromium thickness is monitored in situ with a quartz crystal microbalance through the change in resonance frequency of the quartz crystal [44]. The heater metal is deposited as a sputtered silver film. Two thicknesses were used in the thesis measurements. The $14\ \mu\text{m}$ heater family was fabricated with 200 nm silver and the $6\ \mu\text{m}$ heater family was fabricated with 500 nm silver. Thickness control is based on fixed sputter settings and deposition time, followed by periodic geometry and thickness checks by microscopy. This time based approach was sufficient for reproducible heater resistance and stable 3ω operation in the calibration and coated film measurements.

After metallization, substrates are thermally preconditioned before photoresist coating. The practical sequence is a short dehydration bake followed by rapid cooldown to room temperature to stabilize wetting and resist spread. A positive photoresist, AZ1505, is spin coated at 3000 rpm for 60 s to obtain an approximately $0.5\ \mu\text{m}$ resist layer, followed by soft bake at $100\ ^\circ\text{C}$ for at least 60 s on a hotplate. Pattern transfer is performed by ultraviolet (UV) exposure through the mask on the EVG 610 aligner with a mercury lamp. The exposure was run in top transparency mode with two 10 s pulses separated by a 10 s pause, at an irradiance of approximately $8\ \text{mW cm}^{-2}$ measured at the plane of the photoresist. Development was performed in AZ 726 MIF developer using a visual endpoint criterion and typically required less than 20 s at room temperature. This was followed by hardbake at $100\ ^\circ\text{C}$ for 90 s. After development, the sample is rinsed in deionized water and inspected under an optical microscope before etching. The purpose of this inspection is to reject incomplete or damaged resist patterns before the irreversible metal removal step [44]. The mask region used for heater definition is shown in Figure 3.8. Before that layout is discussed, the process settings are summarized in Table 3.6. These setpoints were selected after repeated process trials and were kept fixed during final sensor production.

Table 3.3: Metal stack used for sensor fabrication.

Layer	Nominal thickness	Magnetron
Chromium adhesion underlayer	0.3 nm	Quorum Q150T Plus
Silver heater film (wide branch)	~200 nm	Pfeiffer Classic 250
Silver heater film (narrow branch)	~500 nm	Pfeiffer Classic 250

Table 3.4: Lithography and etch parameters used during sensor fabrication.

Step	Setpoint	Notes
Spin coat	AZ1505, 3000 rpm, 60 s	Front side coat.
Softbake	100 °C, at least 60 s	Hotplate with steel disk.
Exposure	EVG 610, Hg lamp, 8 mW cm ⁻²	10 s expose, 10 s pause, 10 s expose.
Development	AZ 726 MIF, visual endpoint	Typically under 20 s.
Hardbake	100 °C, 90 s	Post develop bake.
Silver wet etch	Ferric nitrate, 2 mol L ⁻¹	Endpoint checks every second after 5 s.
Resist strip	Acetone then deionized (DI) water dunk	Immediate water dunk avoids stress from rapid evaporation of acetone.

Table 3.5: Primary fabrication tools and process ranges used in this thesis.

Tool	Model	Use and operating range
Mask aligner	EVG 610	Mercury lamp exposure in top transparent mode, with 10 s + 10 s pause + 10 s sequence.
Cr sputter	Quorum Q150T Plus	Chromium adhesion deposition after automatic target pre sputter. Base pressure typically near 1×10^{-5} mbar before Ar. Thickness monitored by an in situ quartz crystal microbalance (QCM).
Ag sputter	Pfeiffer Vacuum Classic 250 (DC)	Silver conductor deposition, typically 10 to 20 minutes at ~ 150 W and 8 sccm Ar. Base pressure near 1×10^{-5} mbar before Ar. No in situ QCM.
Process gas and pressure	Argon, sputter chamber	Ar flow typically 8 to 12 sccm. Power ramp from 40 W. Wait at least 60 s at stable voltage before opening the shutter.

Table 3.6 lists the fixed settings used from substrate cleaning through dicing. The development endpoint determines whether the exposed regions are cleared completely before etching. Incomplete development can leave resist over silver that should be removed. Excessive development can alter the resist edges that define the heater. During the subsequent isotropic silver etch, the exposed silver must be removed completely while lateral undercut beneath the resist is limited. Etch time directly affects the final heater width. Figure 3.8 shows photomask variant 1, an earlier design containing straight heater patterns over a broad

Table 3.6: Compact process windows used in routine fabrication runs.

Step	Setpoint used	Practical window
Pre clean and transfer	1:1 acetone:isopropanol with sonication	~ 10 min, below boiling
Pre sputter bake	Hotplate	$\sim 140^\circ\text{C}$, ~ 1 min
Aluminum plate cooldown		~ 1 min
AZ1505 spin coating	3000 rpm for 60 s	$\sim 0.5 \mu\text{m}$ resist
Soft bake	Hotplate	100°C , at least 60 s
UV exposure	EVG 610 flood mode	10 s + 10 s pause + 10 s
Development	AZ 726 MIF	Visual endpoint, below 20 s
Hard bake	Hotplate	100°C , 90 s
Silver etch	Ferric nitrate, 2 mol L^{-1}	Target completion between 3 and 10 s
Rinsing in 3 separate DI water baths	Removing residual etchant	10 s, 5 min, 5 min
Patterned resist removal	Acetone followed immediately by DI water	Strip AZ1505 after silver etching
Post-etch inspection	Optical microscope	Verify the metal pattern before applying the protective coating
Protective coating	Fresh AZ1505 layer	Applied after inspection and before dicing
Dicing	Diamond saw	Separate the patterned substrate into sensor chiplets
Protective resist removal	Acetone followed immediately by DI water	Strip the protective AZ1505 after dicing

range of widths and lengths. It was used to evaluate the fabrication limits and was not used for the thesis measurements. Based on those trials, photomask variant 2 was restricted to the two heater widths selected for measurement. Variant 2 is shown in Figure 3.11.

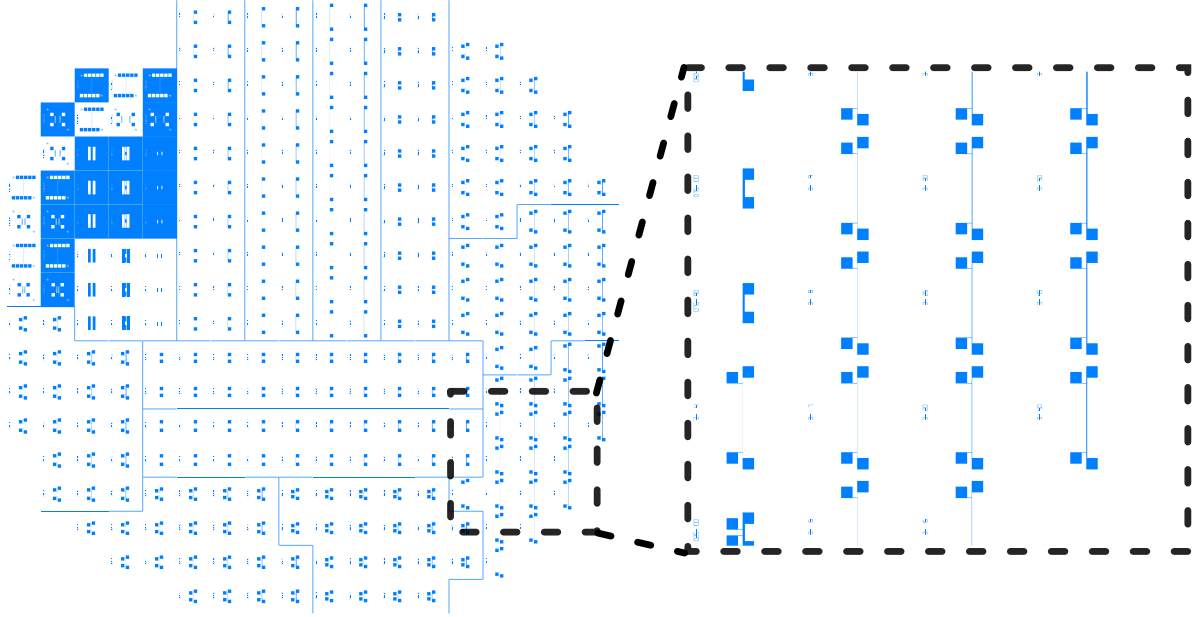


Figure 3.8: Photomask for heater variant 1, showing the microheater families with the range of widths, lengths, and meandering patterns evaluated during sensor development.

For the heater families used in this thesis, nominal mask widths of $10\ \mu\text{m}$ and $20\ \mu\text{m}$ were used to realize final widths around $6\ \mu\text{m}$ and $14\ \mu\text{m}$ after wet etching.

This offset is expected for isotropic silver etching. The final widths are verified by SEM after fabrication, and heaters with consistent width along the full length are selected for testing. Figure 3.9 shows a representative post etch verification result for the wide heater branch. The three mask families used across fabrication trials are shown in Figure 3.10, Figure 3.11, and Figure 3.13.

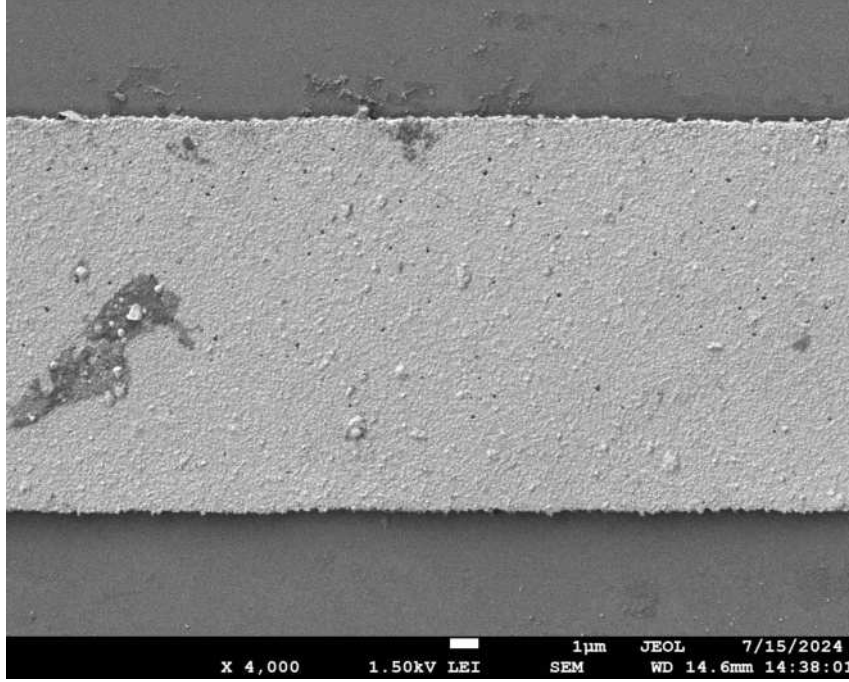


Figure 3.9: Top view SEM image used to verify the etched 14 μm wide microheater.

Figure 3.10 shows the straight heater patterns of photomask variant 1.



Figure 3.10: Heater mask variant 1.

Figure 3.11 shows the four-wire straight heater geometry used for the thesis measurements. The silver thickness was calibrated separately for the two selected widths to control their electrical resistance. The 6 μm heaters used 500 nm silver and the 14 μm heaters

used 200 nm silver. Their placement within the full multi-design photomask is shown in Figure 3.12.



Figure 3.11: Heater mask variant 2 used for the thesis measurements.

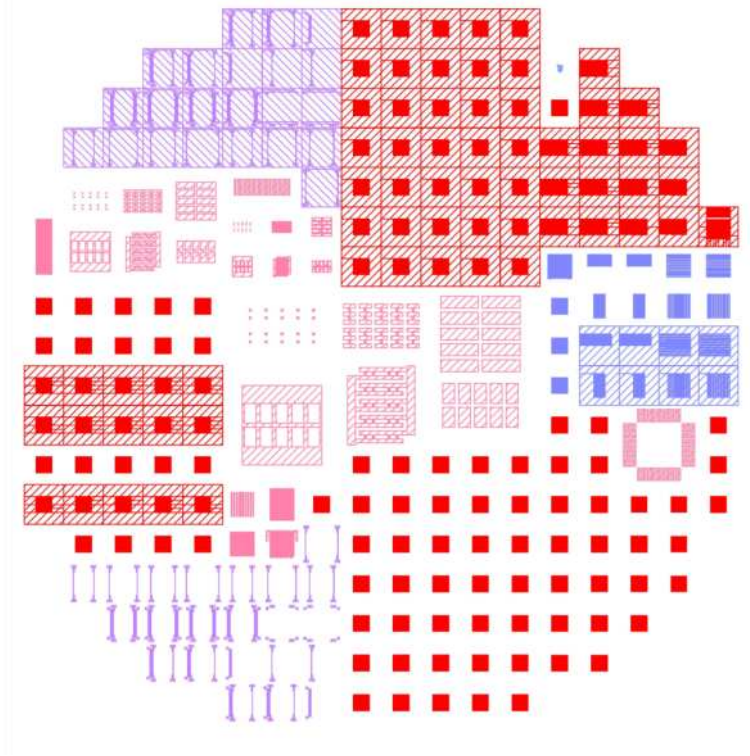


Figure 3.12: Multi-design photomask containing the variant 2 microheater structures used in this thesis. The purple structures in the lower left region contain the two selected four-wire heater geometries. The mask also contains complementary structures for positive- and negative-resist processes and additional structures developed for other applications.

Figure 3.13 shows the third retained family used in the same screening stage. Together with Figure 3.10 and Figure 3.11, it defines the full preselection set from which the final thesis geometry was chosen.

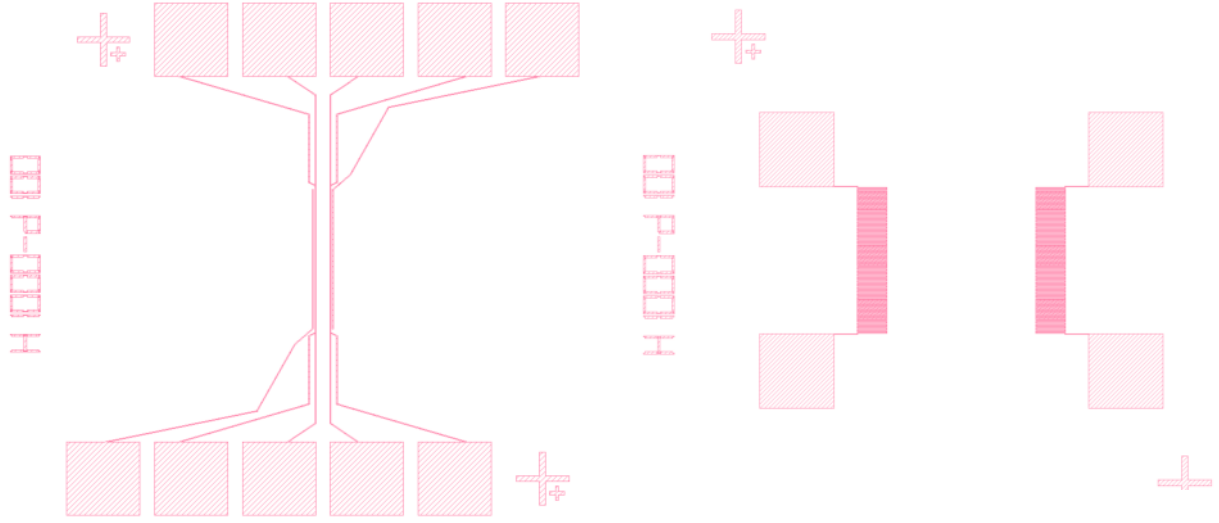


Figure 3.13: Heater mask variant 3. Includes six-wire contacts and a parametrised width and length of the heating strip. The two-step process includes optional symmetrical meandering heaters for substrate heating and gradient formation. The application is for future work on 1D materials and fibers.

Figures 3.10–3.13 show the three photomask designs. Variant 2 was used to fabricate the sensors measured in this thesis.

Silver pattern transfer is performed with a ferric nitrate based wet etchant. The working concentration of etchant used in fabrication was 2 mol L^{-1} at room temperature. Endpoint checks started after approximately 5 s and were repeated every second, with deionized water rinsing between checks. The practical timing target was to complete etching in more than 3 s and less than 10 s for the selected microheater widths. Faster etching makes endpoint control unreliable. Slower etching increases undercut variability and operator dependent spread [44]. Process reproducibility was improved by using a recyclable etchant with controlled refresh intervals. This gave stable etch behavior and reduced line width scatter after mask transfer. Early development included tests with single use nitric acid batches. Ferric nitrate was retained as the main protocol because it gave better practical control in this geometry. Because the etch is isotropic, lateral undercut is unavoidable. The final line width is therefore determined by both the mask opening and the etch time. The analysis does not require the fabricated width to match the nominal mask width exactly. It uses the actual heater width, which is measured by SEM for every heater after fabrication. A heater can therefore be used if its final width differs substantially from the nominal design, provided that the line remains continuous and its geometry can be measured reliably. Heaters are rejected for line breaks, lift-off, or severe edge irregularity. Consistent substrate cleaning and immediate transfer to the sputter chamber reduce these defects.

After the final etchant rinse, the patterned AZ1505 is removed in acetone and the substrate is transferred immediately to DI water. The metal pattern is then inspected by optical microscopy. A fresh protective AZ1505 coating is applied before mechanical cutting to reduce handling damage and edge chipping near the heater structures. Sensors are diced into chiplets on a diamond saw. After dicing, the protective resist is removed in acetone, followed by a DI water rinse. The chiplets are dried and inspected again by optical microscopy. Se-

lected chiplets are screened electrically on a probe station using four point resistance checks to reject damaged or electrically discontinuous lines. The transition from full substrate to individual chiplets is shown in Figure 3.14. Probe station screening is shown in Figure 3.15. Four independently positioned probes contact the four heater pads. Two probes carry the test current and two measure the voltage across the heater, allowing the heater resistance to be checked without including the probe contact resistance. An open or unstable reading indicates a damaged heater or unreliable pad contact. Often defects appear beneath the surface of the heater and are not visible by the optical microscope. Microprobe screening eliminates these defective sensors. Figure 3.16 shows the probe tips aligned with the individual pads.

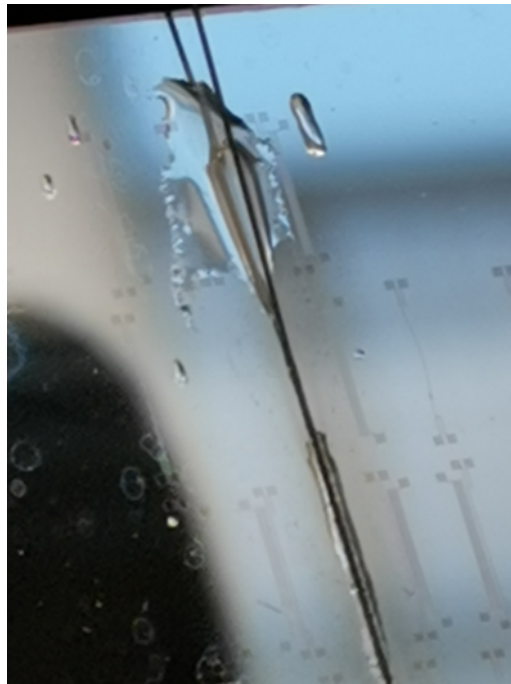


Figure 3.14: Dicing step used to separate the variant 2 wafer into individual 5×5 mm sensor chiplets. The diamond wire diameter is $32 \mu\text{m}$.

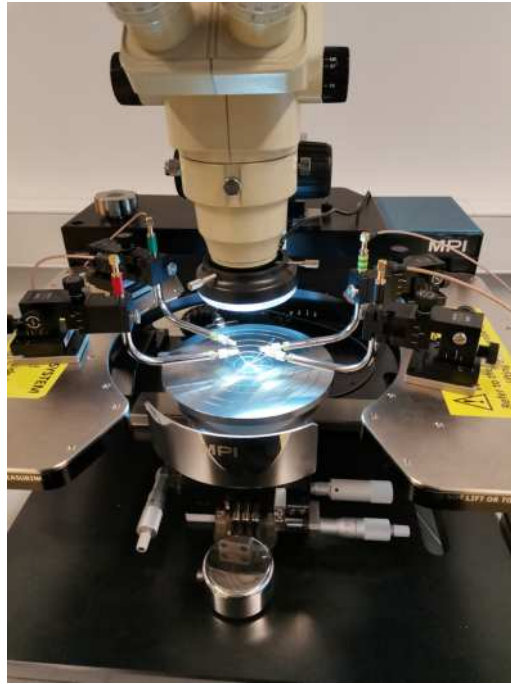


Figure 3.15: Microprobe station screening used for four-point heater resistance checks before SEM measurement and final contacting.

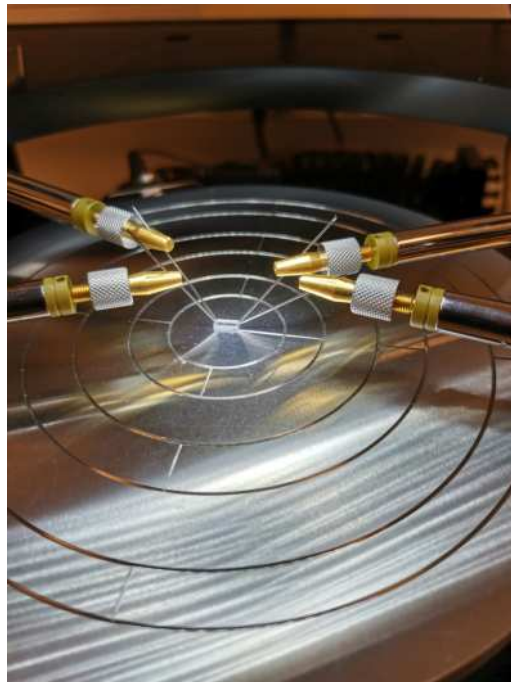


Figure 3.16: Zoomed microprobe contact alignment view showing the four probe tips positioned on the heater contact pads during resistance screening.

After electrical screening, each selected heater is measured by SEM to determine its final width and verify the patterned line geometry. The measured width is used as a heater-geometry input in the subsequent analysis. Final electrical contacting is performed with

the two-component conductive silver paste EPO-TEK EJ2312 [52]. The cure protocol is optimized for low temperature operation to avoid contact induced resistance artifacts, and routine practice is room temperature cure over multiple days before high sensitivity measurements. This route gave stable contacts during thermal cycles and repeatable baseline resistance. Heater resistance is always taken from direct electrical measurement on each chiplet. In thin patterned films, this measured resistance is often different from the ideal bulk estimate $R = \rho_e L / A_{cs}$ because real devices include geometry edge effects, microstructure effects, and contact path contributions. Silver paste contacting was selected for the final measurement sequence because it provided better practical robustness than the tested wire bonding route. The resulting chiplets are reproducible measurement platforms that can be calibrated first and coated with Nafion afterwards, which is central to the inverted geometry strategy used throughout the thesis.

3.3 CALIBRATION AND VALIDATION

This section establishes the substrate baseline and the electrical corrections used in the rest of the thesis. Soda-lime glass is used as the reference substrate, and $\kappa_{\text{glass}}(T)$ is extracted with the classical 3ω logarithmic slope reduction inside the validated frequency window defined in Chapter 2. The calibration uses the measured third harmonic response, heater electrical properties, and the frequency-dependent in-phase temperature amplitude. Calibration on bare substrate data was performed by fitting the in-phase thermal response in the linear part of the ΔT versus $\ln(2\omega)$ curve. Conventions follow Chapter 2, Sec. 2.2. In this thesis ΔT denotes the peak-to-peak heater temperature oscillation at 2ω as introduced in Eq. (2.12). The slope reduction is written for the in-phase component of the complex temperature amplitude $\Delta T(2\omega)$ that appears in the Cahill line source solution (Eq. (2.20)). With the peak-to-peak convention, the peak amplitude is $\Delta T/2$, so the in-phase component used in slope fitting is

$$\Delta T_{2\omega} \equiv \Re\{\Delta T(2\omega)\} = \frac{\Delta T}{2} \cos \phi_{2\omega}, \quad (3.3)$$

where $\phi_{2\omega}$ is the thermal phase lag.

The lock-in amplifier provides the in-phase third harmonic channel $X = \Re\{V_{3\omega}\}$ (Eq. (2.18)). Using the peak-to-peak mapping derived in Chapter 2 (Eq. (2.15)) and the identity $V_{\text{heater}} = I_{\text{rms}} R_0$ for the RMS heater voltage at the operating point, the in-phase thermal amplitude is obtained as

$$\Delta T_{2\omega} = \Re\{\Delta T(2\omega)\} = \frac{2}{\beta V_{\text{heater}}} \Re\{V_{3\omega}\} = \frac{2X}{\beta V_{\text{heater}}}, \quad (3.4)$$

where β is the heater temperature coefficient of resistance (TCR) and R_0 is the heater resistance at the operating point. The electrical transfer corrections described below are applied before forming $\Delta T_{2\omega}$ and its slope.

For each temperature point, the fitted form was

$$\Delta T_{2\omega} = a_T + S \ln(2\omega), \quad (3.5)$$

where a_T is the fitted intercept and $S = d\Delta T_{2\omega}/d\ln(2\omega)$ is the fitted slope used for thermal conductivity extraction.

In the line source and semi-infinite substrate limit, the Cahill solution predicts a log-linear in-phase response in the validated window (Eq. (2.20)). The slope isolates κ through

$$\kappa_{\text{glass}} = \frac{P_{\text{line}}}{2\pi|S|}, \quad P_{\text{line}} = \frac{P_{\text{RMS}}}{L} = \frac{V_{\text{heater}}^2}{R_0 L}, \quad (3.6)$$

where P_{line} is the heater lineic power, P_{RMS} is the average electrical power dissipated in the heater, and L is heater length. This is the Cahill-style reduction in the calibration geometry [28]. The linear fit interval was selected from the validated window discussed in Chapter 2 and from the measured log-linear behavior of the substrate-only sweeps. In this thesis dataset, substrate calibration sweeps were acquired over 30 to 800 Hz and the accepted fit interval for extraction was 30 to 800 Hz when the window linearity criteria were satisfied.

During calibration, the wider heater branch showed a systematic mismatch relative to the narrow heater reference as shown in Figure 3.20. The discrepancy was traced to parasitic series resistance growth in the high temperature wiring and contacts. The mismatch is

electrical in origin because the classical reduction is strongly voltage weighted when expressed in terms of the measured third harmonic slope. Chapter 2 makes this explicit in the closed form $V_{3\omega}$ solution (Eq. (2.21)) and the corresponding slope reduction (Eq. (2.23)). In the notation of Chapter 2, let

$$s = \frac{d\Re\{V_{3\omega}\}}{d\ln(2\omega)} < 0. \quad (3.7)$$

Then the classical slope reduction gives

$$\kappa = -\frac{V_{\text{heater}}^3}{4\pi LR_0} \frac{\beta}{s} = \frac{V_{\text{heater}}^3}{4\pi LR_0} \frac{\beta}{|s|}. \quad (3.8)$$

R_0 , β , and $|s|$ enter linearly. V_{heater} enters as V_{heater}^3 . A modest bias in the effective heater RMS voltage therefore produces a large bias in κ . The same conclusion is obtained if the fit is performed on $\Delta T_{2\omega}$ and then mapped to $V_{3\omega}$. Differentiating Eq. (3.4) gives

$$S = \frac{d\Delta T_{2\omega}}{d\ln(2\omega)} = \frac{2}{\beta V_{\text{heater}}} s, \quad (3.9)$$

which links the thermal slope defined above to the electrical slope used in Eq. (3.8). Both views lead to the same sensitivity issue: electrical amplitude errors must be corrected before comparing results quantitatively. Published datasets often report normalized responses or effective thermal conductivities. These quantities support trend analysis. Quantitative comparison across heater geometries and against reference data requires explicit treatment of wiring parasitics [32, 33, 44]. The parasitic branch resistance used in the correction was obtained from independent direct current measurements with a Keithley 2100 digital multimeter on the high temperature wiring and contact path. For the 14 μm heater branch, the value used in the calibration correction was $R_p = 3.6 \Omega$, with estimated standard uncertainty $\sigma_{R_p} = 0.001 \Omega$. This uncertainty is propagated in the corrected $V_{3\omega}$ term below. The coax in the current insert remained usable for this thesis after correction and periodic verification. Any future hardware rebuild would use a new high temperature insert with new coaxial routing. Figure 3.17 shows representative resistance versus temperature traces before and after 3ω measurements for both heater families. The measured drift pattern is consistent with contact path evolution and supports the need for explicit series resistance correction in the reduction procedure.

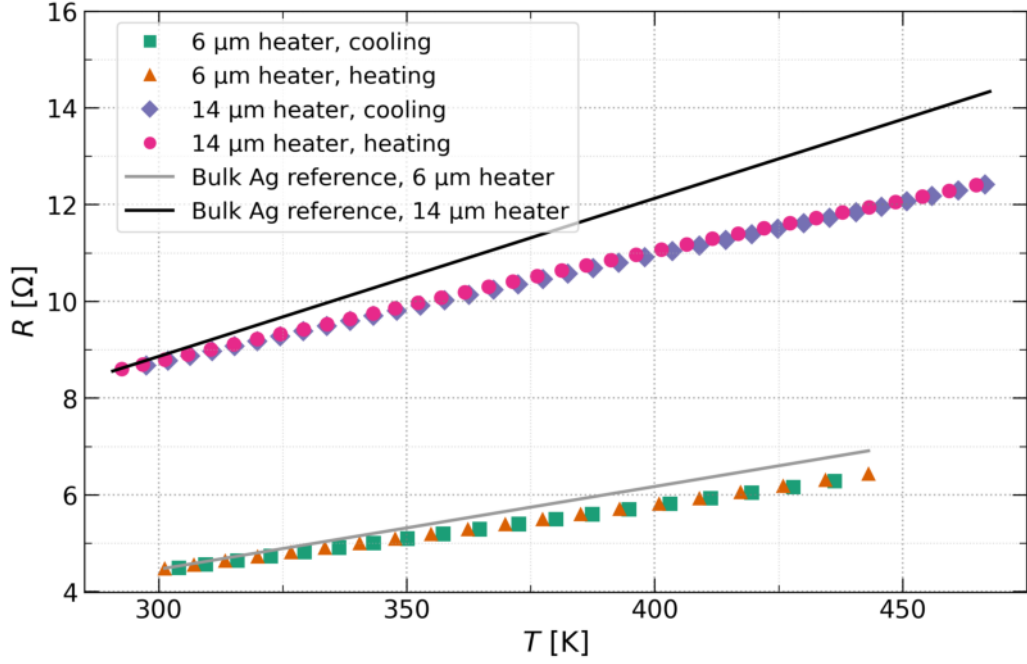


Figure 3.17: Measured heater resistance versus temperature for 6 μm and 14 μm heaters, with bulk silver reference trends. The bulk silver reference has a slightly higher temperature coefficient of resistance. The sputtered heater films remain close to bulk behavior.

Figure 3.18 shows the bridge at the fundamental frequency and its ideal third harmonic equivalent circuit. At the fundamental frequency, the external source drives the complete Wheatstone bridge and the bridge is adjusted by comparing nodes V_A and V_B . At 3ω , the external ideal source has no third harmonic component and is therefore shorted in the equivalent circuit, while its $50\ \Omega$ output resistance remains. The temperature modulated heater is represented by the local source $V_{3\omega}$ in series with R_0 .

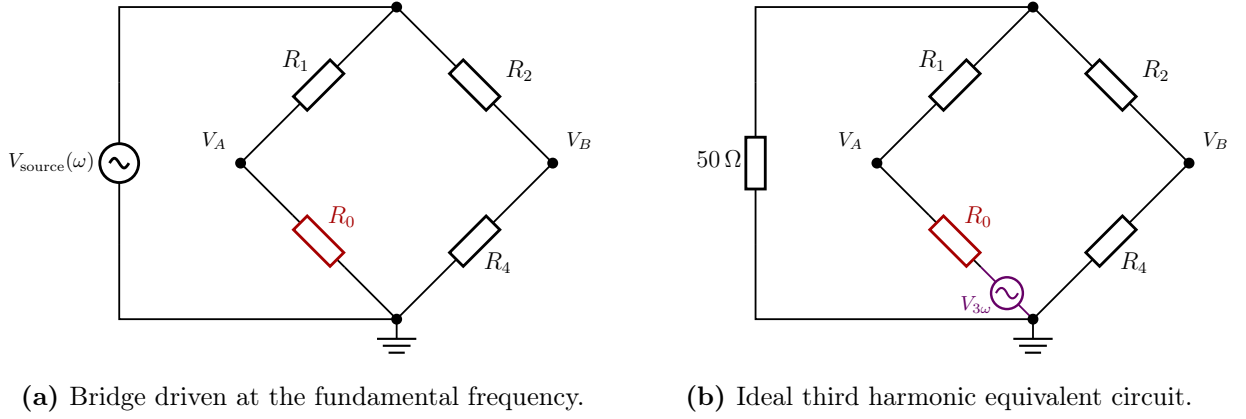


Figure 3.18: Bridge at the fundamental frequency and its ideal third harmonic equivalent circuit. (a) The source $V_{\text{source}}(\omega)$ drives the bridge at the fundamental frequency, R_0 is the heater, and V_A and V_B are the differential measurement nodes. (b) In the ideal 3ω equivalent circuit, the external source is shorted at the third harmonic but its $50\ \Omega$ output resistance remains. The heater generated third harmonic is represented by the local source $V_{3\omega}$.

As viewed from the heater branch in the 3ω equivalent circuit, R_1 is in series with two return paths to ground. One path is through the $50\ \Omega$ source output resistance, while the other is through the series combination $R_2 + R_4$. Since these return paths connect the same two nodes, they are in parallel. The resulting resistance external to R_0 is therefore

$$R_{\text{ext}} = R_1 + [50\ \Omega \parallel (R_2 + R_4)] \simeq 10\ \Omega + 50\ \Omega = 60\ \Omega, \quad (3.10)$$

where the final approximation follows from $R_2 + R_4 \gg 50\ \Omega$. During the 3ω measurement, the heater is connected in a two-wire configuration. The combined resistance of the current-carrying cables, contact wires, connectors, and electrical contacts is therefore lumped into R_p in series with the heater, as shown in Figure 3.19. This additional series resistance causes the voltage divider attenuation. In contrast, R_0 is obtained using a four-wire resistance measurement. The separate voltage-sense leads carry negligible current, so voltage drops along the current leads and contacts are excluded and the heater resistance is isolated.

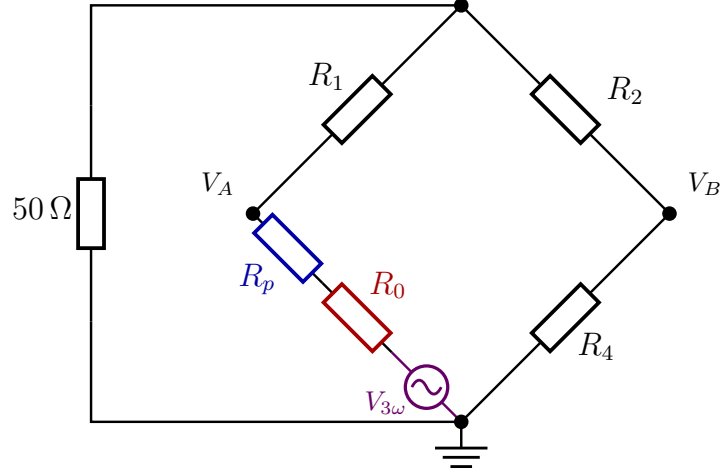


Figure 3.19: Two-wire third harmonic measurement equivalent circuit. The parasitic series resistance R_p , shown in blue, is a lumped representation of the resistances of the cables, connectors, contact wires, and electrical contacts in the current-carrying path to the heater. These contributions attenuate the voltage produced by the local source $V_{3\omega}$. The heater resistance R_0 is determined separately using a four-wire measurement, which excludes voltage drops along the current leads and contacts. With $R_1 = 10 \, \Omega$ and $R_2 + R_4 \gg 50 \, \Omega$, the remaining network contributes approximately $60 \, \Omega$, giving the voltage divider correction in Eq. (3.11).

The measured third harmonic voltage was corrected using

$$V_{3\omega, \text{corr}} = V_{3\omega, \text{meas}} \frac{R_0 + R_p + 60 \, \Omega}{R_0 + 60 \, \Omega}. \quad (3.11)$$

This multiplicative factor corrects the voltage divider attenuation introduced by the parasitic series resistance R_p . The measured bridge voltage is rescaled from the total series path $R_0 + R_p + 60 \, \Omega$ to the nominal bridge arm $R_0 + 60 \, \Omega$. Here the $60 \, \Omega$ term is the external resistance approximation defined in Eq. (3.10). The $10 \, \Omega$ contribution is the precision film resistor R_1 , and the $50 \, \Omega$ contribution is the output impedance of the lock-in amplifier source. R_0 is the heater resistance at the operating temperature, obtained using the four-wire calibration geometry so that lead and contact voltage drops are excluded. R_p is the lumped parasitic series resistance present in the two-wire 3ω measurement path. It includes the current-carrying cables, connectors, contact wires, and electrical contacts. The physical path includes approximately 2 m of room-temperature Bayonet Neill–Concelman (BNC) cable, the high-temperature coaxial cable inside the insert, and approximately 2 cm of $75 \, \mu\text{m}$ diameter gold contact wires at the heater.

The propagated uncertainty includes both measurement scatter and uncertainty of the parasitic resistance estimate:

$$\sigma_{V_{3\omega, \text{corr}}}^2 \approx (\sigma_{\bar{V}_{3\omega}} s_f)^2 + \left(\frac{V_{3\omega, \text{meas}}}{R_0 + 60 \, \Omega} \sigma_{R_p} \right)^2, \quad s_f = \frac{R_0 + R_p + 60 \, \Omega}{R_0 + 60 \, \Omega}. \quad (3.12)$$

Here $\sigma_{\bar{V}_{3\omega}}$ is the standard error of the measured $V_{3\omega}$ mean, σ_{R_p} is the standard uncertainty of parasitic resistance, and s_f is the bridge scaling factor.

In this analysis, κ_{raw} denotes thermal conductivity computed after the $V_{3\omega}$ bridge transfer correction above and before correcting the heater voltage amplitude used in power mapping. The heater voltage amplitude is biased by resistive division when R_p is present in series with the heater. If a branch voltage is interpreted as the heater voltage, the true heater voltage is reduced by

$$V_{\text{heater,true}} = V_{\text{branch,meas}} \frac{R_0}{R_0 + R_p}. \quad (3.13)$$

Because κ scales as V_{heater}^3 in Eq. (3.8), the thermal conductivity level was corrected consistently as

$$\kappa_{\text{corr}} = \kappa_{\text{raw}} \left(\frac{R_0}{R_0 + R_p} \right)^3. \quad (3.14)$$

This correction is applied both to the Wheatstone branch reduction and to the effective heater voltage used in power mapping. After applying this correction, narrow and wide heater trends return to consistent behavior within uncertainty.

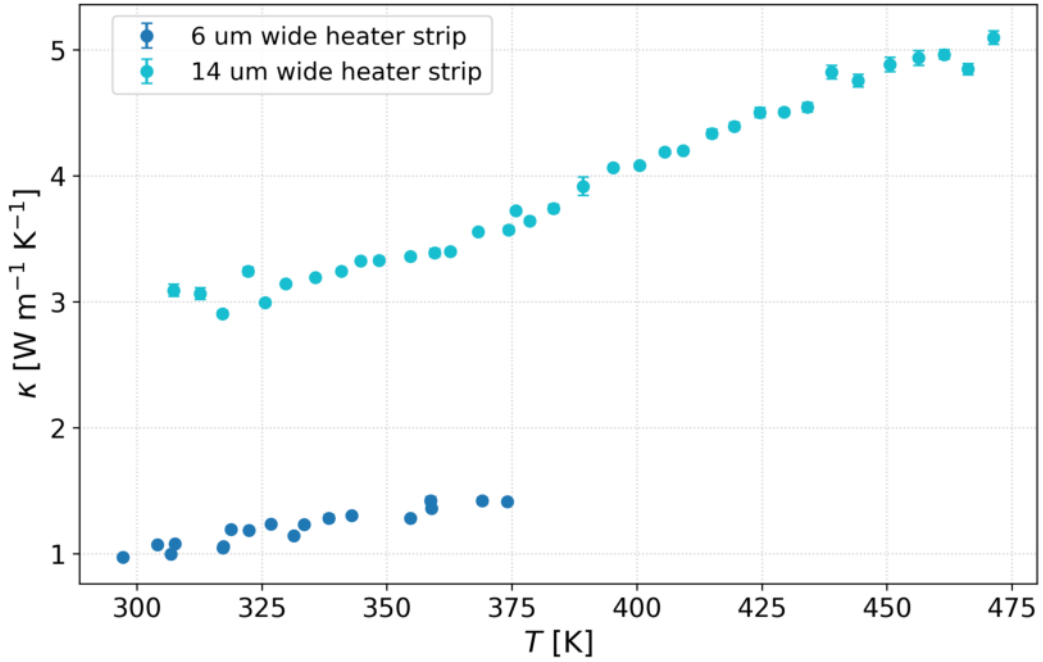


Figure 3.20: Uncorrected glass thermal conductivities for 6 μm and 14 μm heaters.

Figure 3.20 shows the divergence between the uncorrected heater width families. The correction described above is therefore necessary to restore consistency and to ensure that the extracted substrate baseline is suitable for use in later film subtraction and inverse FEM steps.

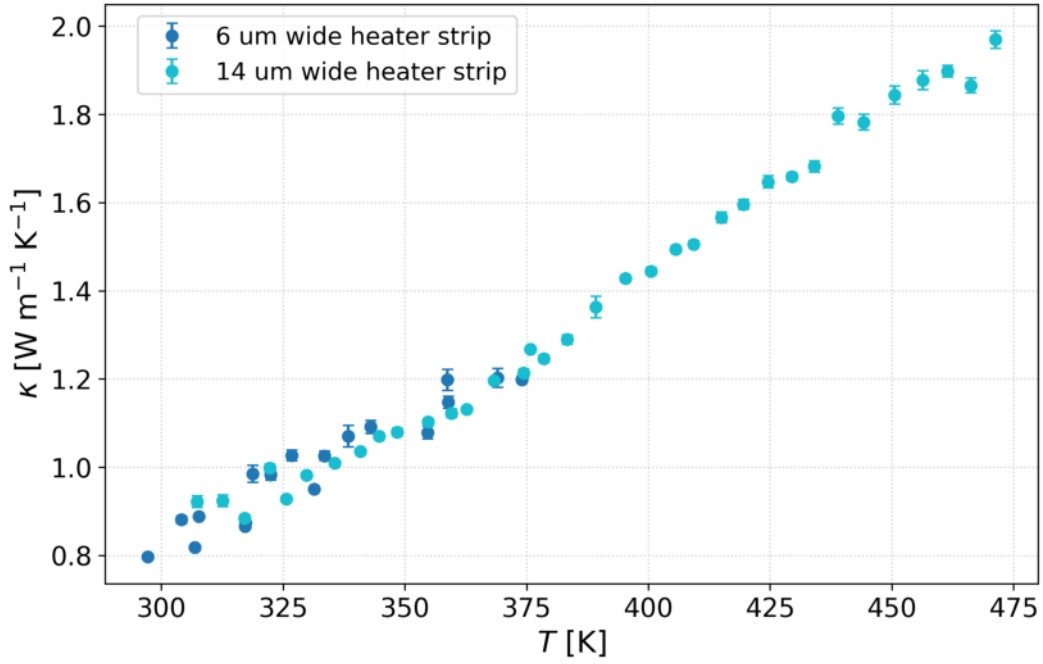


Figure 3.21: Aligned glass thermal conductivities for 6 μm and 14 μm heaters after parasitic resistance correction.

After correction, Figure 3.21 shows the expected convergence of narrow and wide heater estimates within uncertainty. The fitted substrate baseline used for the inverse analysis increases from approximately 0.812 to $1.234 \text{ W m}^{-1} \text{ K}^{-1}$ over the 305.8 – 368.3 K temperature interval used for the coated-film analysis. The uncertainty statement relevant to the experimental glass measurements is the platform validation reported in the published article [44], included in Appendix D. In that work, the relative uncertainty of each extracted glass κ measurement was propagated from the measured voltage, temperature coefficient of resistance, heater resistance, and fitted-slope contributions, and remained below 2 percent. At 334.2 K , the fitted substrate thermal conductivity is $1.003 \text{ W m}^{-1} \text{ K}^{-1}$, consistent with the reference level used in that validation dataset. An additional numerical cross-check against the Cahill line-source model is presented across Figures A.12–A.16 of Appendix A. In the accepted analytical regime, the substrate-only finite-element response has an RMS relative difference of approximately 1.5–3% for most investigated heater widths. The corresponding deviations are 2.50% and 2.68% for the experimentally used 6 and 14 μm heaters. This benchmark is kept separate from the experimental platform validation described above. The corrected $V_{3\omega}$ data were then checked at the level of the selected fit window. Figure 3.22 summarizes the mean third harmonic voltage for each temperature using the common overlap band $f = 520.1$ – 789.3 Hz , corresponding to the plotted interval 6.95 – 7.36 on the $\ln(2f)$ axis in the individual panels. The equivalent interval is 8.79 – 9.20 when expressed as $\ln(2\omega)$, with $\omega = 2\pi f$. The monotonic decrease with temperature is expected from the combined temperature dependence of heater resistance, TCR, and substrate thermal response. The smooth trend across temperature indicates consistent behavior within the selected window.

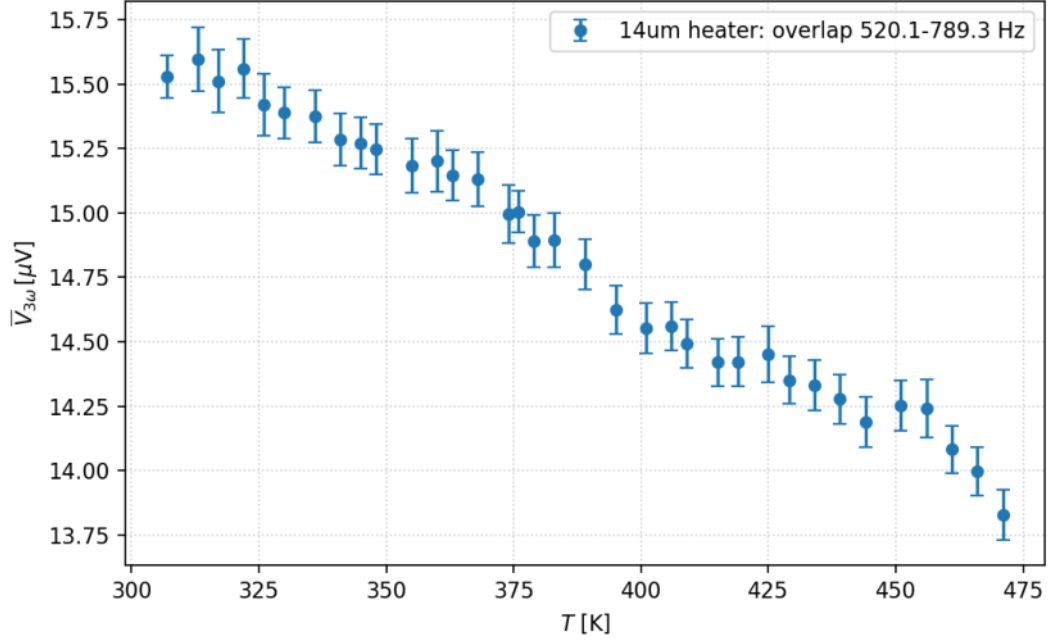


Figure 3.22: 14 μm heater $V_{3\omega}$ voltage averaged over the common 520.1–789.3 Hz overlap band for all measured temperatures.

Sensitivity checks were performed to separate parameters that control the calibration slope from parameters that mainly control regime boundaries. The key test varied volumetric heat capacity ρc in FEM at fixed thermal conductivity in the substrate calibration geometry (Figure A.7). The tested behavior follows the frequency domain relation

$$\alpha = \frac{\kappa}{\rho c}, \quad (3.15)$$

where α is thermal diffusivity, κ is thermal conductivity, ρ is density, and c is specific heat capacity at constant pressure. Changing ρc moves thermal penetration depth and therefore shifts the visible edges of the linear frequency interval. The retained sensitivity calculation in Figures A.7 and A.8 show that this effect is concentrated at the regime boundaries, with a smaller residual variation in the fitted mid-band slope. Thermal conductivity remains the principal parameter controlling that slope, while ρc controls the thermal penetration depth and therefore the placement of the accepted interval. The two parameters are not treated as equally identifiable from the slope alone. Volumetric heat capacity is therefore treated as a prescribed model input. The calibration section provides both the corrected electrical input basis and the parameter-identifiability basis for the inverse FEM methodology used on coated films.

3.4 NUMERICAL 3ω MODEL

The numerical finite-element model developed in this thesis is implemented as a suite of command-line tools composed primarily of Bash and Python scripts. General-purpose geometry construction, meshing, linear algebra, storage, and visualization are supplied by established open-source libraries. The developed tools orchestrate these libraries. They translate the physical description into solver inputs, invoke the numerical stages in the required order, automate frequency and material property sweeps, monitor convergence, manage intermediate states, and direct the calculated fields into 3ω signal extraction and inverse analysis. Together, the tools can serve as a general-purpose thermal FEM solver, but they are optimized and specialized for the 3ω methodology and will remain focused on this application. Reproducibility is supported through a separate JavaScript Object Notation with Comments (JSONC) model definition for each case. Each definition is loaded by the orchestration tools and specifies the physical model, numerical controls, and output.

The overall workflow follows the sequence common in commercial finite-element environments. A parametric physical problem is defined, a mesh is generated, the governing system is assembled and solved, parameter studies are automated, and the resulting fields are reduced to the required observable. The distinction is that the present implementation uses domain-specific command-line orchestration instead of a general graphical solver environment. The custom layer encodes the assumptions and operations needed for the layered heater-film-substrate problem, including material and source mapping, boundary condition assignment, steady and transient execution, periodic convergence assessment, heater temperature averaging, harmonic extraction, and construction of the inverse response map.

Each forward calculation represents a specific 3ω specimen and measurement condition. The physical inputs include the cross-sectional dimensions of the substrate, heater, and film together with the thermal conductivity and volumetric heat capacity assigned to each region. They also include the heater resistance, heater length, applied RMS voltage, operating temperature, and electrical excitation frequency. From these quantities, the orchestration tools construct a two-dimensional conformal mesh, distribute the Joule source over the heater, and solve the transient heat equation until the heater temperature reaches a periodic response. The final cycles are spatially averaged over the heater and fitted at the thermal frequency $2f$, producing $\Delta T(f)$ and the corresponding modeled $V_{3\omega}(f)$.

For a film measurement, this forward calculation is repeated over a prescribed range of candidate film thermal conductivities. Each candidate produces a frequency-dependent modeled response. Reduction over the same logarithmic frequency interval used for the experiment creates a forward map between film thermal conductivity and the measured observable. The intersection of that map with the experimental target provides the inferred film thermal conductivity and its uncertainty interval. Figure 3.23 summarizes the five stages of this workflow, which also define the organization of this section.

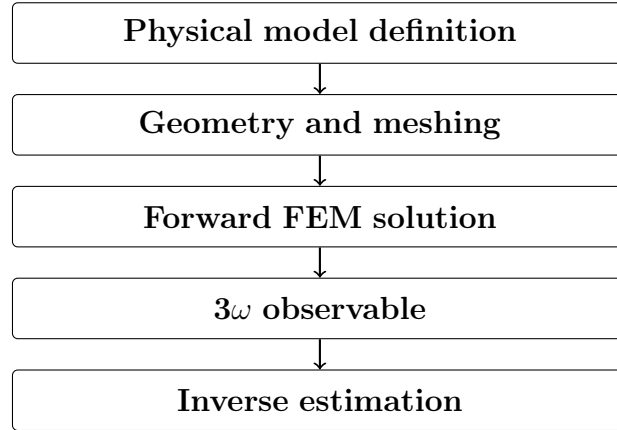


Figure 3.23: Five-stage numerical workflow connecting the physical model to the film thermal conductivity estimate.

The main open source components are summarized in Table 3.7.

Table 3.7: Main open-source components used in the numerical architecture.

Function	Component
Geometry and mesh	Gmsh [54], meshio [55]
Numerical operations	NumPy [56], Numba [57]
Sparse linear algebra	SciPy/SuperLU [58], PyAMG [59], CuPy/CuPyX [60]
Data storage	Hierarchical Data Format version 5 (HDF5), h5py [61]
Analysis and visualization	NumPy [56], SciPy [58], Matplotlib [62]

Gmsh constructs the geometry and mesh on the CPU. The stationary thermal system is solved by default with the CuPy/CuPyX CUDA conjugate gradient solver. If that solve is unavailable, the code uses a CPU solver. The rough and fine transient stages use CPU SuperLU and reuse one sparse factorization throughout the time stepping. PyAMG and SciPy provide additional CPU solver paths.

3.4.1 Physical model definition

Each simulated case begins with the measured specimen dimensions and electrical conditions together with the thermophysical properties assigned to the substrate, heater, and film. The orchestration tools translate the layer order and dimensions into geometric regions, assign thermal conductivity and volumetric heat capacity to those regions, convert the heater voltage and resistance into a volumetric Joule source, and apply the prescribed thermal boundaries. The electrical frequencies and candidate film thermal conductivities complete the case definition. A thermal conductivity sweep retains the same specimen geometry, excitation, boundary conditions, and frequency range while changing only the candidate film thermal conductivity passed to the forward model.

The physical model follows from the long strip geometry of the experiment. The heater length is much larger than its width and thickness, and the dominant thermal gradients relevant to the measured response occur in the cross section. The model is solved in two

spatial dimensions per unit depth along the heater length. The computational domain contains the substrate, the metallic heater, and, for coated measurements, the polymer film. Material properties are treated as piecewise constant within each region at a selected operating temperature, and the baseline model assumes perfect thermal contact at conformal interfaces [32].

The governing transient heat equation is [45, 63]

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \dot{q}(x, y, t), \quad (3.16)$$

where T is temperature, κ is thermal conductivity, ρc is volumetric heat capacity, and $\dot{q}$ is the volumetric heat source density. The bottom boundary is held at the operating temperature. The remaining external boundaries are treated as adiabatic, consistent with the vacuum measurement environment. Temperature and heat-flux continuity are enforced through the shared mesh at internal interfaces.

The electrical excitation is represented by a volumetric heating source within the heater cross section. In the two-dimensional formulation, the measured electrical inputs define the power per unit heater length

$$P_{\text{line}} = \frac{V_{\text{rms}}^2}{R_{\text{heater}} L_{\text{heater}}}, \quad (3.17)$$

where V_{rms} is the RMS heater voltage, R_{heater} is the heater resistance, and L_{heater} is the heater length. The corresponding source density over the heater cross section is

$$q_{\text{heater}} = \frac{P_{\text{line}}}{W_{\text{heater}} H_{\text{heater}}}, \quad (3.18)$$

where W_{heater} and H_{heater} are the heater width and thickness. Joule heating contains equal steady and second-harmonic components, giving

$$\dot{q}(t) = \frac{q_{\text{heater}}}{2} [1 + \cos(4\pi f t)], \quad (3.19)$$

Here f is the electrical drive frequency in hertz and $\omega = 2\pi f$ is its angular frequency. Because Joule heating is quadratic in the drive current, the oscillatory heat source and the resulting temperature response occur at $2f$, equivalently at angular frequency $2\omega = 4\pi f$.

3.4.2 Geometry and meshing

The layered geometry is constructed as conformal material regions, so the nodes on either side of an internal interface are shared. Local mesh refinement is concentrated near the heater, across thin films, and along material interfaces, where the largest temperature gradients occur. Away from the heater the mesh is gradually coarsened.

A representative mesh and the corresponding mesh independence checks are presented in Appendix A.

3.4.3 Forward FEM solution

With the physical problem defined, multiplication of Eq. (3.16) by a test function v , followed by integration over the computational domain $\mathcal{D}$, gives the weak form [64, 65]

$$\int_{\mathcal{D}} \rho c v \frac{\partial T}{\partial t} dA + \int_{\mathcal{D}} \kappa \nabla v \cdot \nabla T dA = \int_{\mathcal{D}} v \dot{q} dA. \quad (3.20)$$

Using linear triangular elements gives the semidiscrete system

$$\mathbf{M} \frac{d\mathbf{T}}{dt} + \mathbf{K}\mathbf{T} = \mathbf{Q}(t). \quad (3.21)$$

Here, $\mathbf{M}$ describes how much heat can be stored at each node. The matrix $\mathbf{K}$ describes how readily heat flows between nodes and is constructed from the thermal conductivity assigned to each material region. The vector $\mathbf{Q}$ describes how the Joule heat is distributed among the nodes. A lumped representation is used for $\mathbf{M}$, meaning that each node receives its own heat storage value.

The element contributions are assembled according to the mesh connectivity. Material labels determine the thermal conductivity and heat capacity used in each element, while elements in the heater receive the Joule source. Their contributions form the global matrices in Eq. (3.21). Adiabatic boundaries require no additional boundary term, and the prescribed bottom temperature is applied before solution.

Time integration uses the Crank–Nicolson method [66]. With $t^{n+1} = t^n + \Delta t$ and $\theta = 0.5$, the update matrices are

$$\mathbf{A}_{\text{CN}} = \mathbf{M} + \theta \Delta t \mathbf{K}, \quad \mathbf{B}_{\text{CN}} = \mathbf{M} - (1 - \theta) \Delta t \mathbf{K}, \quad (3.22)$$

and the temperature update is

$$\mathbf{A}_{\text{CN}} \mathbf{T}^{n+1} = \mathbf{B}_{\text{CN}} \mathbf{T}^n + \Delta t \left[(1 - \theta) \mathbf{Q}^n + \theta \mathbf{Q}^{n+1} \right]. \quad (3.23)$$

The meaning of this update is easiest to see in one dimension. Imagine three neighboring points along a bar, with the middle temperature denoted by T_i . Heat conduction changes T_i according to the difference between it and its two neighbors:

$$\left. \frac{\partial^2 T}{\partial x^2} \right|_i \approx \frac{T_{i-1} - 2T_i + T_{i+1}}{\Delta x^2}.$$

An explicit method would calculate the new temperature using only these differences at the beginning of the timestep, whereas a fully implicit method would use only the unknown differences at its end. Crank–Nicolson averages the two. In the present two-dimensional FEM model, $\mathbf{K}\mathbf{T}$ plays the role of these neighbor-to-neighbor conduction differences, $\mathbf{M}$ accounts for the heat stored around each node, and $\mathbf{Q}$ adds the Joule heat. Averaging the conduction and source terms between t^n and t^{n+1} gives second-order temporal accuracy without requiring prohibitively small timesteps. The bottom node temperatures are held at the operating temperature during every update, and the complete field is reconstructed after the remaining nodal temperatures are solved.

The numerical workflow consists of the following steps:

1. construct the geometry and assign material, heater, and boundary labels.
2. assemble the heat storage, heat conduction, and Joule source terms.
3. solve the steady problem using the mean Joule power to obtain a physical initial temperature field.
4. advance the transient problem with coarse and then fine Crank–Nicolson timesteps until the heater response is periodic and stable.

5. average the final temperature cycles over the heater, extract the 2ω temperature oscillation, and convert it to the modeled 3ω voltage.
6. repeat the forward calculation over frequency and candidate film thermal conductivity, then compare the resulting response map with the experiment.

The heater area observable is constructed by selecting elements whose centroids lie inside the heater and collecting their nodes into a unique averaging set, as illustrated in Figure 3.24.

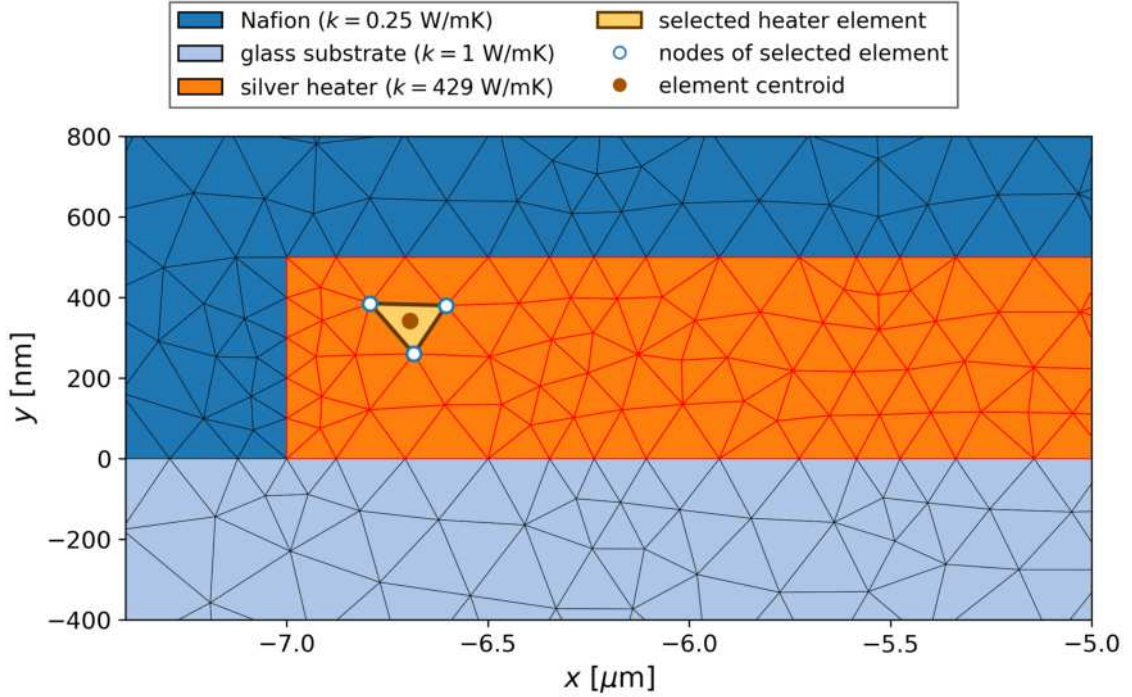


Figure 3.24: Local finite element mesh used to construct the heater area temperature observable. The highlighted triangle illustrates one element selection step.

The calculation is divided into three stages. A steady solution provides a physically consistent initial temperature field. A coarse transient stage approaches the periodic regime efficiently, and a subsequent fine stage resolves the final oscillation used for signal extraction. The timestep is tied to the excitation period,

$$\Delta t = \frac{1}{f N_{\text{pp}}}, \quad (3.24)$$

where N_{pp} is the number of time steps per electrical period. Periodic stabilization is assessed from changes in the spatially averaged heater temperature and its standard deviation over the most recent electrical period. The convergence criteria and the handoff from the rough to the fine stage are detailed in Appendix A.1.

At $f = 237.1 \text{ Hz}$, the rough stage removes the initial transient and the fine stage resolves the response at $2f = 474.2 \text{ Hz}$, as shown for exposed and Nafion-covered heaters in Figures 3.25 and 3.26.

The rough stage monitors the mean temperature and oscillation at a fixed time step, whereas the fine stage continues from the final rough temperature field using a smaller time

step. The two stages therefore resolve the same physical response at different temporal resolutions, so their amplitudes can differ slightly. Only the final five thermal cycles of the fine response are used to determine $A_{2\omega}$. Complementary numerical consistency checks are reported in Appendix A.

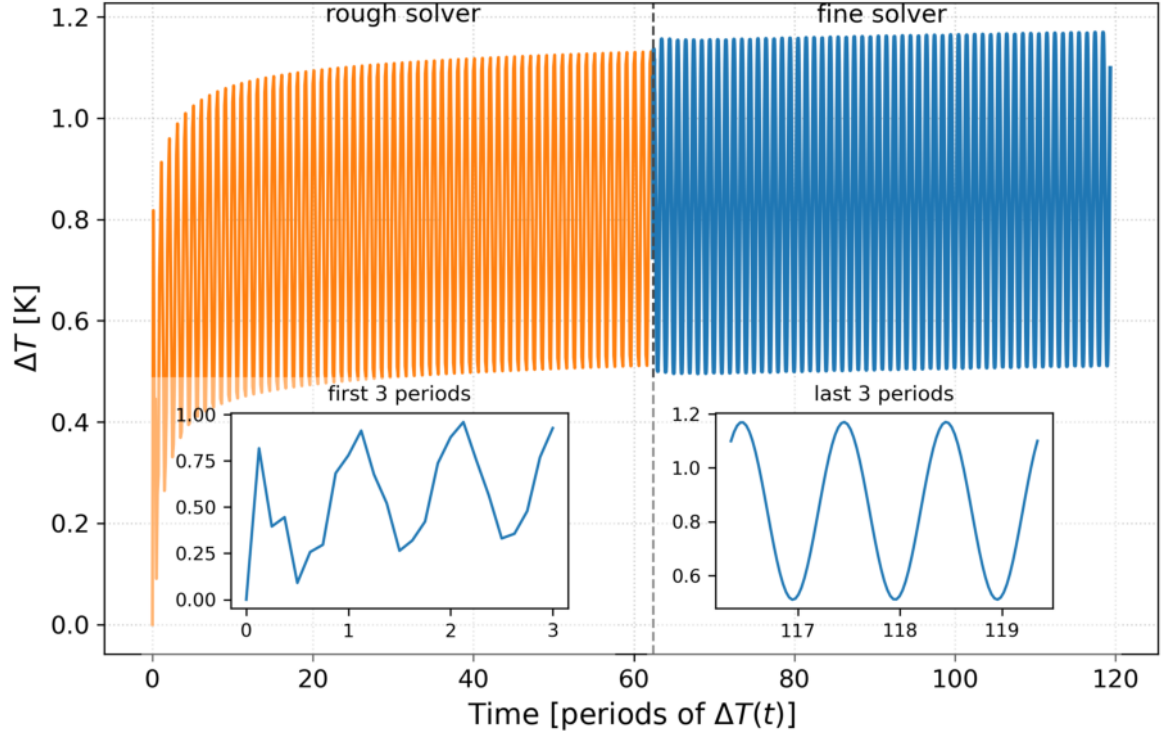


Figure 3.25: Rough-to-fine periodic stabilization for the exposed $6 \mu\text{m}$ wide heater at $f = 237.1 \text{ Hz}$.

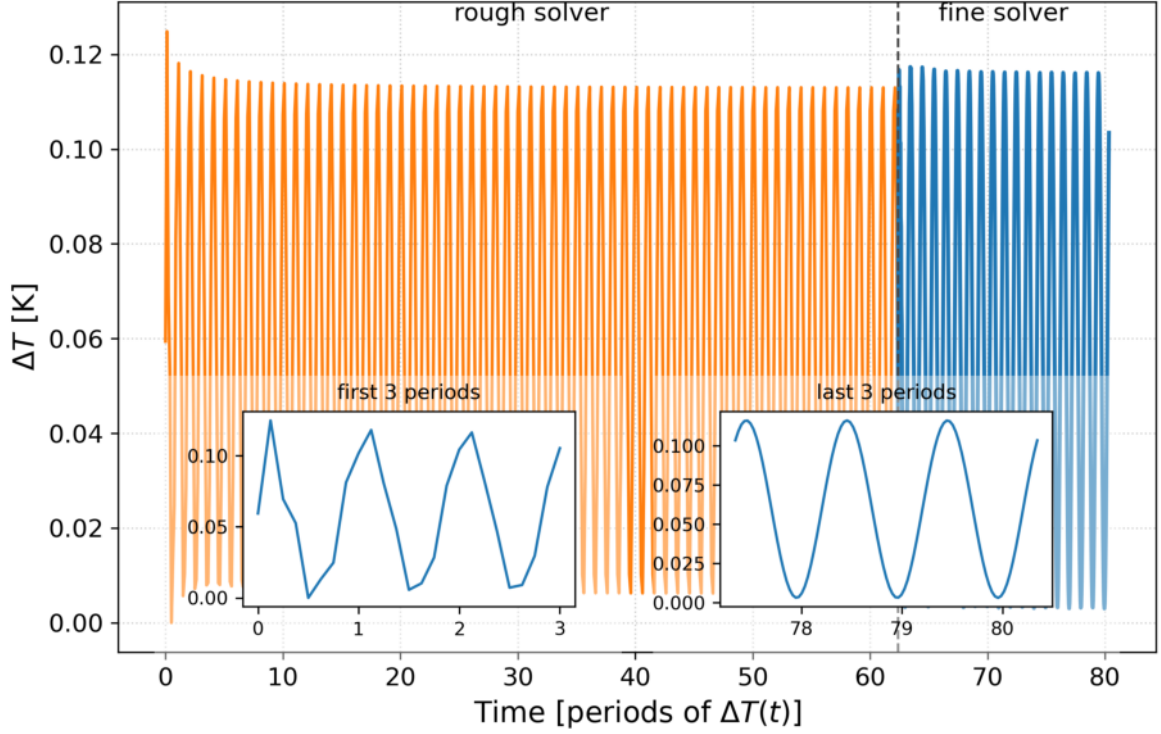


Figure 3.26: Rough-to-fine periodic stabilization for the Nafion-covered $14 \mu\text{m}$ wide heater at $f = 237.1 \text{ Hz}$.

During these stages, intermediate results are stored in a structured hierarchical data model containing the mesh, temperature fields, time samples, geometry attributes, physical inputs, and convergence information. An interrupted calculation can continue from a saved physical state, and the same converged temperature history can be examined using alternative heater averaging definitions or signal reductions without repeating the forward solution. Metadata is recorded for every simulation, including the physical inputs, numerical controls, and the final convergence status.

3.4.4 3ω observable

Once the periodic solution is obtained, it must be reduced to the temperature observable used in the subsequent electrical analysis. The direct numerical result is the temperature field $T(x, y, t)$, whereas the experiment measures the electrical response of the heater. Conceptually, the effective heater temperature is represented by the spatial average over the heater domain,

$$\bar{T}_{\text{heater}}(t) = \frac{1}{A_{\text{heater}}} \int_{A_{\text{heater}}} T(x, y, t) dA. \quad (3.25)$$

In the numerical implementation, heater elements are selected when their centroids lie inside the heater domain. The nodes belonging to all selected elements are then collected, and duplicate node indices are removed. The effective heater temperature is evaluated as the arithmetic mean over the resulting unique-node set,

$$\bar{T}_{\text{heater}}(t) = \frac{1}{N_{\text{heater}}} \sum_{i \in \mathcal{N}_{\text{heater}}} T_i(t), \quad (3.26)$$

where $\mathcal{N}_{\text{heater}}$ is the set of unique nodes associated with the selected heater elements and $N_{\text{heater}} = |\mathcal{N}_{\text{heater}}|$. Thus, the implemented observable is an unweighted nodal average. The same node set is retained throughout the transient calculation and used for the subsequent sinusoidal fit.

After periodic convergence, the heater response is fitted directly in the time domain as

$$\bar{T}_{\text{heater}}(t) = C + A_{2\omega} \sin(4\pi ft + \phi_{2\omega}), \quad (3.27)$$

where C is the mean temperature, $A_{2\omega}$ is the peak temperature amplitude, and $\phi_{2\omega}$ is the thermal phase relative to the sine reference. The reported thermal oscillation is

$$\Delta T_{\text{pp}} = 2A_{2\omega}. \quad (3.28)$$

Using the same RMS and peak-to-peak conventions as in the experimental reduction, the modeled third-harmonic voltage follows Eq. (2.15):

$$V_{3\omega, \text{model}} = \frac{I_{\text{rms}} R_0 \beta}{4} \Delta T_{\text{pp}}, \quad (3.29)$$

where R_0 is the heater resistance at the operating temperature and β is its temperature coefficient of resistance.

In practice, the harmonic model is evaluated as a linear least-squares problem using sine, cosine, and offset components. If

$$\bar{T}_{\text{heater}}(t) = a \sin(4\pi ft) + b \cos(4\pi ft) + C,$$

then

$$A_{2\omega} = \sqrt{a^2 + b^2}, \quad \phi_{2\omega} = \arg(a + ib).$$

The fitted oscillation can equivalently be written as $A_{2\omega} \sin(4\pi ft + \phi_{2\omega})$, where $\phi_{2\omega}$ is its phase shift relative to the sine reference. Numerically, the phase is evaluated as $\phi_{2\omega} = \text{atan2}(b, a)$ using NumPy's `arctan2` function in Python [56]. This function uses the signs of both fitted coefficients to select the correct quadrant. Fitting the final cycles in the time domain retains the amplitude, phase, in-phase component, and quadrature component of the response. The regression covariance provides the statistical contribution to the uncertainty of the extracted amplitude.

Figures 3.27 and 3.28 show that the fitted sinusoid closely follows the final five thermal cycles for both modeled geometries. The faster stabilization of the 14 μm Nafion-covered heater is physically consistent with its less localized thermal response. For the same total lineic heating power, the wider heater distributes heat over a larger area and therefore produces a lower power density and a smaller temperature rise. Its larger contact area also provides stronger thermal coupling to the substrate, allowing heat to be removed from the heater more effectively. Furthermore, averaging the temperature over the larger heater area suppresses localized and rapidly decaying spatial variations, while the Nafion layer additionally damps the oscillatory response. As a result, the changes in the spatially averaged temperature and its period-wise standard deviation fall below the prescribed convergence tolerances sooner. The convergence criteria are defined in Appendix A.1. This does not imply that a wider heater always stabilizes faster, because heater width and layer arrangement differ simultaneously in the two modeled cases. Here, faster convergence means that the heater average satisfies the numerical criteria sooner.

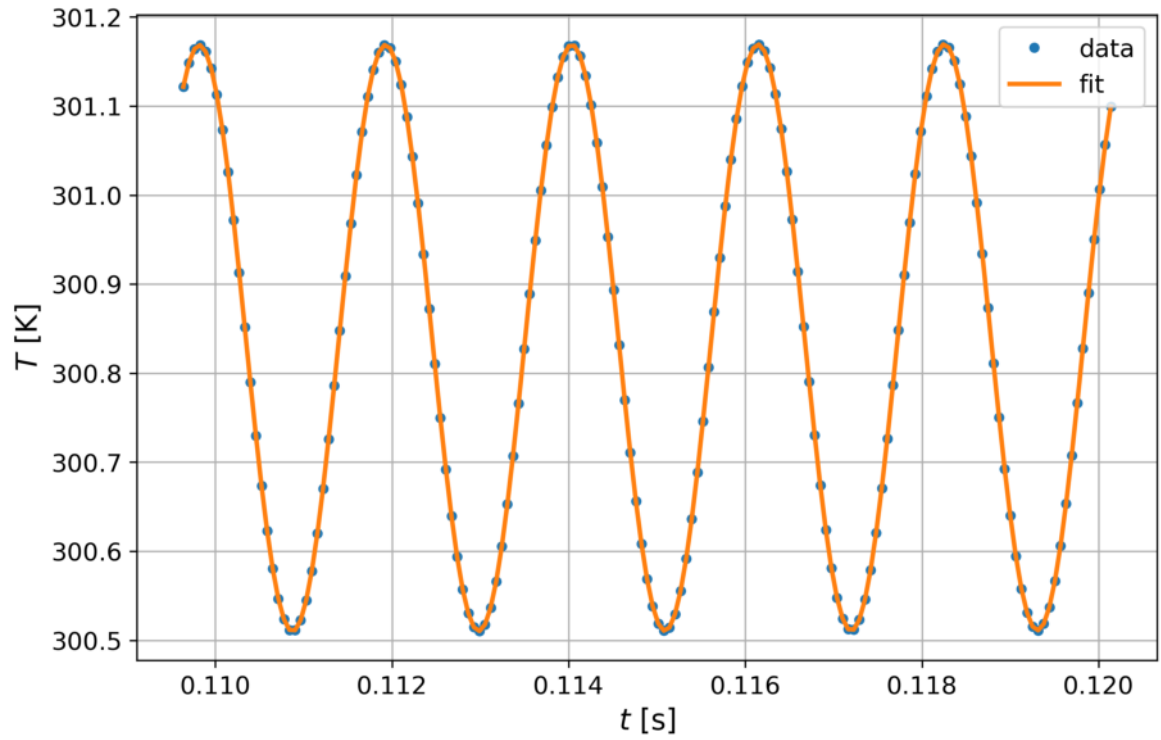


Figure 3.27: Sinusoidal fit to the final five thermal cycles of the exposed 6 μm heater response.

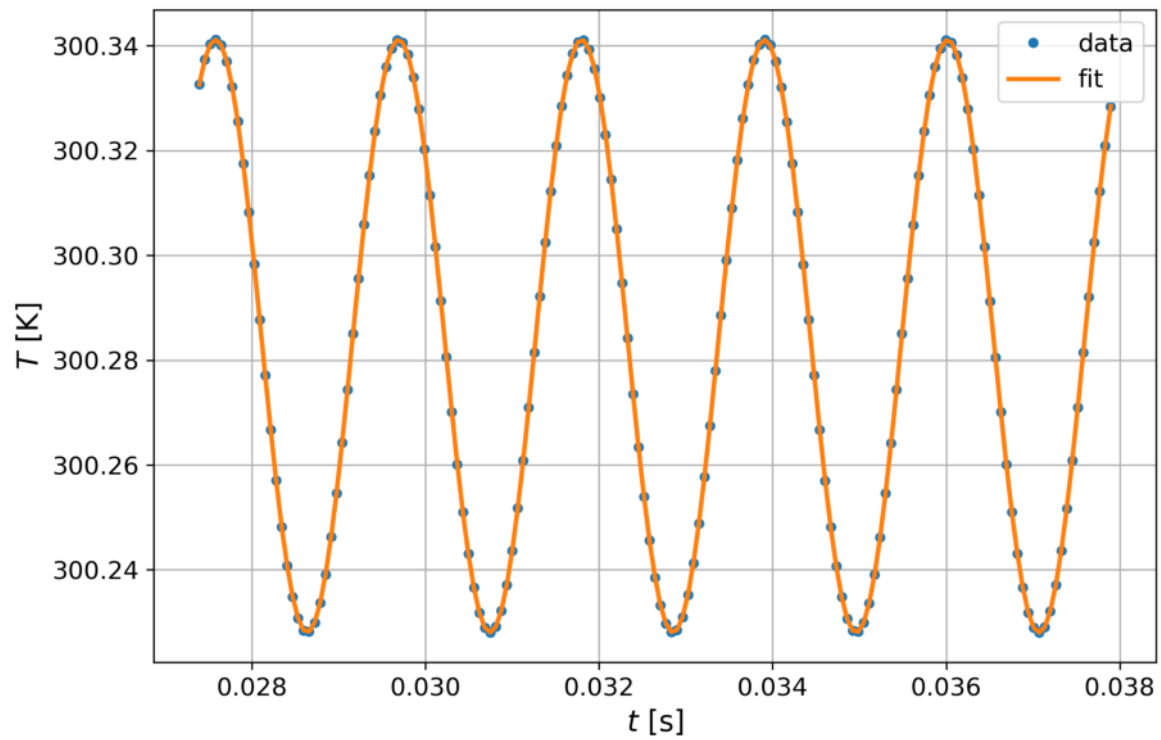


Figure 3.28: Sinusoidal fit to the final five thermal cycles of the Nafion-covered 14 μm heater response.

The same forward solution also provides the spatial temperature field. Figures 3.29–3.34 compare exposed and Nafion-covered 14 μm heaters from 0.01 Hz to 100 kHz. Each panel shows the peak temperature rise field and marks the selected operating point on the corresponding $\Delta T(2f)$ response. The thermal field becomes progressively localized around the heater as frequency increases. In the field plots, the gray rectangle is the heater, the white solid lines are material interfaces, and the black dashed rectangle in the full-domain view marks the region enlarged immediately below it. The blue dashed contours are isotherms drawn at successive fractions of the maximum temperature rise. The cyan and magenta dashed horizontal lines denote the calculated thermal penetration depths in the substrate and film, respectively. If a calculated depth exceeds the corresponding layer thickness, the displayed line is limited by the material interface. In the frequency response plots, the blue curve is the simulated $\Delta T(2f)$, the blue and green shaded regions are the theoretical linear ranges associated with the substrate and film, and their dashed and dotted vertical lines mark the respective range boundaries. The orange line and yellow marker identify the thermal frequency and response shown in the field plot above.

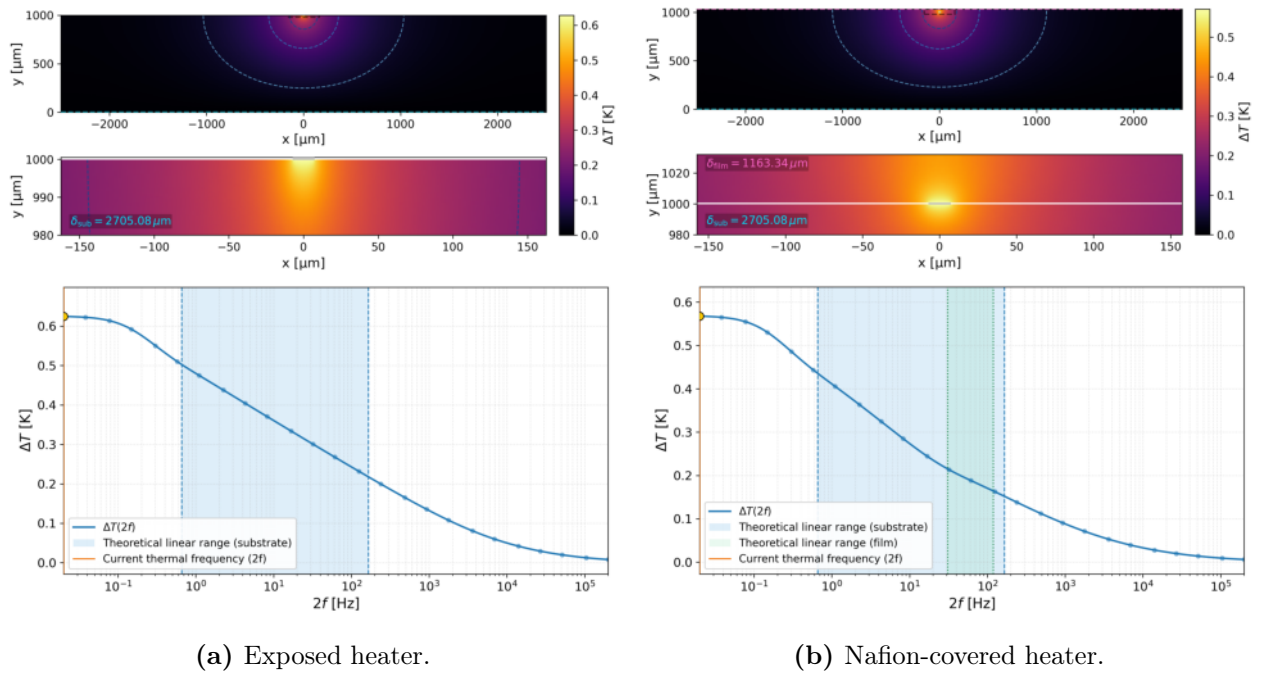


Figure 3.29: Peak temperature-rise fields at $f = 0.01$ Hz (upper panels) and the corresponding marked points on $\Delta T(2f)$ (lower panels). Panel (a) shows the exposed heater, and panel (b) shows the Nafion-covered heater.

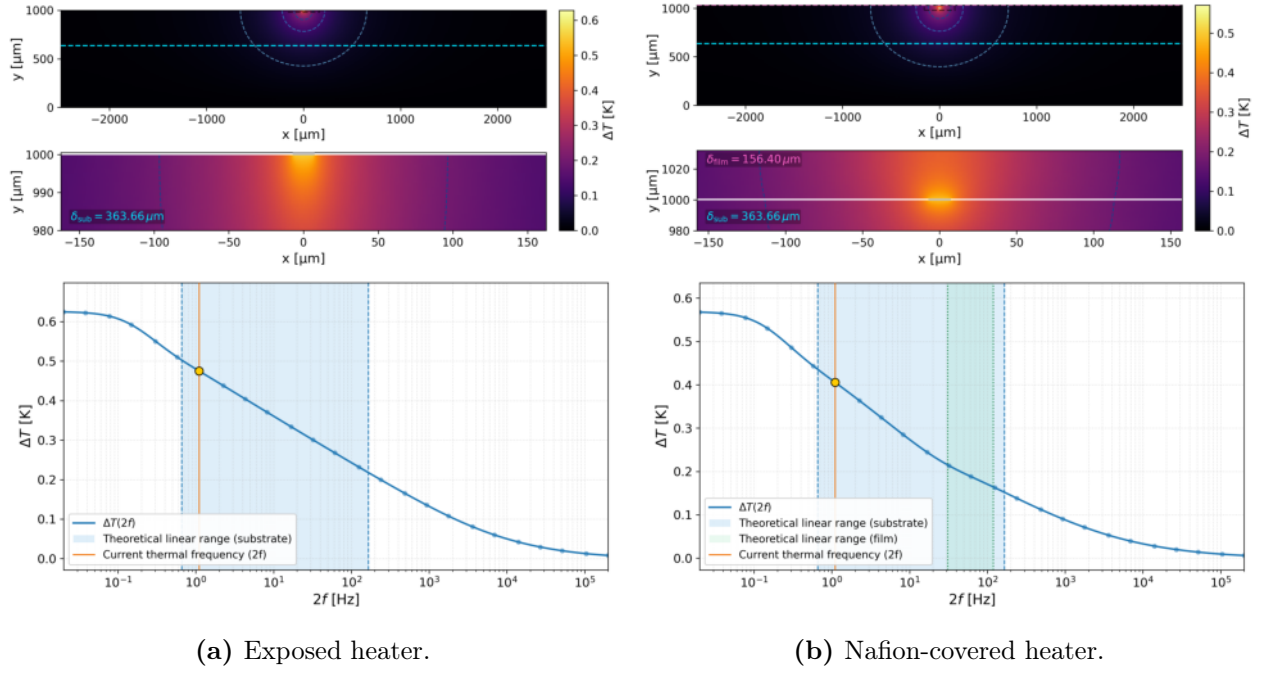


Figure 3.30: Peak temperature-rise fields at $f = 0.5533$ Hz (upper panels) and the corresponding marked points on $\Delta T(2f)$ (lower panels). Panel (a) shows the exposed heater, and panel (b) shows the Nafion-covered heater.

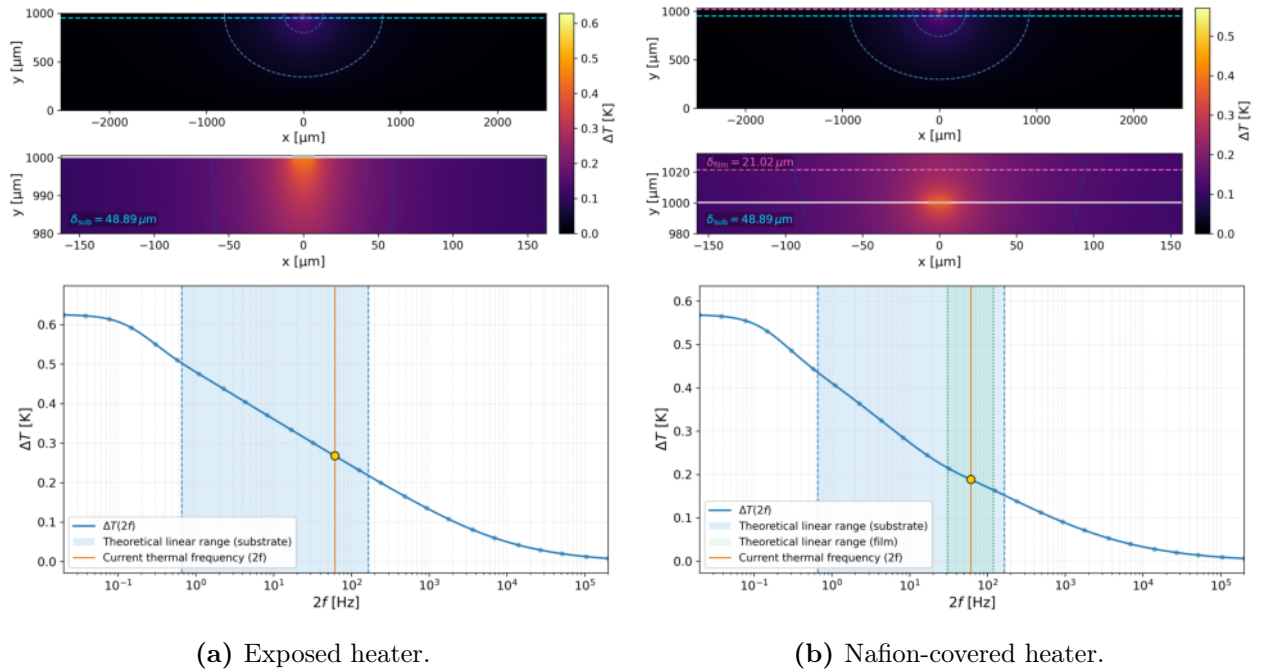


Figure 3.31: Peak temperature-rise fields at $f = 30.62$ Hz (upper panels) and the corresponding marked points on $\Delta T(2f)$ (lower panels). Panel (a) shows the exposed heater, and panel (b) shows the Nafion-covered heater.

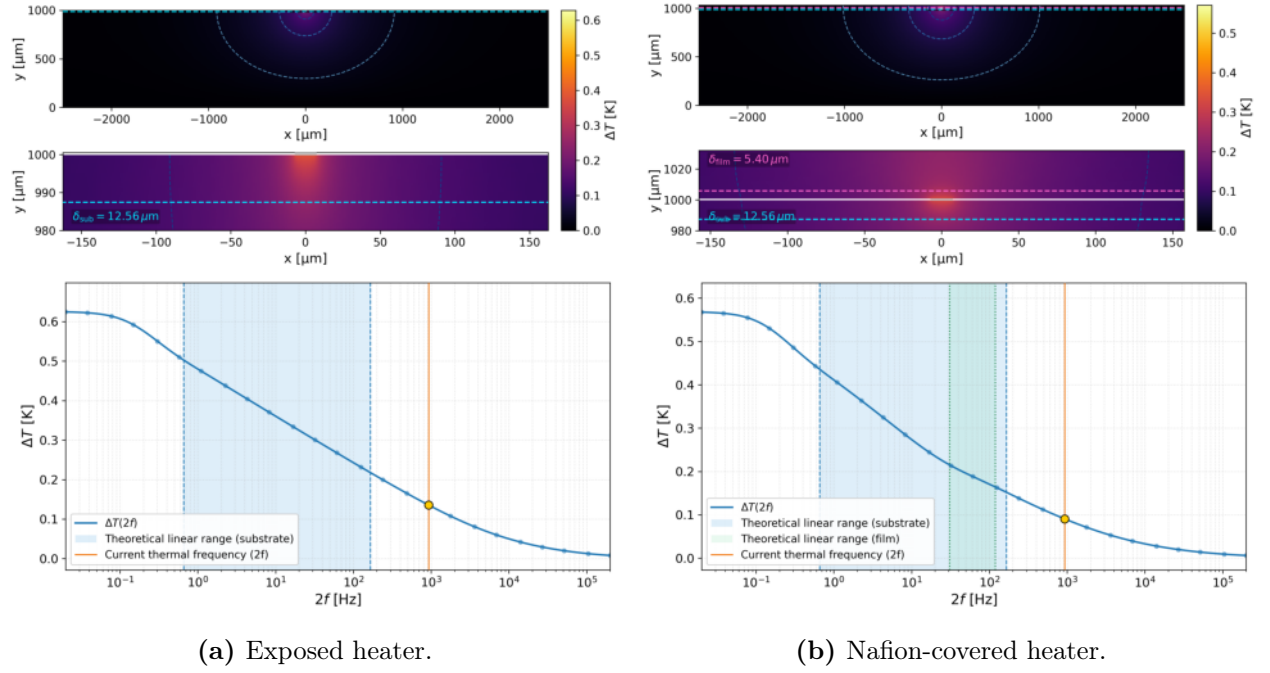


Figure 3.32: Peak temperature-rise fields at $f = 464.2$ Hz (upper panels) and the corresponding marked points on $\Delta T(2f)$ (lower panels). Panel (a) shows the exposed heater, and panel (b) shows the Nafion-covered heater.

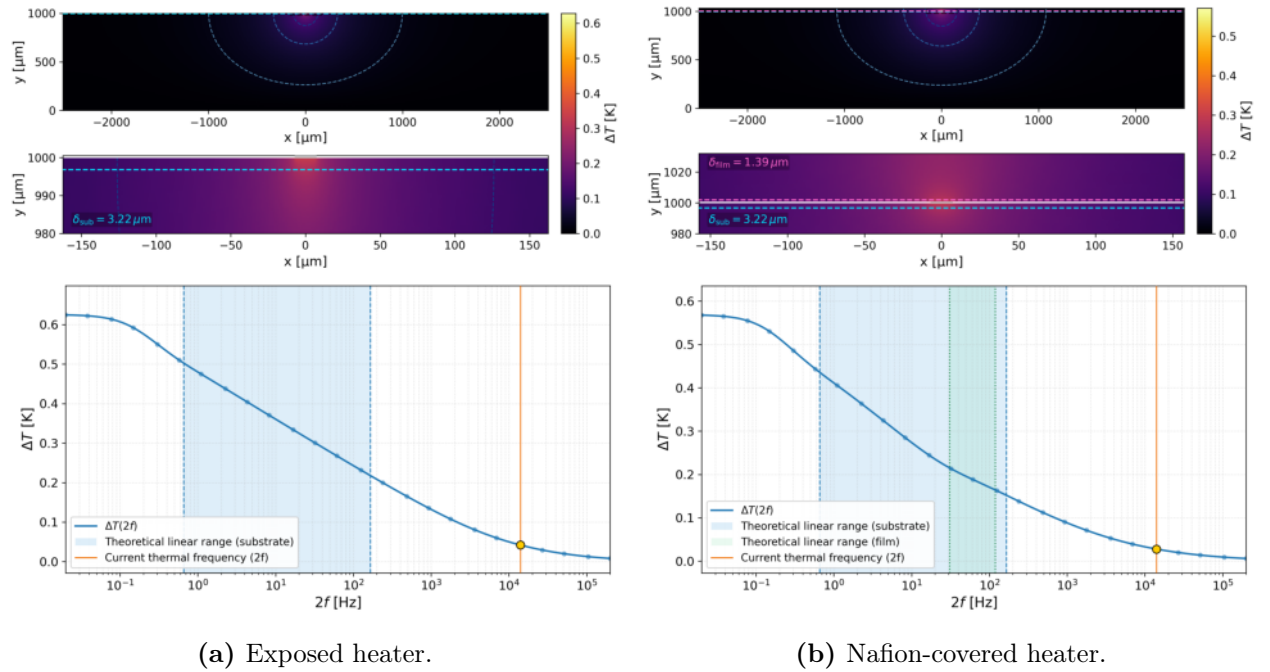


Figure 3.33: Peak temperature-rise fields at $f = 7.037$ kHz (upper panels) and the corresponding marked points on $\Delta T(2f)$ (lower panels). Panel (a) shows the exposed heater, and panel (b) shows the Nafion-covered heater.

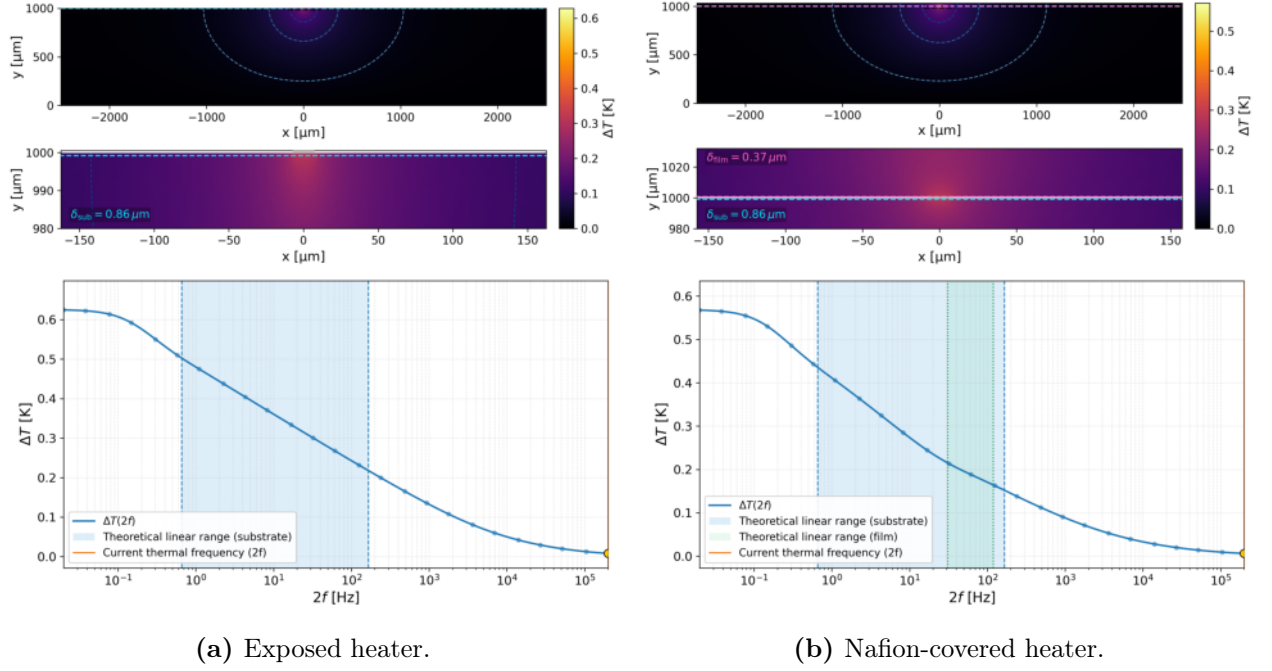


Figure 3.34: Peak temperature-rise fields at $f = 100$ kHz (upper panels) and the corresponding marked points on $\Delta T(2f)$ (lower panels). Panel (a) shows the exposed heater, and panel (b) shows the Nafion-covered heater.

3.4.5 Inverse estimation

The complete forward workflow can be regarded as an operator

$$\mathbf{y}_{\text{FEM}} = \mathcal{F}(\kappa_{\text{film}}, \kappa_{\text{sub}}, \rho c, \text{geometry}, \text{boundary conditions}, \text{power}, \text{frequency}),$$

where $\mathbf{y}_{\text{FEM}}$ is defined in the same measurement space as the experimental observable. Depending on the reduction, this observable may be the full $\Delta T(f)$ response, its in-phase and quadrature components, a logarithmic slope, an effective conductivity, or a differential temperature response. The inversion used for the coated measurements is based on the effective thermal conductivity obtained from the selected logarithmic interval.

The resulting observable provides the connection to the inverse problem. The inversion is evaluated through a parameterized forward sweep. At each experimental temperature, the forward model is evaluated for a range of candidate film thermal conductivities. Each candidate produces a frequency-dependent heater response that is reduced using the same logarithmic frequency band as the experimental data,

$$\Delta T_{\text{pp}}(f) = s_{T,\text{pp}} \ln(4\pi f) + b_T = s_{T,\text{pp}} \ln(2\omega) + b_T, \quad \kappa_{\text{eff,FEM}} = \frac{P_{\text{line}}}{2\pi |s_{T,\text{pp}}|}. \quad (3.30)$$

Here b_T is the fitted temperature response intercept. This gives a discrete forward map $\kappa_{\text{eff,FEM}}(\kappa_{\text{film}})$. The film thermal conductivity is obtained from the crossing condition

$$\kappa_{\text{eff,FEM}}(\kappa_{\text{film}}) = \kappa_{\text{eff,exp}}(T), \quad (3.31)$$

using interpolation between neighboring forward points.

Only the physically admissible branch of the forward map is used. This is important when weak sensitivity or finite-geometry effects produce a non-monotonic response at the edge of the candidate range. The retained crossing interval uses the experimental target and its fitting uncertainty. A steep and unique crossing gives a well-identified film thermal conductivity, whereas a shallow, absent, or multiple crossing indicates limited identifiability.

The forward solutions are calculated for a prescribed range of candidate thermal conductivities and are then reused to construct the inverse map. The approach makes the response sensitivity and the existence, location, and uniqueness of the crossing directly visible.

The local sensitivity of the modeled observable to film thermal conductivity is

$$S_{\kappa} = \left. \frac{\partial y_{\text{FEM}}}{\partial \kappa_{\text{film}}} \right|_{\hat{\kappa}_{\text{film}}}.$$

Here $\hat{\kappa}_{\text{film}}$ is the film thermal conductivity estimated from the crossing of the modeled forward map and the experimental target. The derivative is evaluated locally at that inferred value. For a locally monotonic forward map, the corresponding first-order uncertainty estimate has the form

$$\sigma_{\kappa_{\text{film}}} \approx \frac{\sigma_y}{|S_{\kappa}|}.$$

The final interval accounts for uncertainty in the experimental target, fitting uncertainty, and the local slope of the forward map. Numerical variation established by the validation studies is reported separately. A flat forward map can produce a large thermal conductivity interval even when the fitted temperature response has a small statistical uncertainty. If no crossing occurs within the simulated range, the film thermal conductivity cannot be identified within that range. This can indicate either that the simulated candidate interval is too narrow or that the experiment contains an effect not represented by the model.

Finally, the substrate-only numerical response is checked against the analytical Cahill line-source solution in its accepted frequency regime [28]. For the retained 6 and 14 μm heater comparisons, the root-mean-square relative differences are 2.50% and 2.68%, respectively. These experimentally used widths provide a traceable benchmark of the forward thermal calculation without relying on the experimental inversion.

The complete numerical validation is presented in Appendix A. It includes mesh sensitivity, same-property layer partitioning, the discrete Crank–Nicolson residual, global energy balance, bottom-temperature invariance, volumetric heat-capacity sensitivity (Figures A.7 and A.8), substrate thermal conductivity sensitivity, analytical comparison, and monotonicity of the film thermal conductivity map. The appendix also shows the direct substrate-response overlay between experiment, FEM, and the Cahill solution. The complete experimental substrate calibration is treated in Section 3.3.

Chapter 4

RESULTS AND DISCUSSION

4.1 NAFION THERMAL CONDUCTIVITY

This chapter presents the dry depositable Nafion dataset and the extracted thermal conductivity in the operating range of polymer electrolyte hydrogen fuel cells. The experimental signals were corrected with the calibration workflow from Section 3.3, and thermal conductivity was estimated with the inverse finite element methodology defined in Section 3.4.

4.1.1 Nafion deposition and curing protocol

The Nafion film was deposited only after electrical calibration of each sensor chiplet was complete. The polymer layer is chemically sensitive, and the lithography steps used for heater fabrication would alter the deposited film. Using these calibrated sensors, we avoid altering the deposited film and test pristine films.

The precursor solution was Nafion NS-5 in the 5 wt% PFSA dispersion class. The liquid was dispensed by micropipette so that the heater and the full active sensing length were fully covered. The final thesis dataset uses dry films prepared in ambient laboratory conditions and then measured in vacuum at elevated temperatures.

Room temperature curing was performed for 48 hours in a dust-free environment. This protocol was developed together with Dr. Krešimir Dželalija to minimize film disturbance during solvent evaporation and to obtain stable films for repeated thermal scans. An optional multilayer lamination procedure was also defined, but it was not used for the dataset reported in this thesis.

Film thickness was estimated after thermal measurements by optical microscopy as $32\text{ }\mu\text{m}$. This value is treated as a process estimate for and is not propagated as a separate term in the final inversion uncertainty budget of this thesis. Heater resistance was measured before and after each complete film measurement to verify that the electrical state of the heater remained stable during deposition, curing, and thermal cycling. The realized polymer on 3ω -sensor geometry used for this sequence is shown in Figure 4.1.

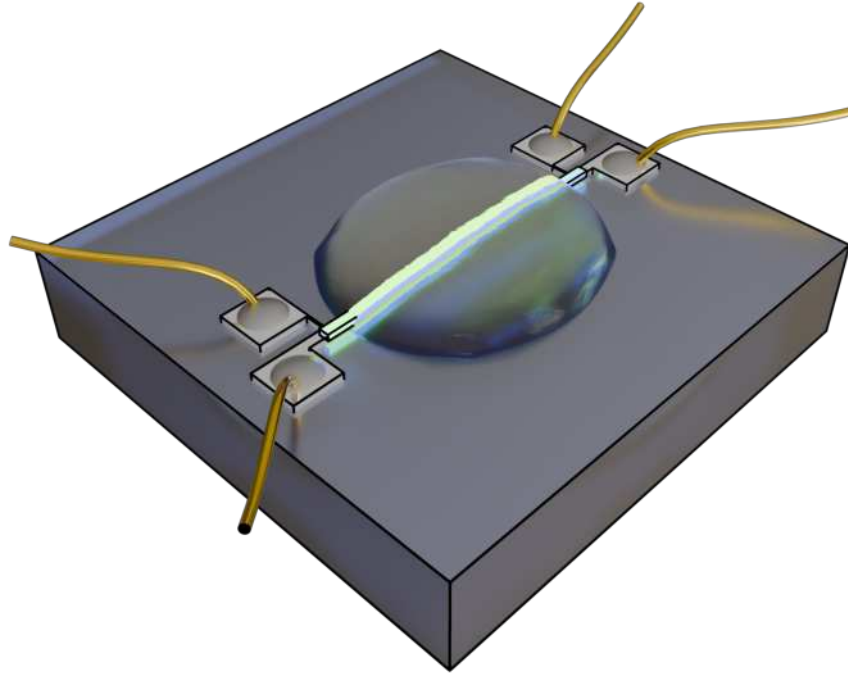


Figure 4.1: Rendered inverted geometry used for Nafion measurements, where a thin polymer film is deposited on top of the thermal conductivity sensor after electrical calibration. In reality the film covers the entire sensor area.

The local mesh evolution around the heater is illustrated in Figure 4.2. Increasing the mesh factor progressively resolves the heater edges and adjoining material regions while retaining conformal interfaces.

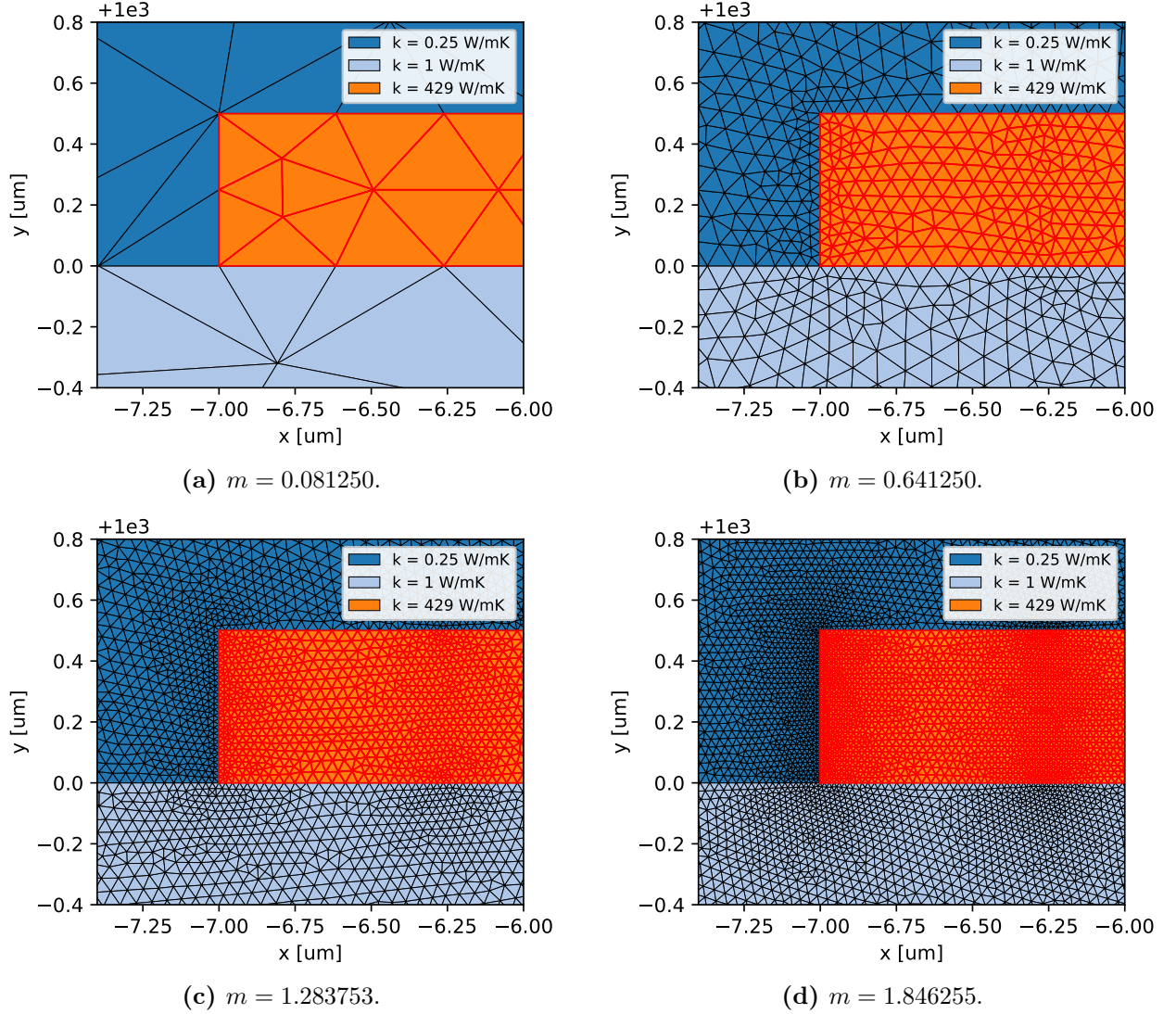


Figure 4.2: Mesh refinement around the heater at 500 Hz. Increasing m produces progressively finer triangular elements while preserving conformal material interfaces.

The frequency-dependent thermal power amplitudes provide additional physical context for the inverted geometry. For material region j , the plotted quantity is

$$\eta_j(f) = 100 \frac{\left| \tilde{P}'_{j,2\omega}(f) \right|}{\left| \tilde{P}'_{\text{src},2\omega}(f) \right|}, \quad (4.1)$$

where $\tilde{P}'_{j,2\omega}$ is the complex amplitude of the fitted 2ω thermal power component per unit heater length and $\tilde{P}'_{\text{src},2\omega}$ is the corresponding source power amplitude. Because the material components generally have different phases, their magnitudes are not required to sum to 100%. In the heater–substrate reference calculation shown in Figure 4.3, the substrate dominates at low frequency, while the heater contribution becomes appreciable only at the highest frequencies. Introducing the Nafion film adds a separate contribution, as shown in Figure 4.4, and changes the frequency-dependent distribution underlying the difference between the coated and uncoated configurations.

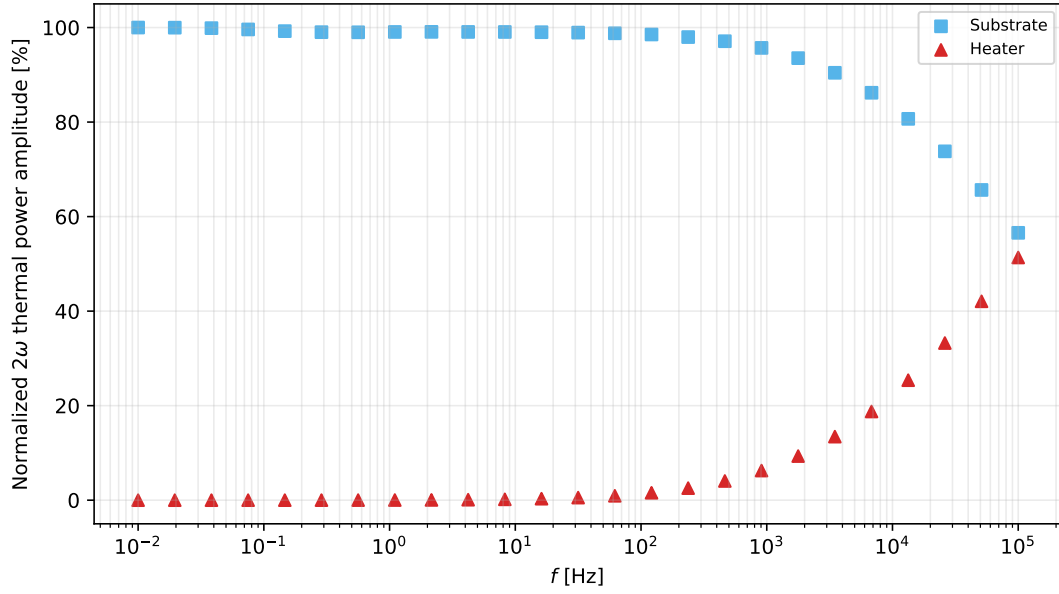


Figure 4.3: Normalized 2ω thermal power amplitudes from Eq. (4.1) for the uncoated heater–glass geometry. Light-blue squares denote the glass substrate and red triangles denote the heater.

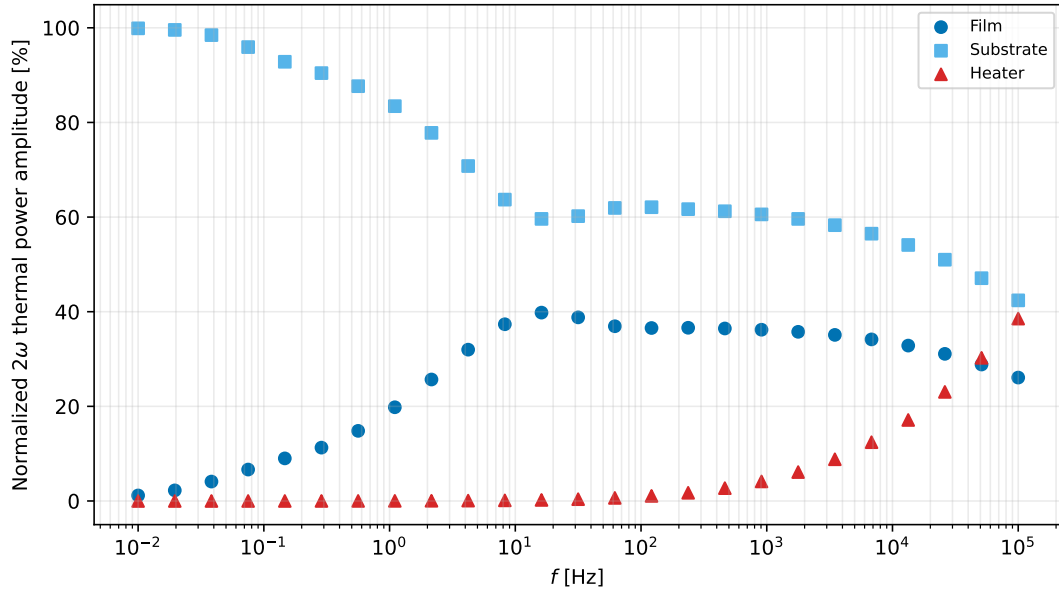


Figure 4.4: Normalized 2ω thermal power amplitudes from Eq. (4.1) for the coated Nafion–film–heater–glass geometry. Dark-blue circles denote the Nafion film, light-blue squares denote the glass substrate, and red triangles denote the heater.

Figures 4.3 and 4.4 are consistent with the temperature fields shown in Figures 3.29–3.34. At low frequencies, the large thermal penetration depth allows the temperature oscillation to extend deeply into the substrate, producing a large thermally active substrate volume and

a dominant substrate contribution. As frequency increases, the penetration depth decreases and the oscillatory response becomes progressively confined to the region near the heater. In the coated geometry, the film maximum and substrate minimum near 20 Hz mark the transition where the penetration depth becomes comparable to the film thickness and the relative oscillatory energy storage shifts from the substrate toward the Nafion layer. The normalized components show how strongly each material participates in the oscillatory thermal response. Their magnitudes do not sum to unity because the components also have different phases. The temperature maps show the associated spatial penetration. When the penetration depth becomes smaller than the film thickness, the power partition between the film and substrate approaches the two medium effusivity estimate $e_f/(e_f + e_s)$, where $e = \sqrt{\kappa\rho c_p}$. The material properties used here give $e_f/(e_f + e_s) \approx 0.37$, close to the film plateau at intermediate frequencies in Figure 4.4. Heater heat storage becomes appreciable at the highest frequencies and changes this partition.

4.1.2 Thermal conductivity of dry depositable Nafion in the operating range

The thermal conductivity extraction in this chapter uses corrected $V_{3\omega}$ data, substrate reference line fits, and the inversion crossing procedure described in Sections 3.3 and 3.4. The analysis range targeted the practical operating window of 25 to 95 °C.

In the current dataset, the available inversion temperatures span 305.75 to 368.34 K, which corresponds to 32.60 to 95.19 °C. The final Nafion results were obtained from the sensor with the 14 μm wide heater using the corrected substrate reference. The 6 μm heaters were used for calibration consistency checks and pilot measurements. Once the automated procedure was established, the entire thermal conductivity measurement campaign took four days, with continuous measurements.

Representative paired glass versus glass plus Nafion frequency sweeps were used in the inversion workflow, and the coated case produced a clear shifted response relative to the bare glass baseline.

The FEM geometry and all prescribed material properties other than thermal conductivity were considered temperature invariant. At each of the 14 experimental temperatures, the measured glass thermal conductivity was assigned to the substrate. The measured thermal conductivity of the coated system supplied the inversion target. A broad scan of film thermal conductivity $\kappa_{\text{film}} = 0.03\text{--}0.70 \text{ W m}^{-1} \text{ K}^{-1}$ located a crossing separately at each temperature. These initial crossings ranged from 0.219 to 0.308 $\text{W m}^{-1} \text{ K}^{-1}$, with a mean of 0.261. The second scan used a refined thermal conductivity grid around each crossing. The resulting values obtained from the fitted experimental targets were confined to 0.2480–0.2518 $\text{W m}^{-1} \text{ K}^{-1}$, with a mean of 0.25.

No temperature trend was resolvable within the propagated uncertainty over the analyzed range. The resulting thermal conductivity of the dry film is nearly constant with temperature in this interval and is centered near 0.25 $\text{W m}^{-1} \text{ K}^{-1}$. The plotted error bars show $\hat{\kappa} \pm u_{\kappa}$, where u_{κ} is the propagated standard uncertainty of the conductivity estimate. They are not prediction intervals. The largest standard uncertainty for a fitted target value is 0.0154 $\text{W m}^{-1} \text{ K}^{-1}$, or approximately 6.1% of the corresponding conductivity estimate. The calculation assumes a locally linear inversion.

A compact uncertainty check identified inversion crossing width as the dominant contri-

bution in this dataset. Run to run electrical scatter in the fitted band is smaller after calibration correction. Radiative loss was evaluated from the net Stefan–Boltzmann exchange in Eq. (2.26). Linearization about the operating temperature gives the radiative heat transfer coefficient $h_{\text{rad}} = 4\varepsilon\sigma T^3$. The heater geometry and the spreading of its temperature field determine the thermally active surface area. For the line heater, this geometry is represented by the thermal penetration depth in Eq. (2.24). At the highest measurement temperature, the blackbody limit $\varepsilon = 1$, $\delta_s \lesssim 35 \mu\text{m}$, and $\kappa_{\text{sub}} \approx 1 \text{ W m}^{-1} \text{ K}^{-1}$ give a radiative loss fraction below 2.0×10^{-4} . Radiative loss is negligible in the selected frequency band [28, 32].

The summary in Table 4.1 shows that the refined second pass crossings collapse into a narrow thermal conductivity interval around $0.25 \text{ W m}^{-1} \text{ K}^{-1}$. The interpolation structure behind that collapse is carried by the inversion figures below, where experimental and modeled effective thermal conductivity curves intersect at the accepted κ_{film} value.

The extracted level is physically plausible for dry fluorinated ionomer systems and is consistent in order of magnitude with dry Nafion literature ranges when differences in preparation route, morphology, thickness, hydration state, and measurement geometry are considered [3, 8]. The result should therefore be interpreted as a controlled dry depositable film property within this methodology.

Figure 4.5 shows the interpolation step used to convert each temperature target into a film thermal conductivity. Each curve represents the FEM-derived effective response as a function of imposed κ_{Nafion} , while the horizontal target level comes from the corrected experimental reduction at the same temperature. The accepted value is the crossing between the modeled branch and the experimental target, which is why clustering of the crossings near $0.25 \text{ W m}^{-1} \text{ K}^{-1}$ directly supports the nearly temperature independent result for the dry film.

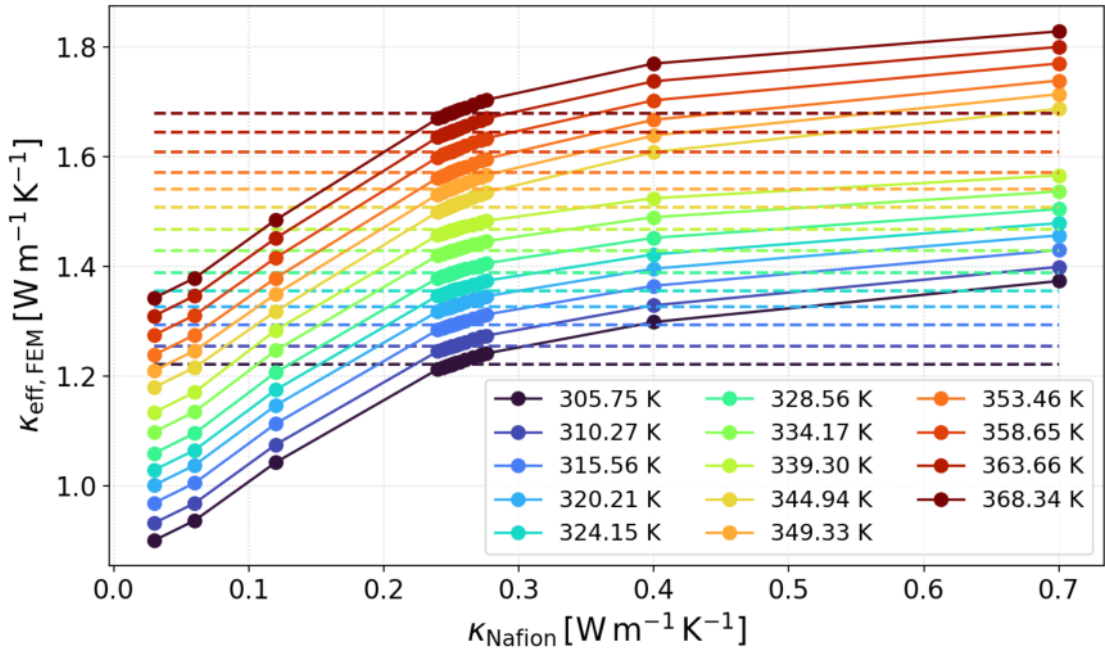


Figure 4.5: Inversion process interpolation across all temperatures.

Figure 4.6 compares the accepted inversion results from 305.75 to 368.34 K. At each

Table 4.1: Summary metrics for dry depositable Nafion film inversion in this thesis dataset.

Quantity	Value
Available inversion temperatures	305.75 to 368.34 K (32.60 to 95.19 °C)
Heater width	14 μm
Heater length	2.6 mm
Film thickness after curing	nominally 32 μm
First pass crossing range	0.219 to 0.308 $\text{W m}^{-1} \text{K}^{-1}$
First pass crossing mean	0.261 $\text{W m}^{-1} \text{K}^{-1}$
Second pass crossing range	0.2480 to 0.2518 $\text{W m}^{-1} \text{K}^{-1}$
Second pass crossing mean	0.2500 $\text{W m}^{-1} \text{K}^{-1}$
Largest standard uncertainty for a fitted target	0.0154 $\text{W m}^{-1} \text{K}^{-1}$ (approximately 6.1%)

temperature, κ_{Nafion} was varied in the FEM model until the calculated system thermal conductivity matched one of two targets. The pointwise experimental target is the system thermal conductivity obtained from the individual measurement at that temperature. The fitted experimental target is the value of the linear fit to the measured system thermal conductivity, evaluated at the same temperature. Each temperature therefore has its own fitted target. The fit is applied to the measured system thermal conductivity. The Nafion thermal conductivity is the inversion variable.

Using the fitted experimental target, the 14 inferred values have a mean of 0.2500 $\text{W m}^{-1} \text{K}^{-1}$ and range only from 0.2480 to 0.2518 $\text{W m}^{-1} \text{K}^{-1}$, a total variation of approximately 1.5%. Their error bars share a common overlap from 0.2368 to 0.2614 $\text{W m}^{-1} \text{K}^{-1}$. Inversions based on individual experimental points scatter more widely, from 0.2162 to 0.2966 $\text{W m}^{-1} \text{K}^{-1}$, and show no monotonic temperature dependence. Pointwise experimental targets carry the measurement scatter through the inversion. Targets obtained from the linear fit retain the measured temperature trend with less scatter. The plotted error bars represent the propagated target and inversion standard uncertainties. The numerical spread among values obtained from the linear fit is smaller than the width of these error bars. The series obtained from the linear fit supports a thermal conductivity of approximately 0.25 $\text{W m}^{-1} \text{K}^{-1}$ over the investigated range.

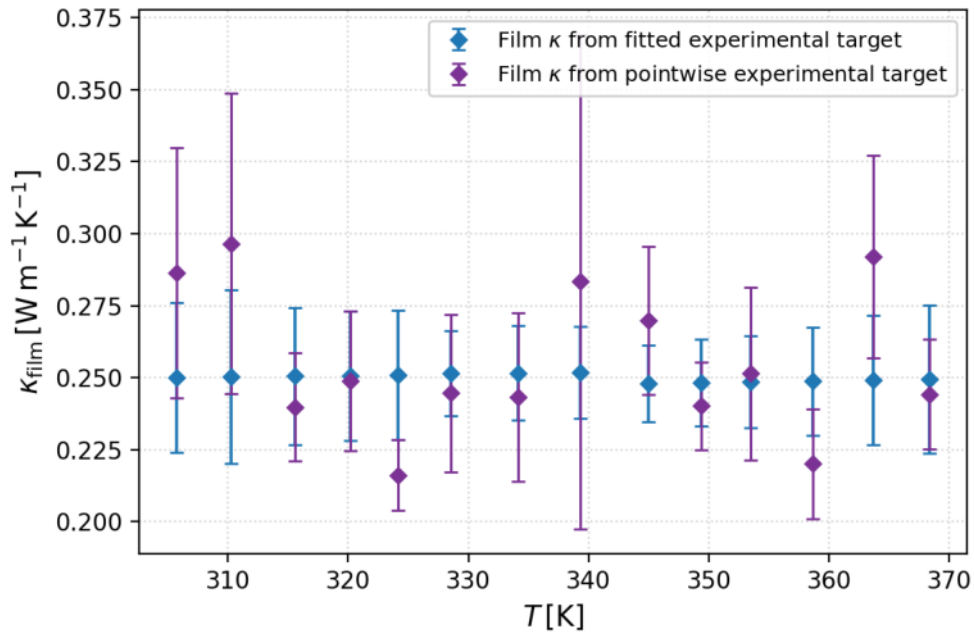


Figure 4.6: Inverse FEM estimates of dry Nafion thermal conductivity obtained using the fitted experimental target and the pointwise experimental target at each temperature. The intervals show propagated target and inversion standard uncertainty. They are not prediction intervals.

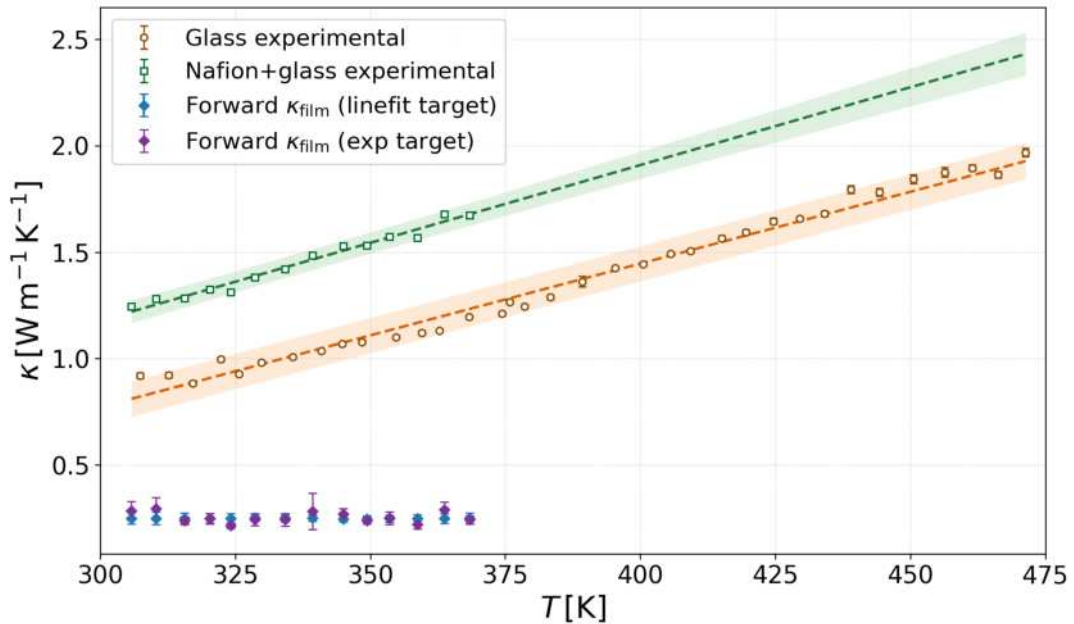


Figure 4.7: Measured thermal conductivity of the glass substrate (orange) and effective stack of Nafion and glass (green), with linear fits and 1σ prediction bands. Inverse FEM estimates of the Nafion film thermal conductivity use either the fitted stack response (blue) or individual experimental points (purple).

Over 305.75–368.34 K, the fitted effective thermal conductivity of the coated stack increases from 1.2215 to 1.6792 W m⁻¹ K⁻¹. This increase cannot be assigned directly to Nafion because the thermal conductivity of glass varies with temperature and the substrate remains part of the measured thermal path. After the inverse FEM model separates the film contribution, the estimates obtained from the fitted targets remain between 0.2480 and 0.2518 W m⁻¹ K⁻¹. Pointwise targets produce the wider 0.2162–0.2966 W m⁻¹ K⁻¹ spread visible in Figure 4.6 because experimental scatter is transferred directly through the inversion.

The error bars shown here use the propagated standard uncertainty directly. The stored summaries assign no additional FEM slope contribution, and uncertainty in the nominal film thickness is not included. The pointwise target series has a larger maximum interval half-width of 0.0858 W m⁻¹ K⁻¹, reflecting its greater sensitivity to individual experimental points.

Figures 4.5–4.7 show the rising effective response of the complete stack and the nearly constant intrinsic film result. The series obtained from the fitted targets is retained as the principal estimate: $\kappa_{\text{film}} \approx 0.25 \text{ W m}^{-1} \text{ K}^{-1}$, with no temperature trend resolvable within the propagated uncertainty over the investigated dry-state range.

4.2 MICROSTRUCTURE DETECTABILITY

4.2.1 Modelling Philosophy and Scope

The purpose of this section is to quantify how controlled microstructural perturbations within a Nafion film modify the measurable thermal response in the inverted 3ω configuration. The analysis is restricted to thermal transport. No attempt is made to model electrochemical degradation pathways, radical chemistry, catalyst reactions, or coupled proton transport. The focus is on structural modifications that can be represented within reduced thermal models and evaluated within the validated measurement and inversion framework developed in this thesis.

Two complementary study groups are used. The first group treats intentional Nafion modification studies, represented here by composite-type perturbations analyzed with mean field effective medium descriptions. The second group treats degradation-oriented thermal transport scenarios and explicit degradation geometries. Within the degradation group, water redistribution and void-like scenarios are represented as mean-field perturbations because they can be approximated as distributed secondary phases in the ionomer volume. In contrast, surface-localized skin formation cannot be captured by mean field theory and is implemented explicitly as a multilayer geometry in the finite element model.

The central objective is to determine detectability limits. For each perturbation scenario, the predicted change in extracted effective thermal conductivity is compared against experimentally established uncertainty bounds. This establishes which classes of structural contrast are thermally resolvable within the present configuration.

4.2.2 Nafion Modification Studies

Controlled changes in filler fraction and thermal contrast provide a quantitative test of how small a deliberate change in the Nafion layer can be resolved by the present sensor. They also establish a reference against which the less controlled degradation scenarios can be interpreted. Each effective composite property is mapped with Maxwell–Eucken theory and then passed through the same FEM and electrical postprocessing used for the degradation studies.

Composite perturbations and thermal contrast sensitivity

Composite films are represented with a first-order Maxwell–Eucken effective medium mapping in the dilute limit [67, 68, 69, 70, 71]. The mapping converts filler-phase thermal conductivity κ_f and filler fraction c_f into effective film thermal conductivity κ_{eff} , which is passed to the forward FEM model.

$$\kappa_{\text{eff}}(c_f) = \kappa_m \frac{\kappa_f + 2\kappa_m + 2c_f(\kappa_f - \kappa_m)}{\kappa_f + 2\kappa_m - c_f(\kappa_f - \kappa_m)}. \quad (4.2)$$

The baseline matrix thermal conductivity is $\kappa_m = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$. Three contrast scenarios are used, with low ($\kappa_f = 0.6$), medium ($\kappa_f = 1.0$), and high filler thermal conductivity ($\kappa_f = 5.0 \text{ W m}^{-1} \text{ K}^{-1}$), each sampled at $c_f = \{0, 0.05, 0.10, 0.15, 0.20, 0.25\}$. Table 4.2 lists the shared numerical and experimental settings, while Table 4.3 gives the mapped film thermal conductivities supplied to the FEM model.

Table 4.2: Composite study setup and shared extraction settings.

Parameter	Value
Mean-field mapping	Maxwell–Eucken (Eq. 4.2)
Matrix thermal conductivity	$\kappa_m = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$
Contrast scenarios	low: $\kappa_f = 0.6$, medium: $\kappa_f = 1.0$, high: $\kappa_f = 5.0$
Concentration sweep	$c_f = \{0, 0.05, 0.10, 0.15, 0.20, 0.25\}$
Base layered model	film $32 \mu\text{m}$, heater $14 \mu\text{m}$, glass substrate 1 mm
Electrical drive	$V_{\text{rms}} = 0.1 \text{ V}$, $R_0 = 10 \Omega$, $L = 3 \text{ mm}$
Frequency sweep	25 points from 10^{-2} to 10^5 Hz
Extraction method	Kabaši overlap
Experimental uncertainty floor	$\langle \sigma_{V_{3\omega}} \rangle = 0.0973 \mu\text{V}$ (11.919–801 Hz), $0.0819 \mu\text{V}$ (200.9–801 Hz)

The uncertainty varies across the frequency sweep. Its average over 11.919–801 Hz is $0.0973 \mu\text{V}$ because this interval includes the noisier points at low frequencies. The detectability calculations use the selected 200.9–801 Hz measurement band, whose average uncertainty is lower at $0.0819 \mu\text{V}$.

Composite figure set

To keep this section consistent with the defect methodology, the same figure categories are shown: grouped thermal response, grouped electrical response, extracted $\kappa_{\text{eff,system}}$, slope trend, baseline-to-maximum $|\Delta V_{3\omega}|$, and concentration resolution.

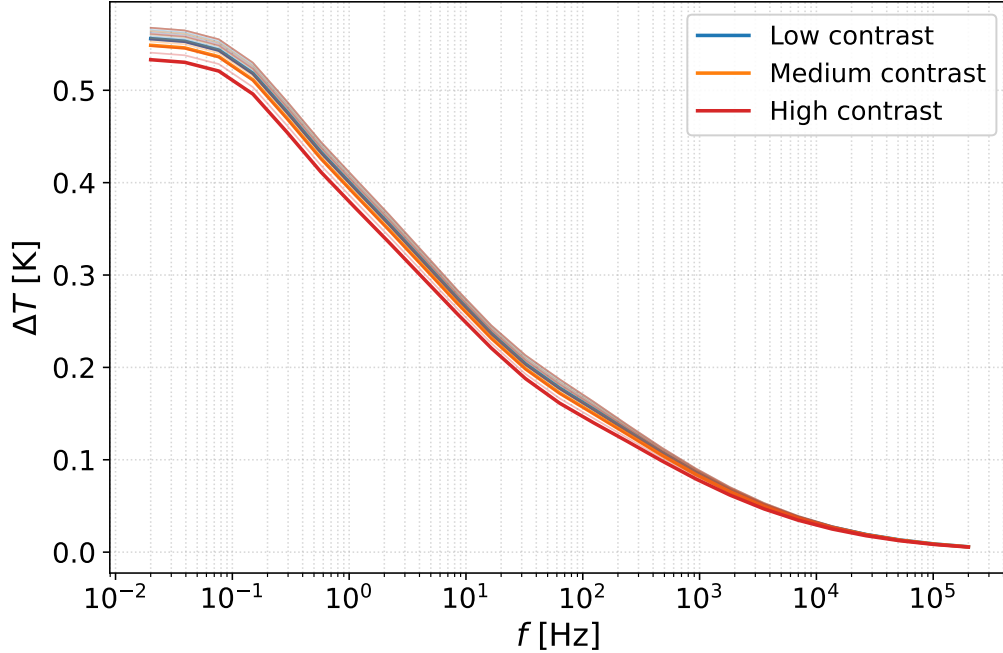

Figure 4.8: Composite study grouped thermal response $\Delta T(f)$ across low, medium, and high contrast families and all concentrations.

Table 4.3: Maxwell–Eucken mapped film thermal conductivity values used as composite FEM inputs.

c_f	low κ_{eff}	medium κ_{eff} [W m ⁻¹ K ⁻¹]	high κ_{eff}
0.00	0.250000	0.250000	0.250000
0.05	0.262125	0.269231	0.283848
0.10	0.274648	0.289474	0.320896
0.15	0.287589	0.310811	0.361619
0.20	0.300971	0.333333	0.406593
0.25	0.314815	0.357143	0.456522

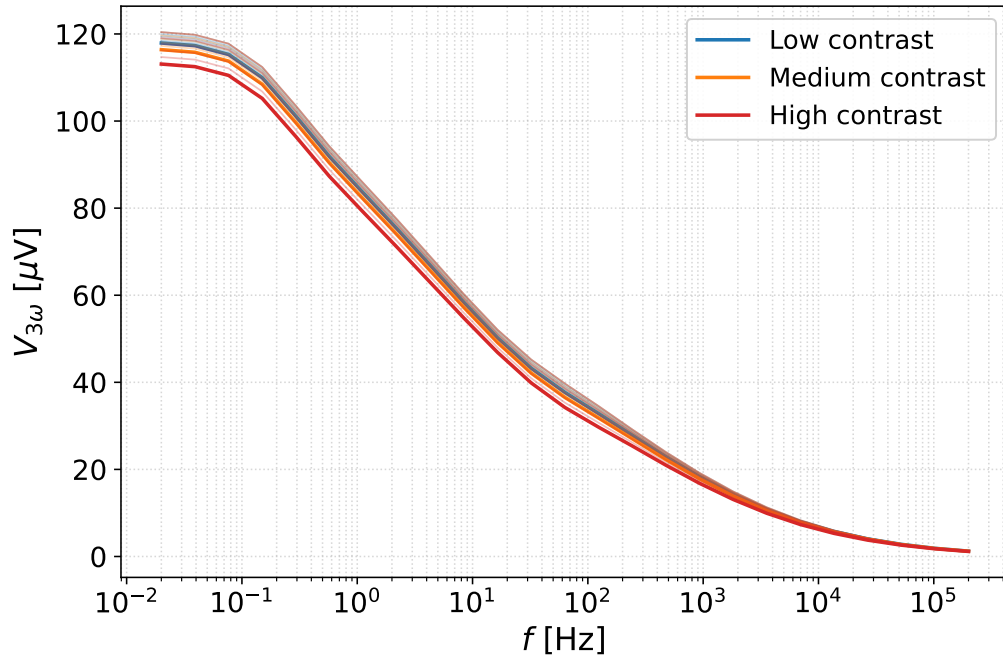


Figure 4.9: Composite study grouped $V_{3\omega}(f)$ across all contrast families and concentrations, using the same electrical conversion and uncertainty baseline as defect studies.

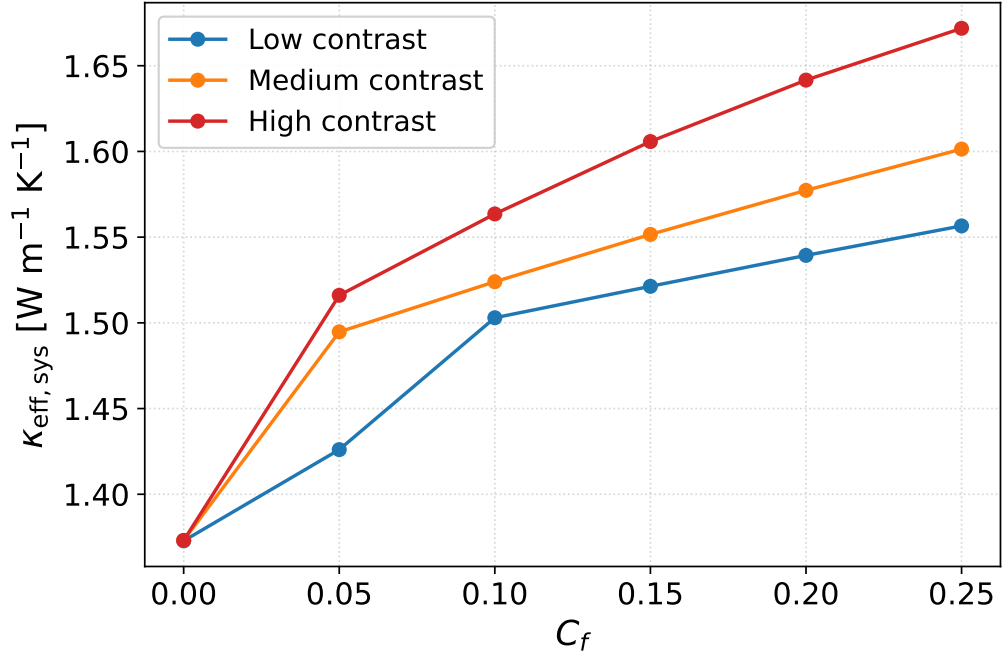


Figure 4.10: Extracted heater-seen effective thermal conductivity $\kappa_{\text{eff,system}}$ versus c_f for all composite contrasts.

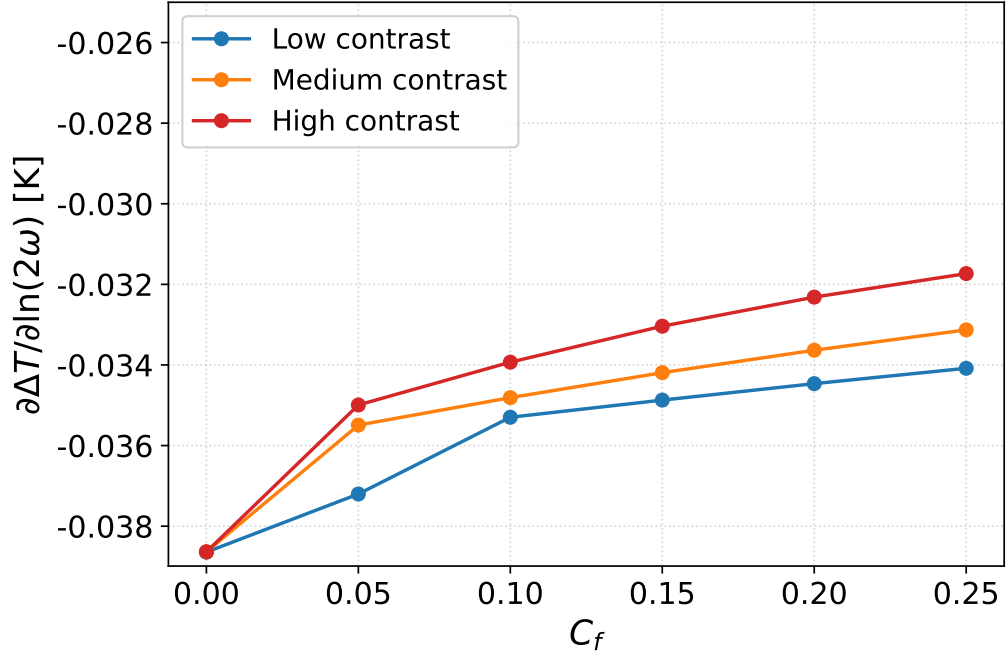


Figure 4.11: Slope of ΔT versus $\ln(2\omega)$ as a function of c_f for all composite contrasts.

At a fixed frequency, the electrical separation between two modeled composite concentrations is defined as

$$|\Delta V_{3\omega}(f)| = |V_{3\omega}(f, c_{f,2}) - V_{3\omega}(f, c_{f,1})|, \quad (4.3)$$

This signal difference is compared with the experimental 1σ uncertainty in $V_{3\omega}$, $\sigma_{V_{3\omega}} = 0.0819 \mu\text{V}$ (81.9 nV). The minimum resolvable concentration change is calculated from the local signal sensitivity as

$$\Delta c_{f,\min}(f) = \frac{\sigma_{V_{3\omega}}}{|\partial V_{3\omega}(f, c_f)/\partial c_f|}. \quad (4.4)$$

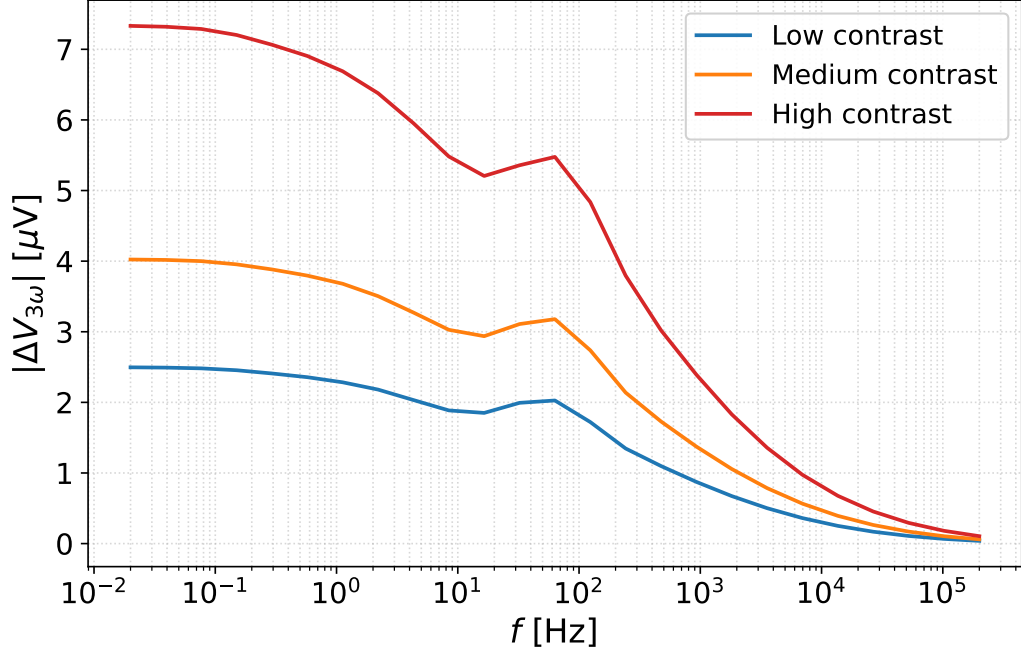


Figure 4.12: Absolute electrical separation $|\Delta V_{3\omega}|$, as defined in Eq. (4.3), between $c_f = 0$ and $c_f = 0.25$. The three curves correspond to the low, medium, and high filler thermal conductivity cases. Each curve gives the difference between the two concentration states.

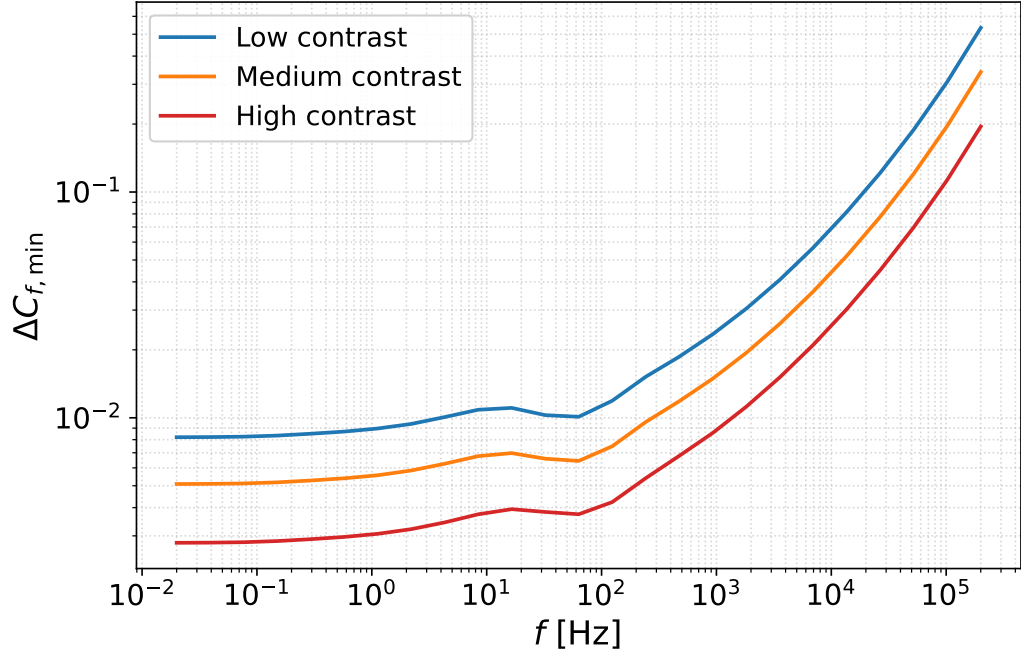


Figure 4.13: Composite concentration resolution $\Delta c_{f,\min}(f)$, calculated from Eq. (4.4) using the local sensitivity of $V_{3\omega}$ and the measured 1σ uncertainty.

Figures 4.8 and 4.9 show increasing separation of the thermal and electrical response families as filler contrast and concentration increase. The corresponding effective thermal conductivity and slope reductions in Figures 4.10 and 4.11 remain monotonic, so the response can be mapped uniquely to concentration over the simulated range. Figures 4.12 and 4.13 translate this separation into the measurable voltage difference and minimum resolvable concentration. The overlap window metrics are collected in Table 4.4.

For the full tested change $c_f = 0 \rightarrow 0.25$, the criterion $\Delta c_{f,\min} \leq 0.25$ is already satisfied at the lowest simulated frequency, 0.020 Hz, for all three contrast branches. That frequency lies outside the interval used to infer thermal conductivity. The overlap used for thermal conductivity analysis begins at 30.688 Hz. The first sampled point inside it is 32.324 Hz, where $\Delta c_{f,\min} = 0.0103$, 0.00659, and 0.00383 for the low, medium, and high contrast branches, respectively. Within the overlap window, the best resolution for all three branches occurs at 63.249 Hz, with corresponding values 0.0101, 0.00644, and 0.00374. Thus the detectable concentration change lies inside the same frequency window that is suitable for thermal conductivity extraction.

Between $c_f = 0$ and $c_f = 0.25$, the extracted $\kappa_{\text{eff,system}}$ shift is +13.38% (low), +16.63% (medium), and +21.76% (high). In electrical space, the mean $|\Delta V_{3\omega}|$ separation in the overlap windows is 1.9138, 3.0084, and 5.2235 μV , corresponding to 23.3675 $\times$, 36.7326 $\times$, and 63.7790 $\times$ the band uncertainty floor 0.0819 μV . This confirms a clear detectability margin for all three composite contrasts in the present setup.

For every composite and degradation case, the FEM temperature amplitude is converted to $V_{3\omega}$ with the small signal relation in Eq. (2.15). The same conversion is used for all cases.

Table 4.4: Composite detectability metrics in the Kabaši overlap windows ($c_f = 0 \rightarrow 0.25$).

Scenario	overlap window [Hz]	$\Delta V_{3\omega, \text{mean}}$ [μV]	$\Delta c_{f, \text{min, mean}}$	$\Delta c_{f, \text{min, min}}$
low	30.688–149.786	1.9138	0.01076	0.01010
medium	30.688–165.929	3.0084	0.00684	0.00644
high	30.688–165.929	5.2235	0.00393	0.00374

4.2.3 Degradation Studies

For degradation cases where the secondary phase can be approximated as a dilute component inside the Nafion film, we use the same Maxwell–Eucken modelling framework as above. This covers gas-phase water redistribution and void formation, treated as water vapor and gas occupancy sweeps, respectively.

Chemical degradation of Nafion by radical species at catalyst interfaces has been reported [72]. Here, this evidence motivates an idealized surface-localized sensitivity case represented as a uniform skin. The cited work does not establish that exact morphology. Because the assumed perturbation is surface-localized, it cannot be represented by mean-field mixing and is therefore implemented as an explicit additional layer in the FEM model. The skin case is treated as a separate scenario family and is not directly comparable to the composite, water vapor, or void results.

Water redistribution as a water vapor volume-fraction sweep

Water redistribution is an established PEMFC transport and degradation concern and provides the physical motivation for this thermal scenario study [22, 73]. The calculation represents gas-phase water vapor and does not model liquid-water flooding. The dedicated mean-field case uses a representative near-300 K, low-pressure water vapor thermal conductivity $\kappa_{\text{H}_2\text{O}} = 0.019 \text{ W m}^{-1} \text{ K}^{-1}$ and $c_{\text{H}_2\text{O}} = \{0, 0.05, 0.10, 0.15, 0.20, 0.25\}$ [74]. Table 4.5 defines the sweep and common extraction settings. The concentration-dependent windows, fitted slopes, and extracted effective thermal conductivities are reported in Table 4.6.

Water vapor redistribution figures

Table 4.5: Water vapor redistribution study setup (frequency sweep).

Parameter	Value
Mean-field mapping	Maxwell–Eucken (Eq. 4.2)
Matrix thermal conductivity	$\kappa_m = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$
Water vapor thermal conductivity at 300 K	$\kappa_{\text{H}_2\text{O}} = 0.019 \text{ W m}^{-1} \text{ K}^{-1}$ [74]
Water vapor fraction sweep	$c_{\text{H}_2\text{O}} = \{0, 0.05, 0.10, 0.15, 0.20, 0.25\}$
Frequency sweep	25 points from 10^{-2} to 10^5 Hz
Substrate window	0.6586–165.929 Hz
Extraction window rule	Kabaši overlap
Uncertainty floor used	$\langle \sigma_{V_{3\omega}} \rangle = 0.0819 \text{ } \mu\text{V}$ in 200.9–801 Hz band

Table 4.6: Water vapor extraction summary from concentration-dependent Kabaši overlap windows.

$c_{\text{H}_2\text{O}}$	$\kappa_{\text{film}} [\text{W m}^{-1} \text{ K}^{-1}]$	overlap window [Hz]	slope	$\kappa_{\text{eff,system}} [\text{W m}^{-1} \text{ K}^{-1}]$
0.00	0.2500	30.688–118.948	-0.038646	1.37275
0.05	0.2337	28.684–111.179	-0.038654	1.37247
0.10	0.2180	26.765–103.742	-0.038720	1.37012
0.15	0.2031	24.927–96.615	-0.038855	1.36536
0.20	0.1887	23.163–89.779	-0.039064	1.35806
0.25	0.1749	21.470–83.217	-0.039354	1.34805

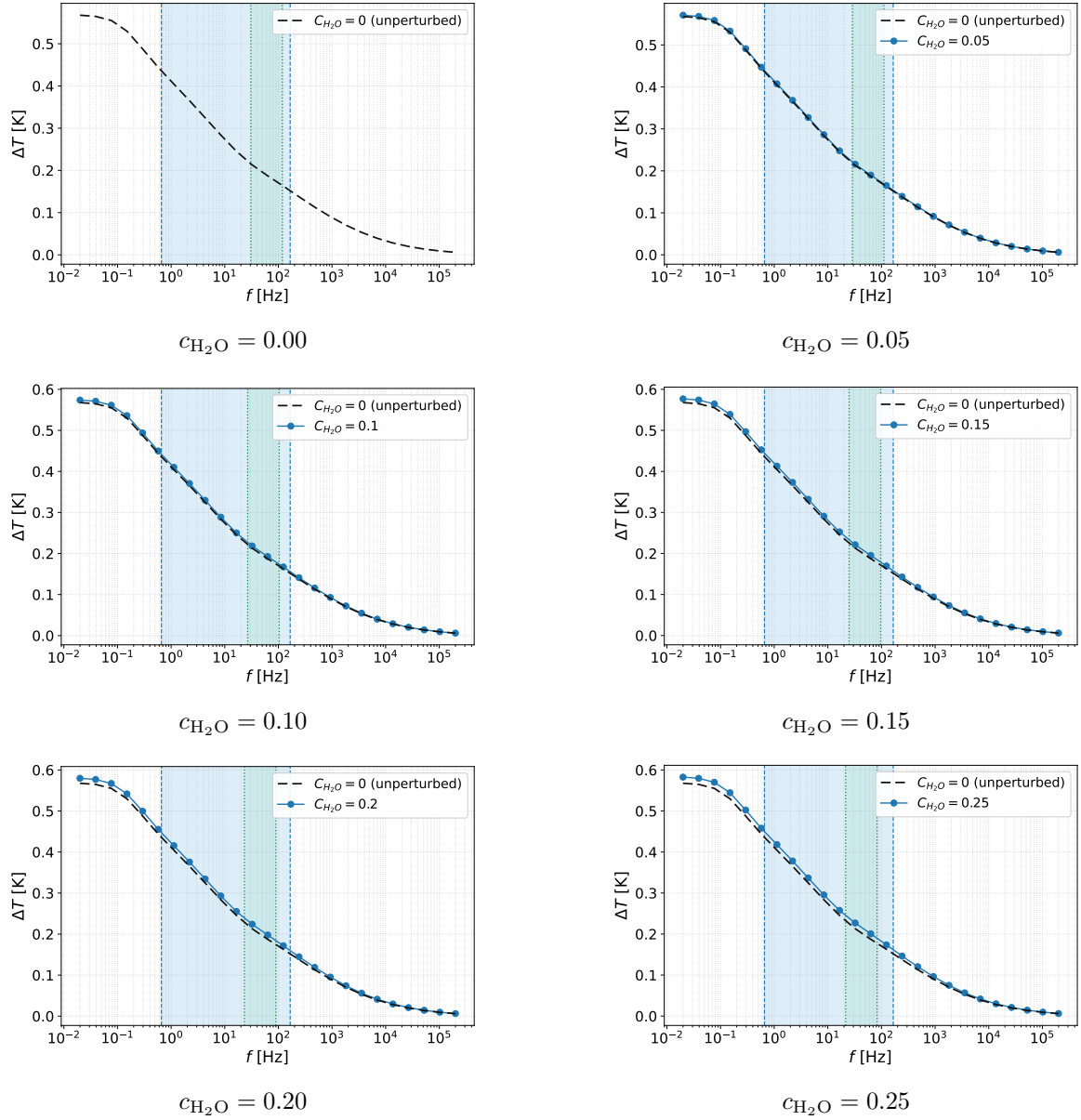


Figure 4.14: Water vapor $\Delta T(f)$ for six concentrations.

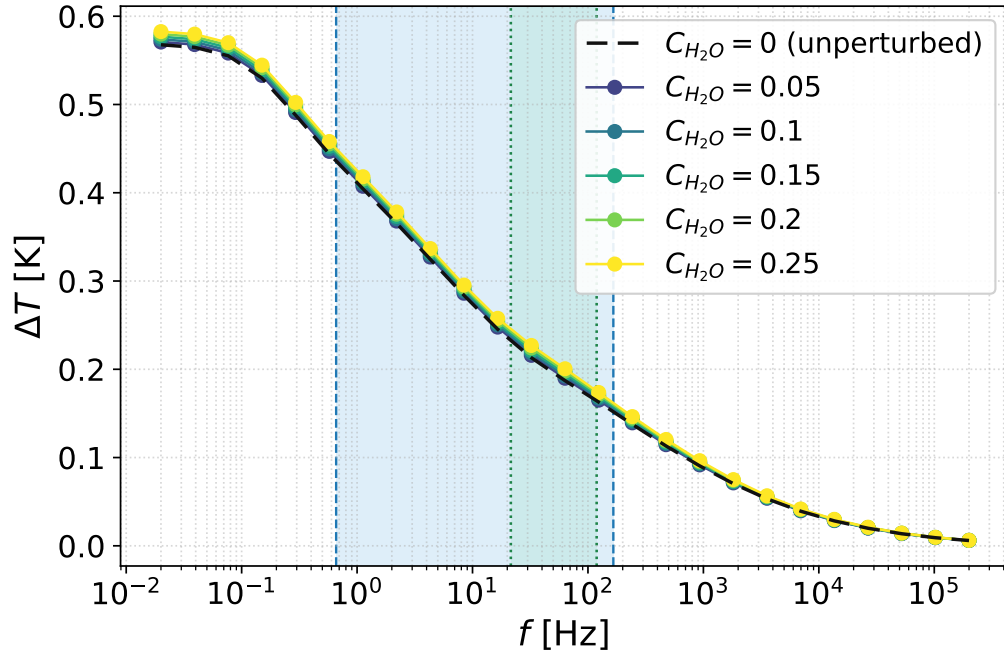


Figure 4.15: Grouped water vapor $\Delta T(f)$ overlay for all c_{H_2O} .

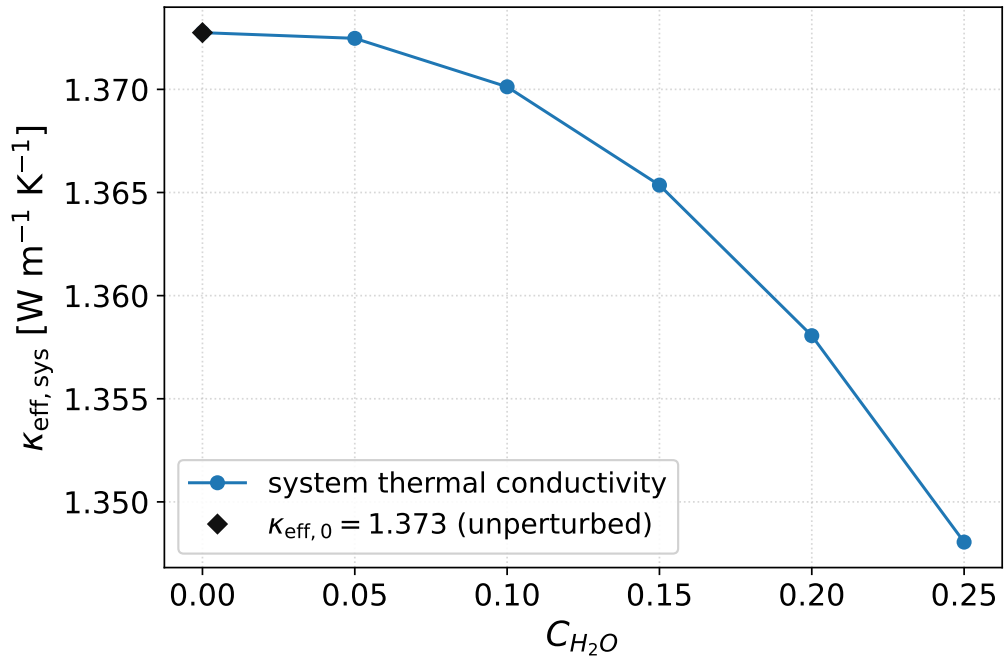


Figure 4.16: Extracted system thermal conductivity versus c_{H_2O} for the water vapor redistribution study.

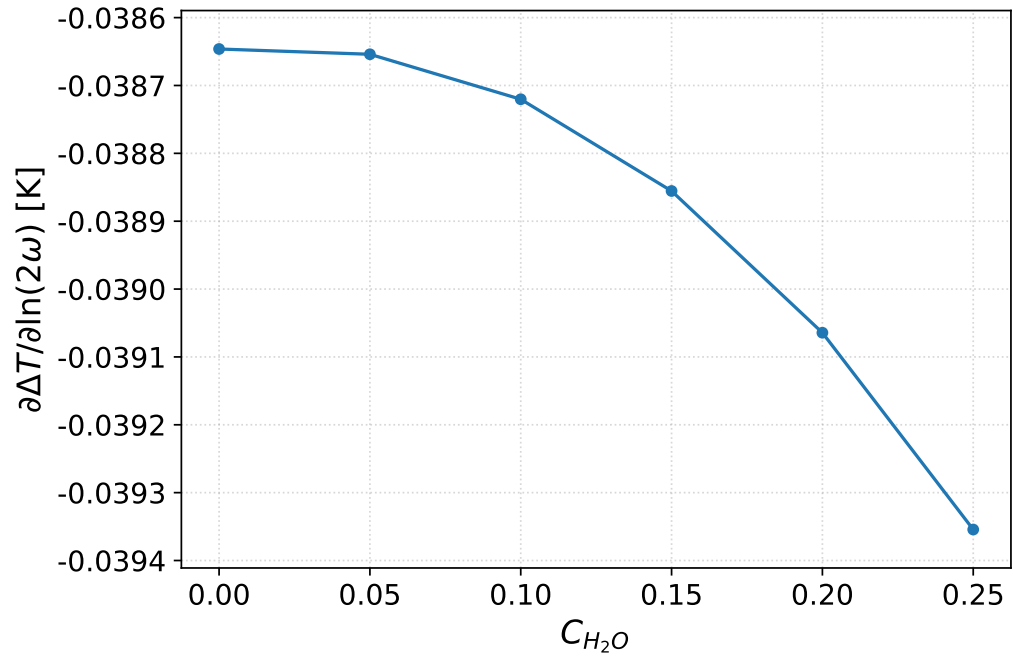


Figure 4.17: Water vapor slope of ΔT versus $\ln(2\omega)$ as a function of c_{H_2O} .

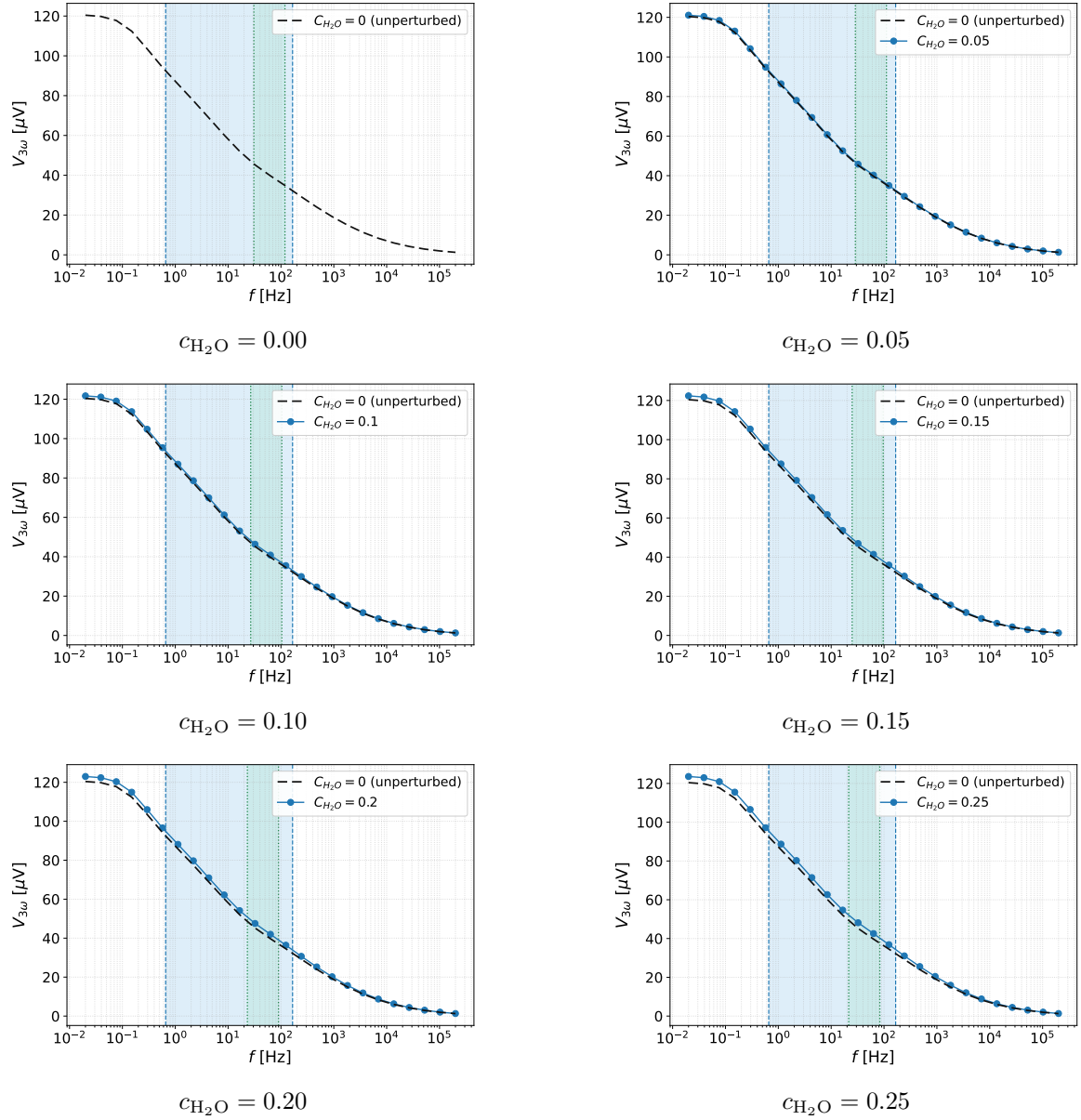


Figure 4.18: Water vapor $V_{3\omega}(f)$ for six concentrations.

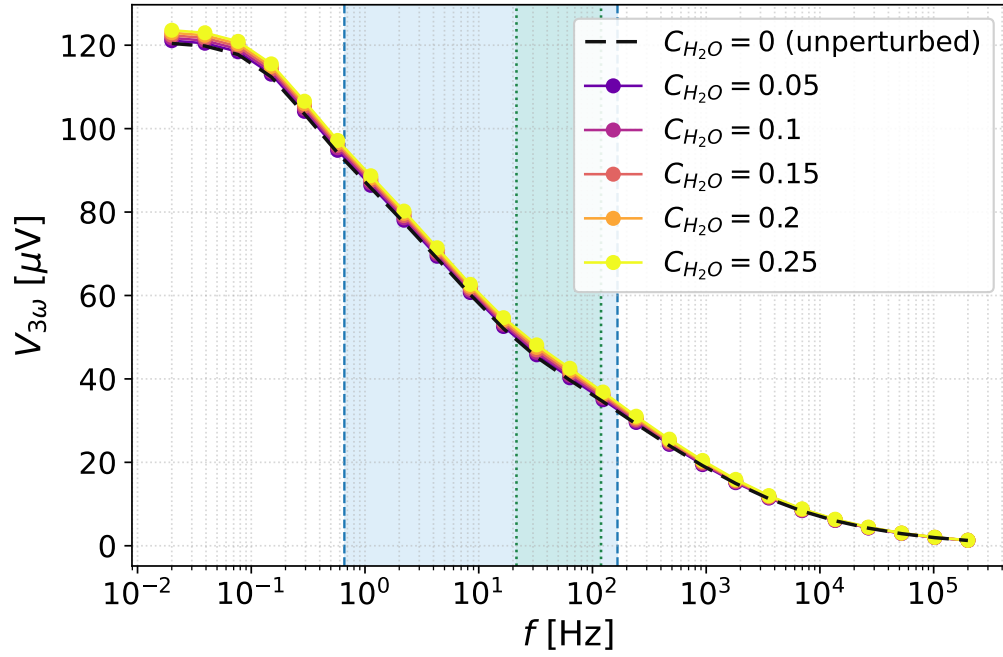


Figure 4.19: Grouped water vapor $V_{3\omega}(f)$ overlay for all c_{H_2O} .

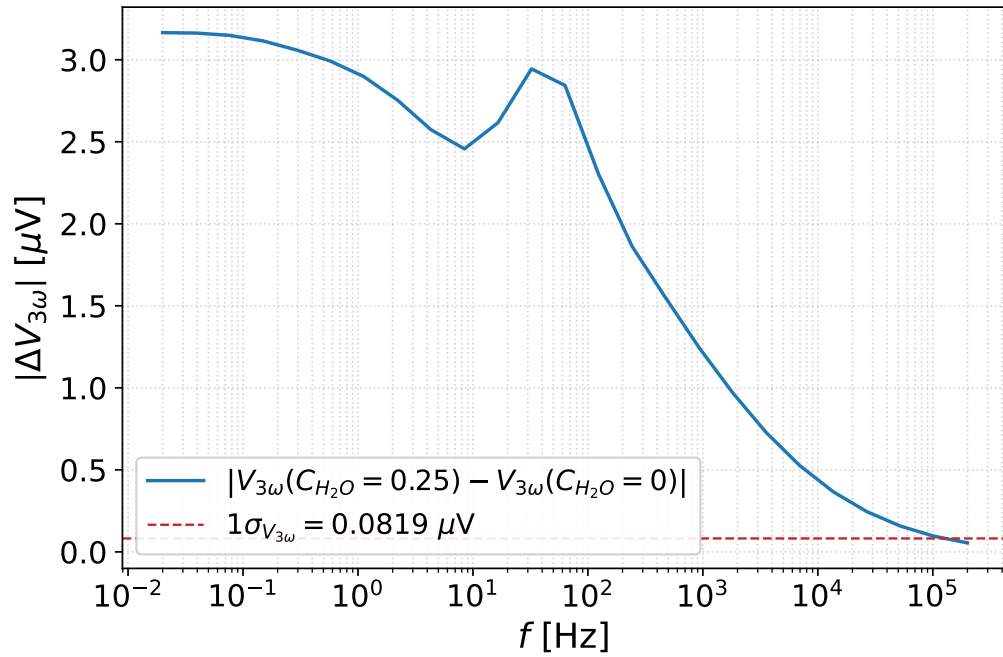


Figure 4.20: Water vapor absolute electrical separation $|\Delta V_{3\omega}|$ between $c_{H_2O} = 0$ and 0.25.

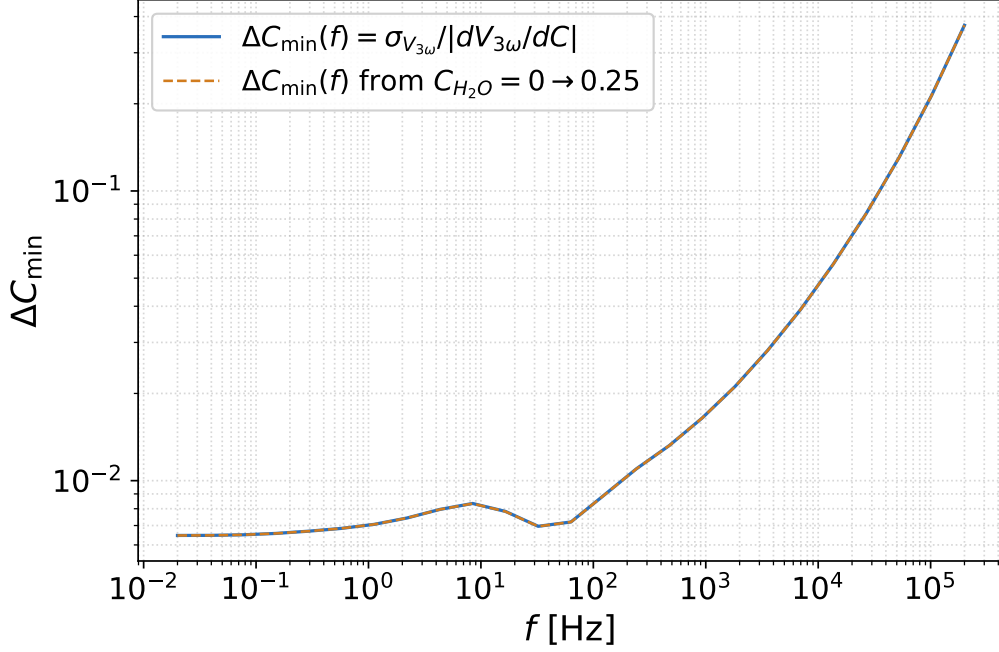


Figure 4.21: Water vapor concentration resolution $\Delta c_{\text{H}_2\text{O},\text{min}}(f)$.

The shaded frequency bands in Figures 4.14, 4.15, 4.18, 4.19, 4.22, and 4.23 denote the theoretical substrate and film linear ranges defined in Chapter 2.

Figure 4.14 and their overlay in Figure 4.15 show a systematic concentration-dependent shift. Figures 4.16 and 4.17 confirm that both the effective thermal conductivity and fitted slope vary monotonically. The same ordering is retained in the individual and grouped electrical responses (Figures 4.18 and 4.19). Finally, Figures 4.20 and 4.21 show that this trend remains above the experimental uncertainty floor. The local maximum in $|\Delta V_{3\omega}|$ and the corresponding minimum in resolvable concentration occur when the thermal penetration depth is comparable to the film thickness. The upper film surface limits heat flow out of the film, so more of the oscillatory heat is stored in the finite film volume during this part of the cycle. A change in film composition then produces its largest difference in heater temperature and voltage. The changing power split between the film and substrate is shown in Figure 4.4.

For the water vapor redistribution case, $\kappa_{\text{eff,system}}$ decreases from 1.37275 to 1.34805 $\text{W m}^{-1} \text{K}^{-1}$ between $c_{\text{H}_2\text{O}} = 0$ and 0.25, a change of -1.79931% . The mean electrical separation across this full span is 2.8939 μV in the overlap window [21.470, 118.948] Hz, corresponding to $35.33455\times$ the 0.0819 μV uncertainty floor. The mean concentration resolution is $\Delta c_{\text{H}_2\text{O},\text{min}} = 0.00708$, indicating that small but finite filling-fraction changes remain thermally and electrically resolvable in this setup.

Void formation as gas-occupancy sweep

Void formation is treated as a low thermal conductivity secondary-phase family with different possible gas occupancies. The same concentration sweep is used for each gas case, $c_{\text{gas}} = \{0, 0.05, 0.10, 0.15, 0.20, 0.25\}$, and only film thermal conductivity is changed through Maxwell–Eucken mapping. The gas thermal conductivities and their contrast relative to

Nafion are listed in Table 4.7. The corresponding detectability metrics are summarized in Table 4.8. The gas values are rounded representative thermal conductivities near 300 K from low-pressure reference data [74]. The $0.001 \text{ W m}^{-1} \text{ K}^{-1}$ vacuum entry is a numerical approximation to the limiting case of a void with no gas.

Void figure set by gas

Each panel below shows one gas case as a grouped concentration sweep, using the same evidence categories as the composite and water vapor sections.

Table 4.7: Rounded near-300 K gas-phase thermal conductivity inputs used in the mean-field void study. The vacuum entry is a numerical limiting surrogate.

Void occupancy	phase thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	ratio to $\kappa_m = 0.25$
vacuum surrogate	0.001	0.004
air	0.026	0.104
N ₂	0.025	0.100
O ₂	0.026	0.104
H ₂	0.180	0.720

Table 4.8: Void detectability summary for $c_{\text{gas}} = 0 \rightarrow 0.25$ in each gas case.

Void occupancy	overlap window [Hz]	$\Delta V_{3\omega, \text{mean}}$ [μV]	$\Delta c_{\text{gas}, \text{min}, \text{mean}}$	$\Delta c_{\text{gas}, \text{min}, \text{min}}$
vacuum	20.513–118.948	3.2409	0.00632	0.00619
air	21.830–118.948	2.7668	0.00740	0.00728
N ₂	21.779–118.948	2.7854	0.00735	0.00723
O ₂	21.830–118.948	2.7669	0.00740	0.00728
H ₂	28.379–118.948	0.6596	0.03104	0.03097

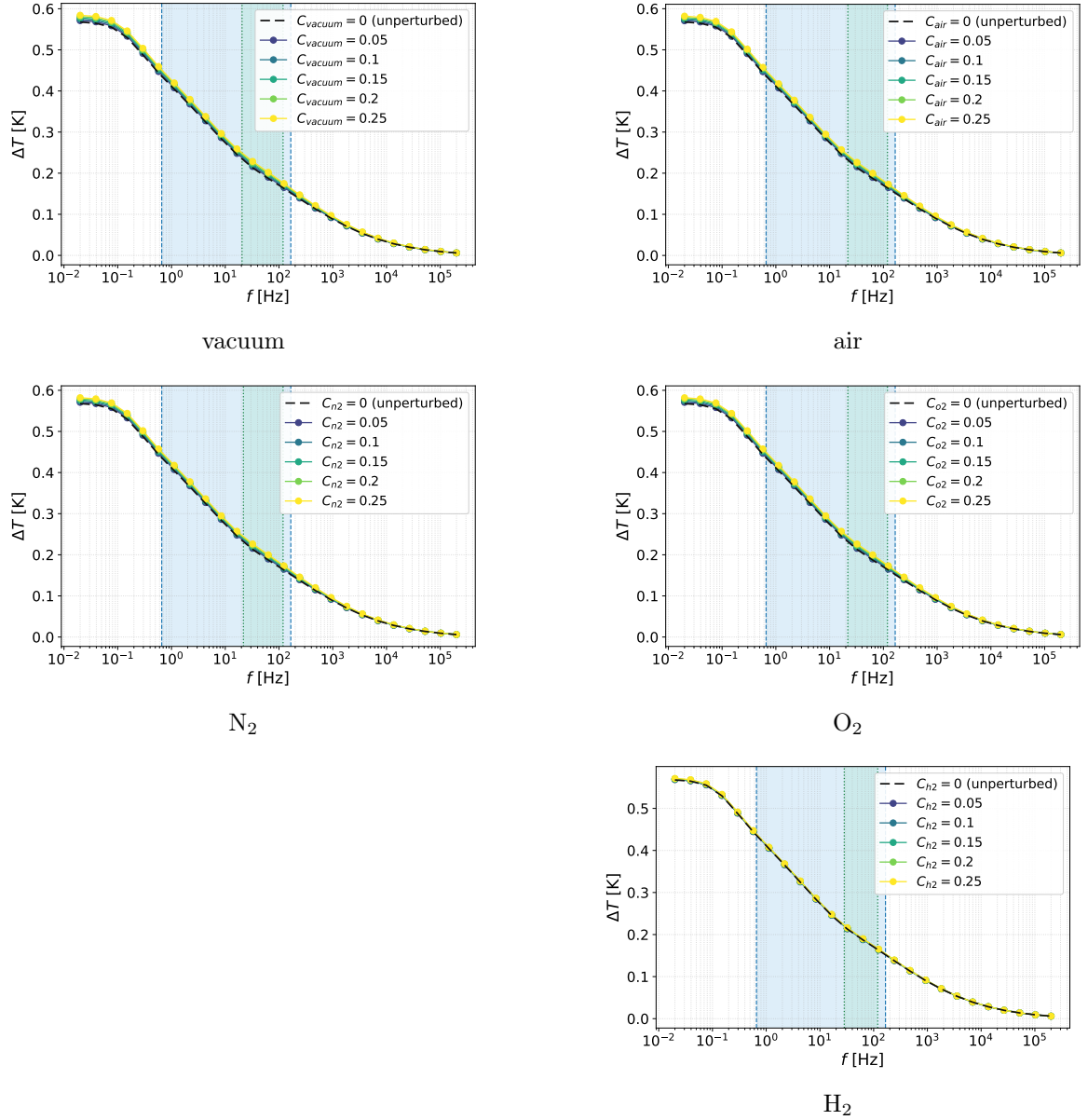


Figure 4.22: Void study grouped $\Delta T(f)$ families by gas occupancy.

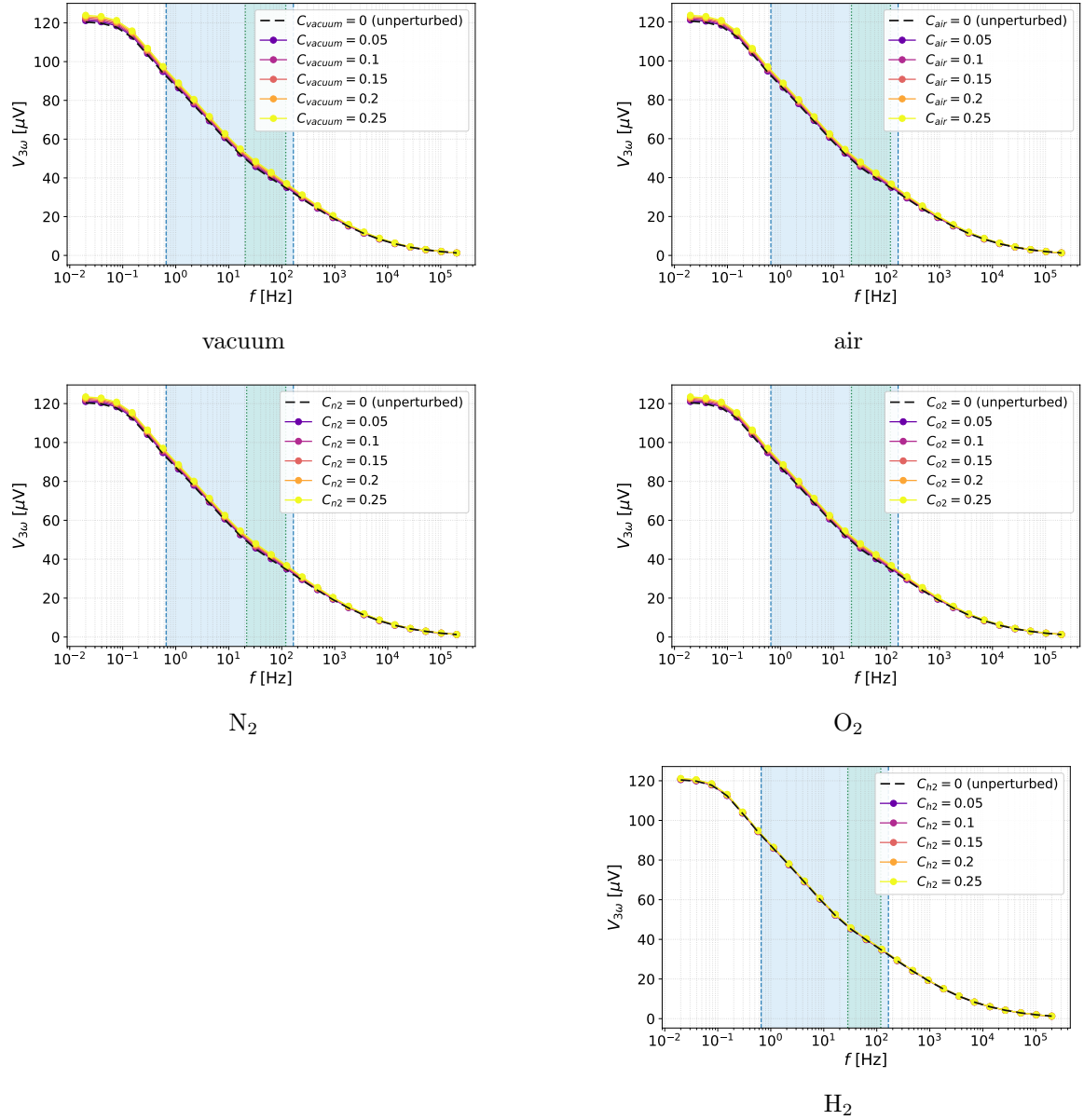


Figure 4.23: Void study grouped $V_{3\omega}(f)$ families by gas occupancy.

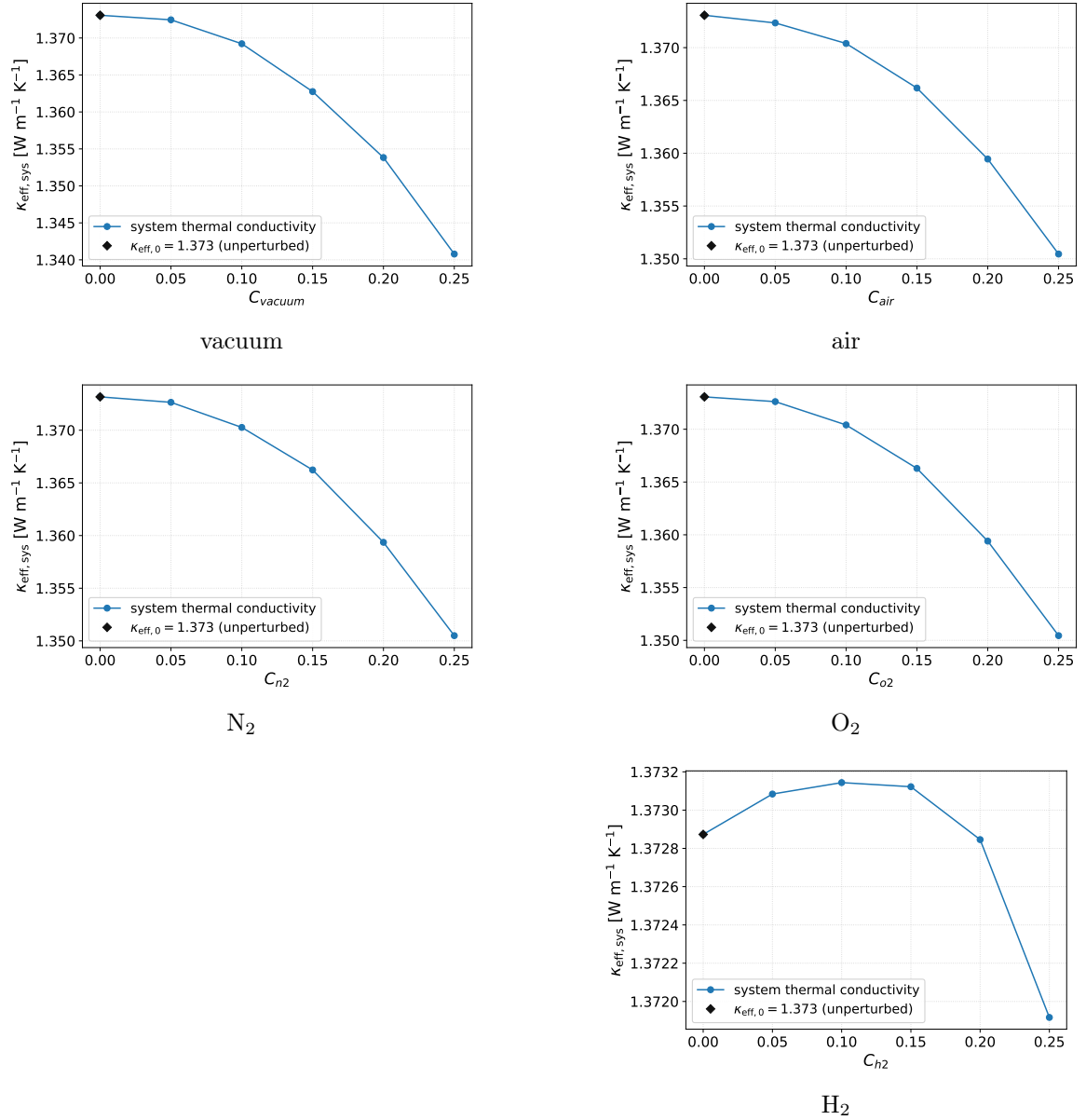


Figure 4.24: Void study extracted $\kappa_{\text{eff,system}}$ versus concentration by gas occupancy.

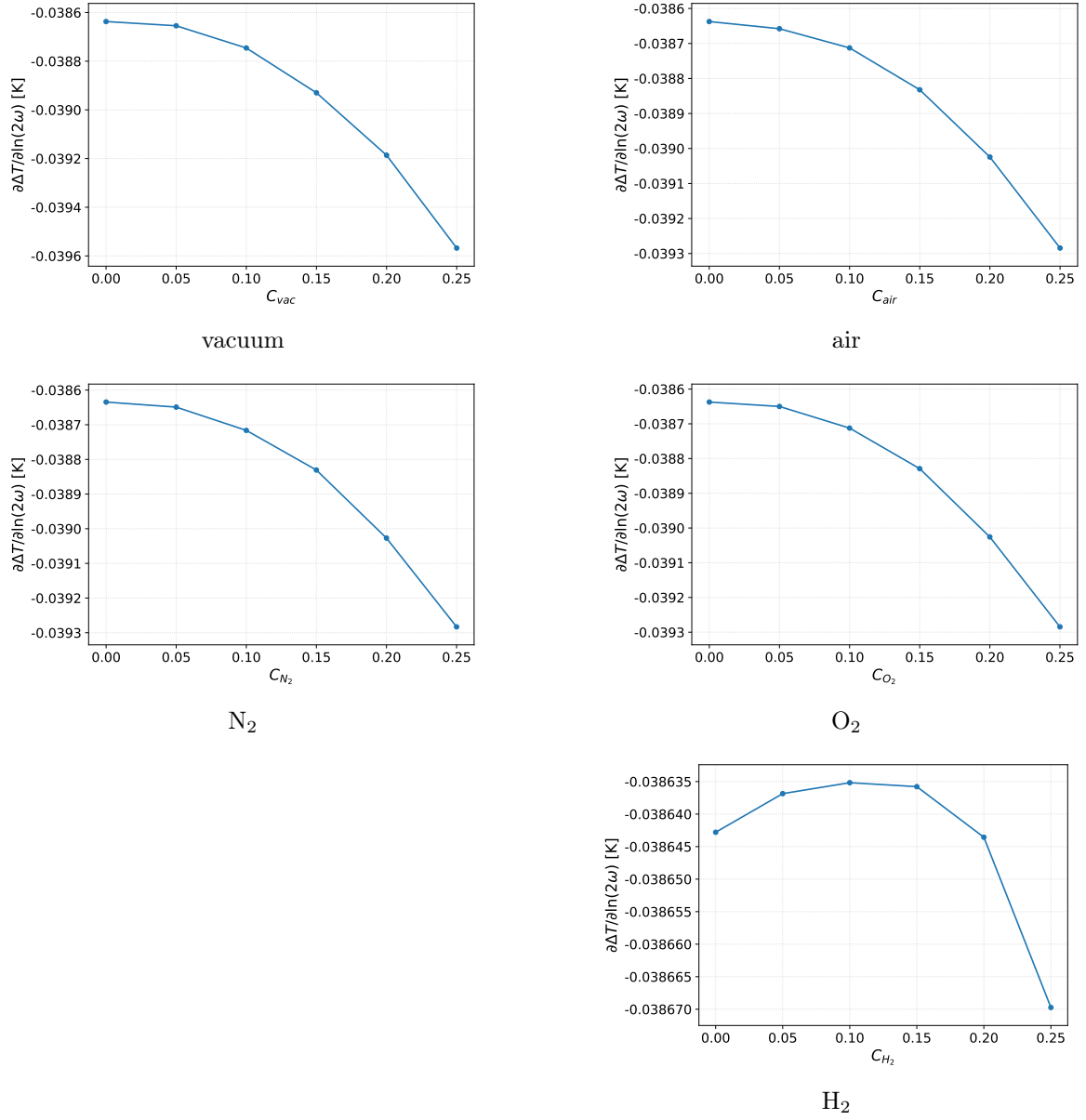


Figure 4.25: Void study slope $\partial\Delta T/\partial\ln(2\omega)$ versus concentration by gas occupancy.

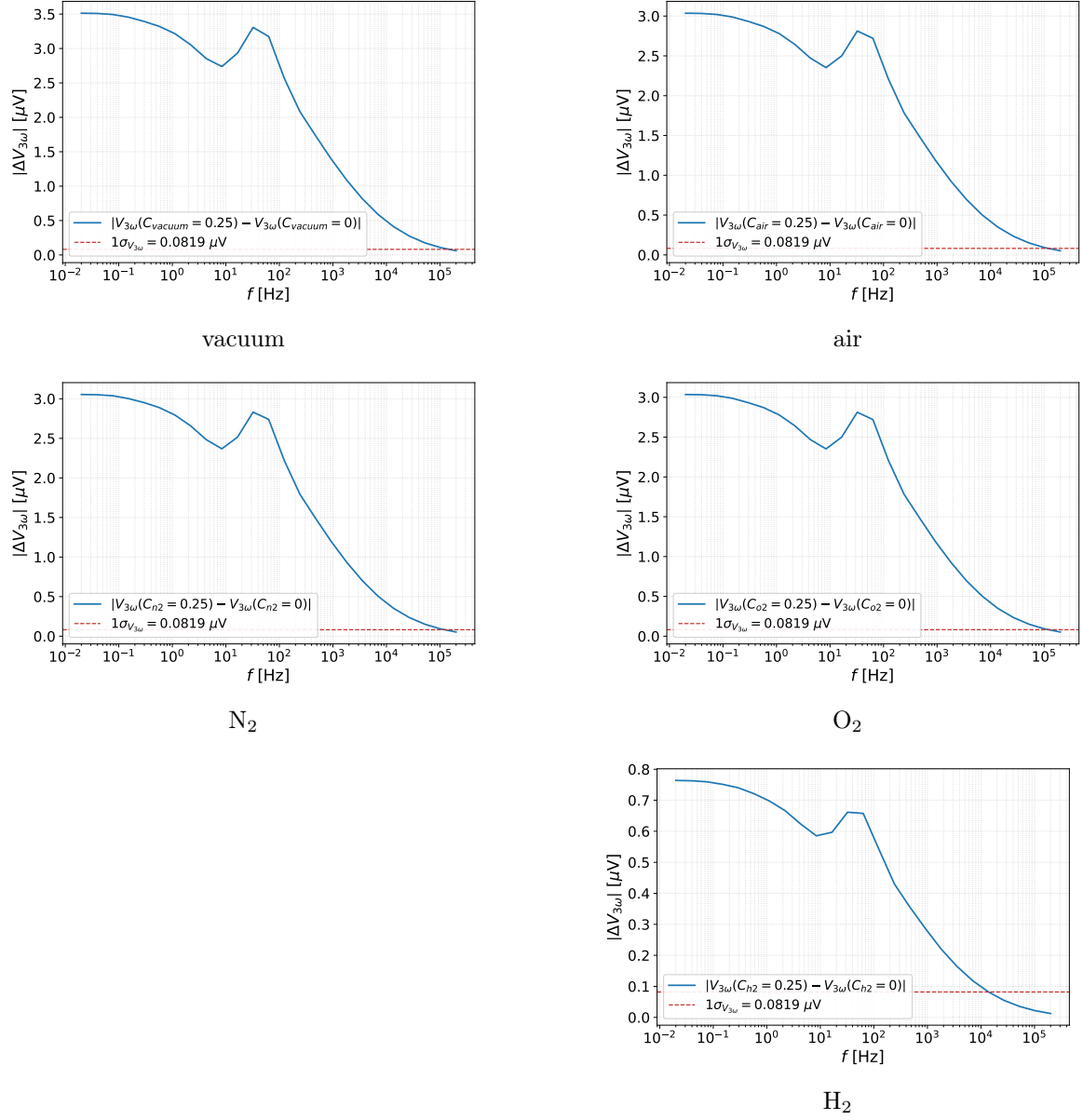


Figure 4.26: Void study $|\Delta V_{3\omega}|$ between baseline and maximum concentration by gas occupancy. The red dashed line is the experimental 1σ uncertainty in $V_{3\omega}$, $0.0819 \mu\text{V}$ (81.9 nV). This value is the limit of detection used in the resolution calculation.

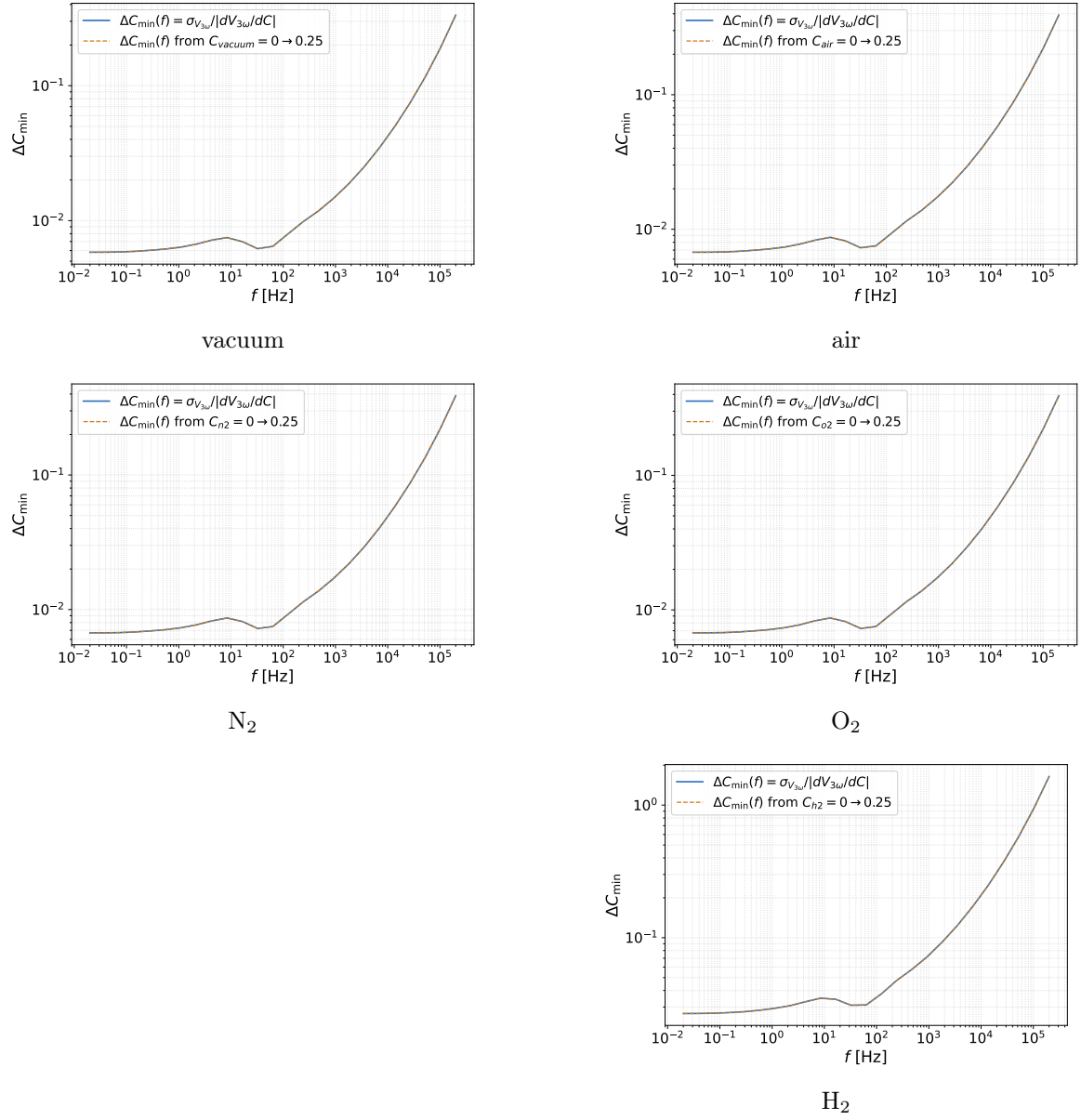


Figure 4.27: Void study concentration resolution $\Delta C_{\text{gas},\min}(f)$ by gas occupancy, calculated using the experimental 1σ limit of detection, $0.0819 \mu\text{V}$ (81.9 nV).

The thermal and electrical response families in Figures 4.22 and 4.23 separate most strongly for vacuum and least strongly for H_2 . The effective thermal conductivity and slope reductions (Figures 4.24 and 4.25) preserve this gas-dependent ordering. Figures 4.26 and 4.27 show the resulting experimental consequence: lower gas thermal conductivity produces greater voltage separation and a smaller resolvable void fraction. The broad local maximum in $|\Delta V_{3\omega}|$ occurs when the penetration depth becomes comparable to the film thickness. The finite film volume then stores a larger part of the oscillatory heat, which makes the heater temperature most sensitive to redistribution within the film. The changing power split is shown in Figure 4.4 and the analogous water vapor response in Figure 4.20. The greater signal separation in this frequency range improves concentration resolution.

Void results follow the expected thermal-contrast ordering. Vacuum gives the strongest mean separation ($3.2409 \mu\text{V}$, $\Delta c_{\min} = 0.00632$). Air, N_2 , and O_2 are nearly identical (mean separation $2.767\text{--}2.785 \mu\text{V}$, $\Delta c_{\min} = 0.00735$ to 0.00740). H_2 is much weaker ($0.6596 \mu\text{V}$, $\Delta c_{\min} = 0.0310$). This is consistent with the higher gas-phase thermal conductivity of H_2 , which reduces Maxwell–Eucken contrast relative to Nafion.

Skin formation: multilayer skin model

Surface-localized degradation cannot be represented by mean field theory because it introduces spatially resolved layering. This perturbation is implemented as an explicit multilayer FEM case.

The top skin study is implemented as a two-sweep family in the same film-heater-substrate geometry used in the previous sections. The first sweep varies skin thickness at fixed skin thermal conductivity ($\kappa_{\text{skin}} = 0.1 \text{ W m}^{-1} \text{ K}^{-1}$). The second sweep varies skin thermal conductivity at fixed thickness ($t_{\text{skin}} = 1 \mu\text{m}$). The skin thickness, thermal conductivity, and volumetric heat capacity are prescribed sensitivity study inputs. Table 4.9 defines both sweeps, and Table 4.10 summarizes their electrical separation and parameter resolution.

RESULTS AND DISCUSSION

Table 4.9: Top skin multilayer study setup (frequency sweep).

Parameter	Value
Base layered model	film 32 μm , heater 14 μm , glass substrate 1 mm
Skin placement	explicit top layer on Nafion film
Thickness sweep	$t_{\text{skin}} = \{0.1, 0.25, 0.5, 1, 2, 5\} \mu\text{m}$ at $\kappa_{\text{skin}} = 0.1$
Thermal conductivity sweep	$\kappa_{\text{skin}} = \{0.05, 0.10, 0.15, 0.20, 0.25\} \text{ W m}^{-1} \text{ K}^{-1}$ at $t_{\text{skin}} = 1 \mu\text{m}$
Skin volumetric heat capacity	$\rho c_{\text{skin}} = 2.94 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$
Extraction window rule	Kabaši overlap
Uncertainty floor used	$\langle \sigma_{V_{3\omega}} \rangle = 0.0819 \mu\text{V}$ in 200.9–801 Hz band

Table 4.10: Top skin detectability summary for thickness and thermal conductivity sweeps.

Sweep (overlap window 30.688–118.948 Hz)	parameter span	$\Delta V_{3\omega, \text{mean}} [\mu\text{V}]$	$\Delta p_{\text{min, mean}}$
$t_{\text{skin-sweep}}, \kappa_{\text{skin}} = 0.1$	0.1 $\rightarrow$ 5 μm	0.1273	5.7907 μm
$\kappa_{\text{skin-sweep}}, t_{\text{skin}} = 1 \mu\text{m}$	0.25 $\rightarrow$ 0.05 $\text{ W m}^{-1} \text{ K}^{-1}$	0.0065	2.4527 $\text{ W m}^{-1} \text{ K}^{-1}$

Top skin figure set

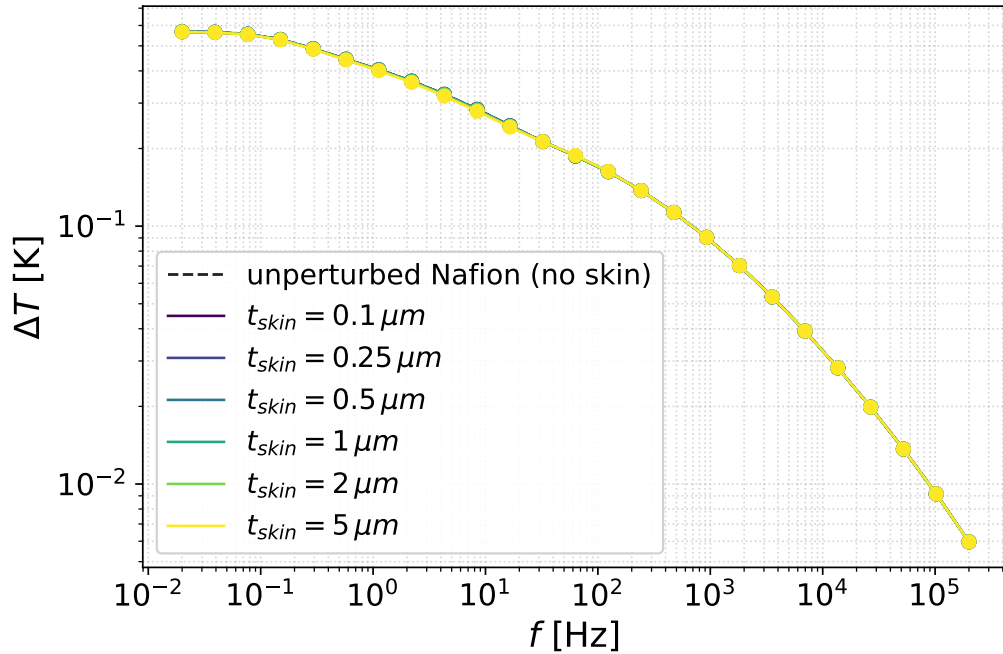


Figure 4.28: Top skin grouped $\Delta T(f)$ for thickness sweep at fixed $\kappa_{\text{skin}} = 0.1 \text{ W m}^{-1} \text{ K}^{-1}$.

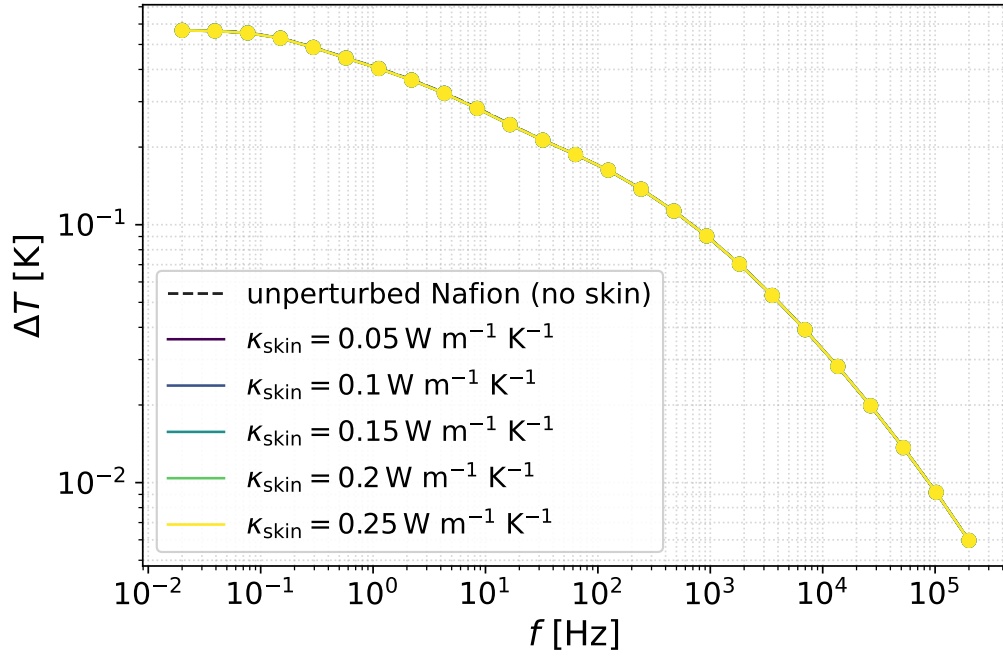


Figure 4.29: Top skin grouped $\Delta T(f)$ for thermal conductivity sweep at fixed $t_{\text{skin}} = 1 \mu\text{m}$.

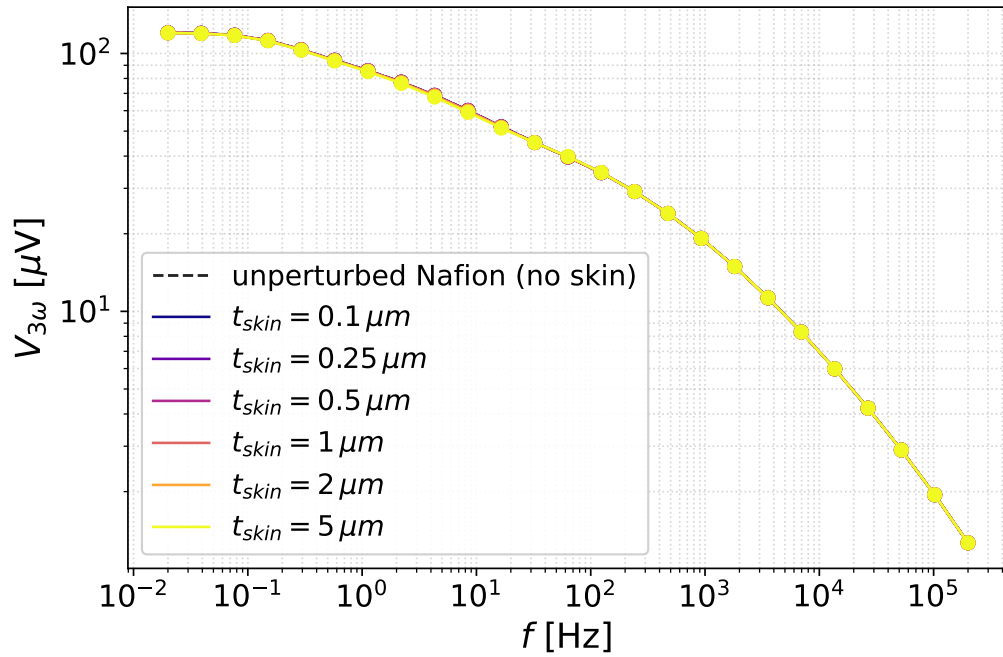


Figure 4.30: Top skin grouped $V_{3\omega}(f)$ for thickness sweep at fixed $\kappa_{\text{skin}} = 0.1 \text{ W m}^{-1} \text{ K}^{-1}$.

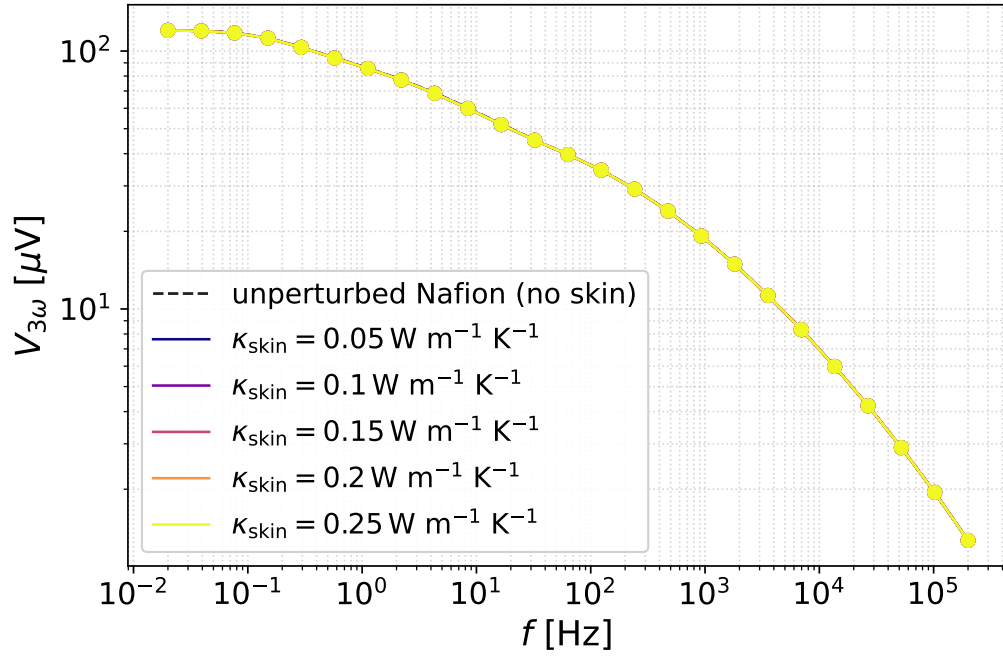


Figure 4.31: Top skin grouped $V_{3\omega}(f)$ for thermal conductivity sweep at fixed $t_{\text{skin}} = 1 \mu\text{m}$.

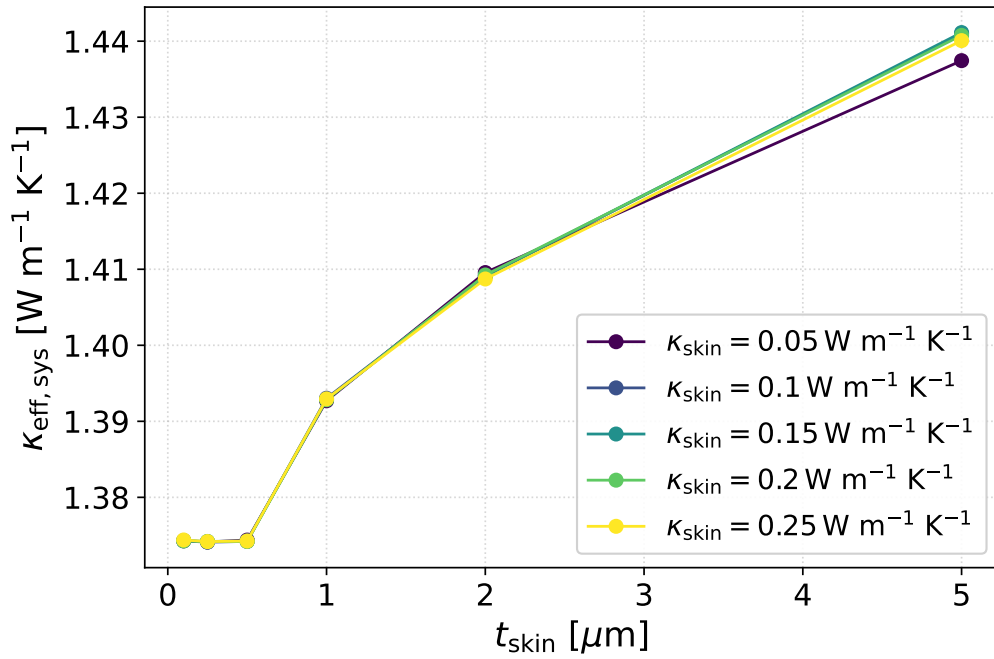


Figure 4.32: Top skin extracted $\kappa_{\text{eff, system}}$ versus t_{skin} for all κ_{skin} branches.

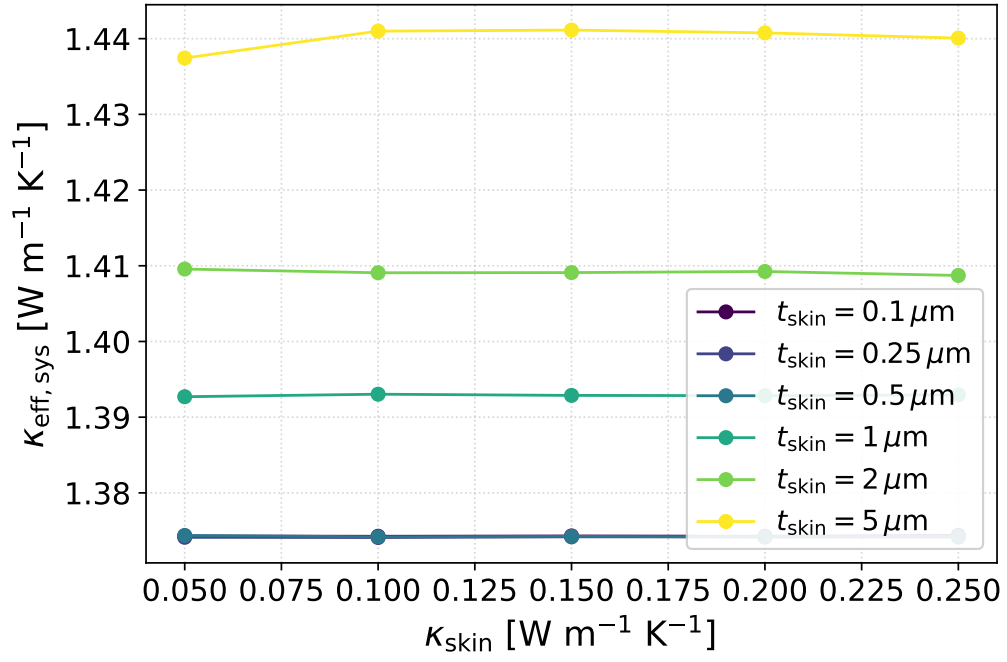


Figure 4.33: Top skin extracted $\kappa_{\text{eff,system}}$ versus κ_{skin} for all t_{skin} branches.

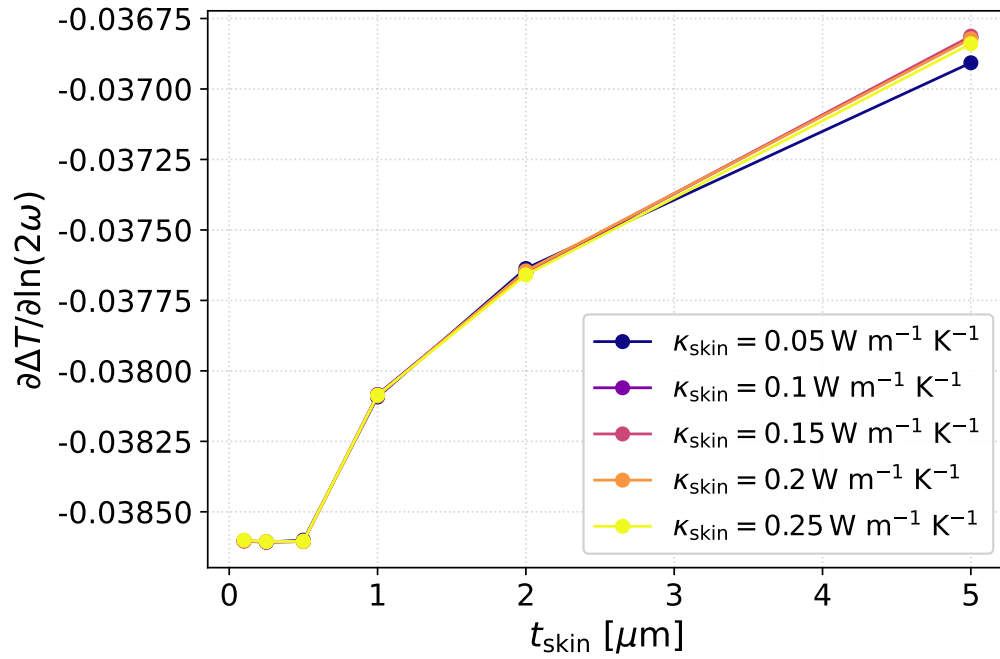


Figure 4.34: Top skin slope $\partial\Delta T/\partial\ln(2\omega)$ versus t_{skin} by κ_{skin} branch.

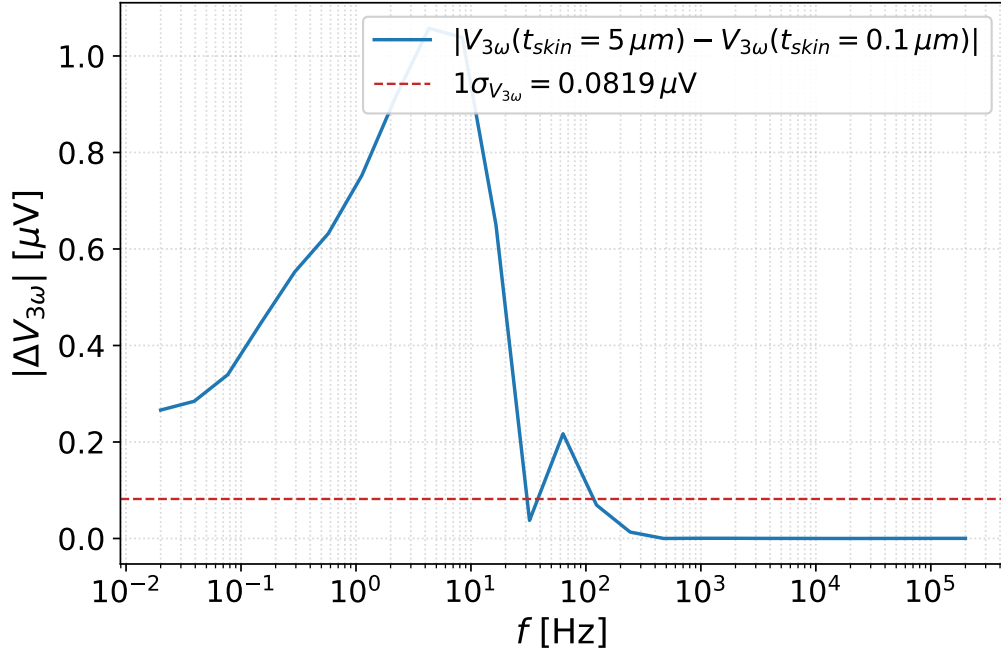


Figure 4.35: Top skin absolute electrical separation $|\Delta V_{3\omega}|$ for $t_{\text{skin}} : 0.1 \rightarrow 5 \mu\text{m}$ at $\kappa_{\text{skin}} = 0.1 \text{ W m}^{-1} \text{ K}^{-1}$. The red dashed line marks the experimental 1σ uncertainty in $V_{3\omega}$, $0.0819 \mu\text{V}$ (81.9 nV).

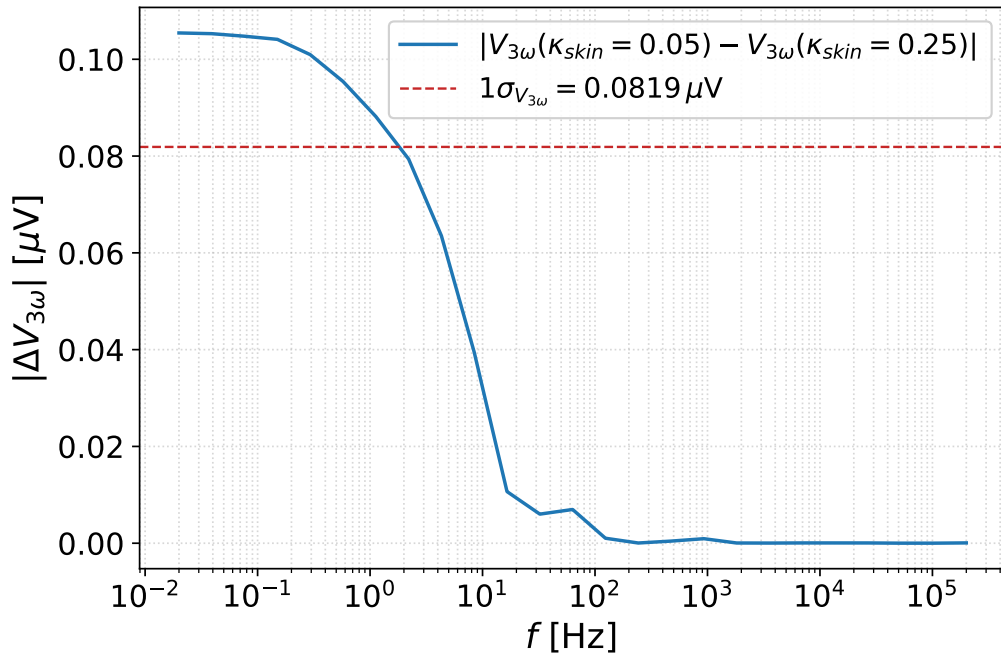


Figure 4.36: Top skin absolute electrical separation $|\Delta V_{3\omega}|$ for $\kappa_{\text{skin}} : 0.25 \rightarrow 0.05 \text{ W m}^{-1} \text{ K}^{-1}$ at $t_{\text{skin}} = 1 \mu\text{m}$. The red dashed line is the experimental 1σ uncertainty in $V_{3\omega}$, $0.0819 \mu\text{V}$ (81.9 nV).

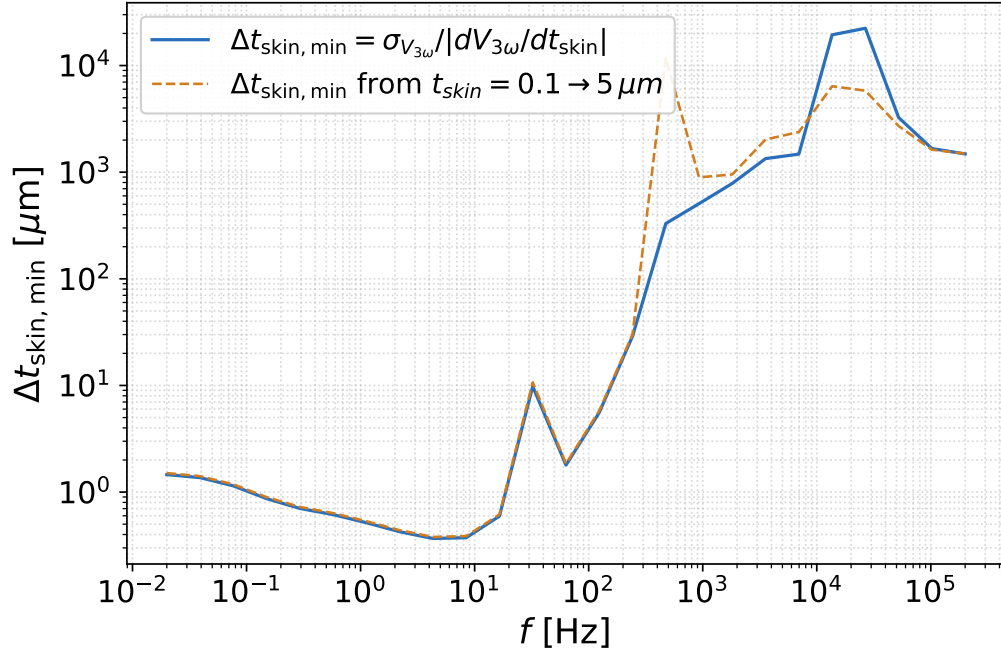


Figure 4.37: Top skin thickness resolution $\Delta t_{\text{skin},\text{min}}(f)$ at $\kappa_{\text{skin}} = 0.1 \text{ W m}^{-1} \text{ K}^{-1}$.

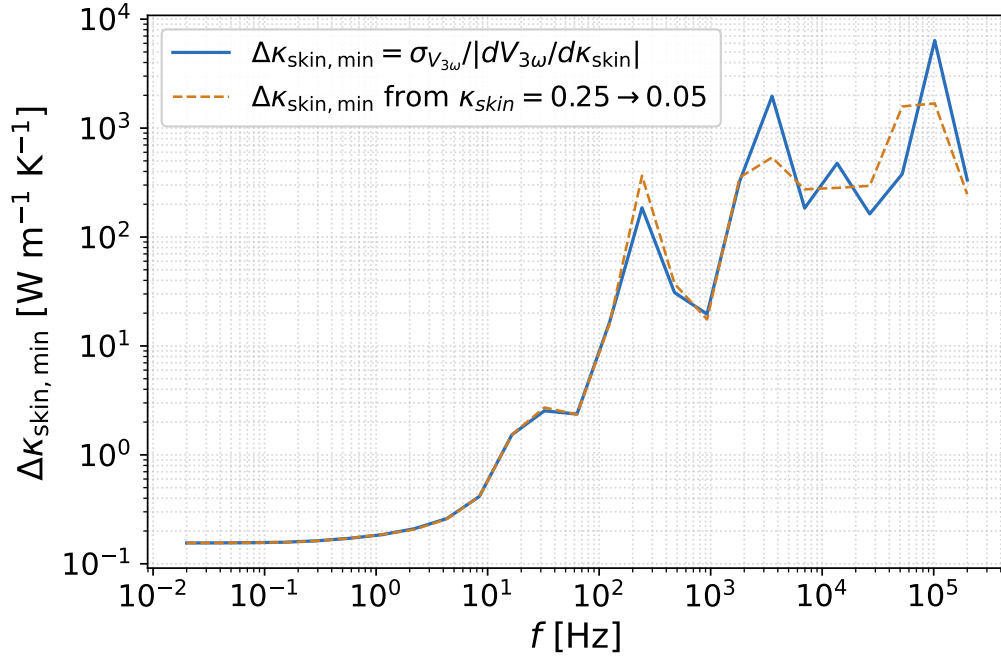


Figure 4.38: Top skin thermal conductivity resolution $\Delta \kappa_{\text{skin},\text{min}}(f)$ at $t_{\text{skin}} = 1 \text{ μm}$.

For the thickness sweep, Figures 4.28 and 4.30 show only a small progressive separation of the response curves. The derived effective thermal conductivity and logarithmic slope in Figures 4.32 and 4.34 vary systematically, but the electrical separation and resolution in Figures 4.35 and 4.37 show that the effect remains near the measurement limit.

At fixed $\kappa_{\text{skin}} = 0.1 \text{ W m}^{-1} \text{ K}^{-1}$, increasing t_{skin} from 0.1 to 5 μm shifts extracted $\kappa_{\text{eff,system}}$ from 1.37410 to 1.44099 $\text{W m}^{-1} \text{ K}^{-1}$, an increase of 4.86791%. The mean electrical separation for this span is 0.1273 μV in 30.688–118.948 Hz, corresponding to 1.55433 $\times$ the 0.0819 μV uncertainty floor. The inferred mean minimum resolvable thickness increment is $\Delta t_{\text{skin,min}} = 5.7907 \mu\text{m}$, larger than the simulated sweep span.

For the thermal conductivity sweep, the near overlap of the thermal and electrical curves in Figures 4.29 and 4.31 is also reflected in the weak effective thermal conductivity response of Figure 4.33. The voltage separation in Figure 4.36 remains below the uncertainty floor, and Figure 4.38 consequently places the required thermal conductivity resolution far outside the simulated range.

The small point-to-point irregularities in the two resolution curves arise from the resolution definition, which divides the experimental uncertainty by a local numerical sensitivity. The sensitivity is evaluated from differences between discretely sampled FEM response curves. Consequently, small numerical changes between adjacent frequency points are amplified when the response derivative is small. The effect is most visible for the weakly identifiable skin parameters and does not represent an additional physical resonance.

At fixed $t_{\text{skin}} = 1 \mu\text{m}$, the thermal conductivity sweep $\kappa_{\text{skin}} : 0.25 \rightarrow 0.05 \text{ W m}^{-1} \text{ K}^{-1}$ produces a mean electrical separation of only 0.0065 μV , corresponding to 0.07937 $\times$ the uncertainty floor. The inferred $\Delta\kappa_{\text{skin,min}} = 2.4527 \text{ W m}^{-1} \text{ K}^{-1}$ is far above the imposed sweep range, indicating that thermal conductivity contrast in this skin configuration is not practically resolvable in the present setup.

4.2.4 Thermal Detectability and Sensitivity Limits

Table 4.11 places all studies on the same electrical-sensitivity basis. The high-contrast composite case gives the largest mean separation (5.2235 μV), followed by vacuum-surrogate voids (3.2409 μV). The water vapor redistribution case and air-, N_2 -, or O_2 -filled voids remain clearly detectable, with mean resolvable fractions from 0.00632 to 0.00740. H_2 -filled voids have lower contrast and a mean resolvable fraction of 0.03104.

The explicit skin layer is the limiting case. Its thickness sweep produces only 0.1273 μV mean separation and requires a resolvable increment larger than the simulated thickness span. Its thermal conductivity sweep produces 0.0065 μV , below the experimental uncertainty floor of 0.0819 μV (81.9 nV). Under the present geometry and noise level, composite loading, gas-phase water redistribution, and most void scenarios are detectable, whereas the investigated skin-property changes are not reliably identifiable.

Table 4.11: Overview of detectability metrics by study type in the present chapter.

Study type	Phase/parameter term	overlap [Hz]	$\Delta V_{3\omega, \text{mean}}$ [μV]	$\Delta p_{\text{min, mean}}$
Composite low	$\kappa_f = 0.6$	30.688–149.786	1.9138	0.01076
Composite medium	$\kappa_f = 1.0$	30.688–165.929	3.0084	0.00684
Composite high	$\kappa_f = 5.0$	30.688–165.929	5.2235	0.00393
Water vapor	$\kappa_{\text{H}_2\text{O}} = 0.019$	21.470–118.948	2.8939	0.00708
Void vacuum surrogate	$\kappa_{\text{sur}} = 0.001$	20.513–118.948	3.2409	0.00632
Void air	$\kappa_{\text{air}} = 0.026$	21.830–118.948	2.7668	0.00740
Void N ₂	$\kappa_{\text{N}_2} = 0.025$	21.779–118.948	2.7854	0.00735
Void O ₂	$\kappa_{\text{O}_2} = 0.026$	21.830–118.948	2.7669	0.00740
Void H ₂	$\kappa_{\text{H}_2} = 0.180$	28.379–118.948	0.6596	0.03104
Skin t -sweep	$\kappa_{\text{skin}} = 0.1, t : 0.1 \rightarrow 5 \mu\text{m}$	30.688–118.948	0.1273	5.7907 μm
Skin κ -sweep	$t_{\text{skin}} = 1 \mu\text{m}, \kappa : 0.25 \rightarrow 0.05$	30.688–118.948	0.0065	2.4527 $\text{W m}^{-1} \text{K}^{-1}$

4.3 DISCUSSION

This chapter interprets the Nafion results in physical terms, positions them against prior reports, and summarizes what this methodology contributes beyond a single dataset.

4.3.1 What we learned about Nafion

The central experimental outcome of this thesis is that no temperature trend was resolvable within the propagated uncertainty for dry depositable Nafion in the analyzed operating range. The extracted thermal conductivity remains nearly constant over the available inversion range from 32.60 to 95.19 °C, centered near 0.25 $\text{W m}^{-1} \text{K}^{-1}$.

This result is physically plausible for a matrix-dominated amorphous fluoropolymer in this temperature interval. In the dry state, heat transport is largely controlled by the polymer framework, so weak temperature dependence is expected compared with systems where an evolving fluid phase affects transport properties. The result is also consistent in order of magnitude with dry Nafion and related fluoropolymer ranges reported in literature when differences in preparation and measurement geometry are considered [8, 9, 75].

The measurement conditions used in this thesis were designed to reduce nonintrinsic drift terms that can masquerade as a thermal conductivity trend. The Nafion film was measured in vacuum after controlled curing, with a defined bottom thermal boundary and automated pointwise balancing during frequency sweeps. This combination reduced long dwell times and improved repeatability of the fitted response.

4.3.2 Relation to prior work

Quantitatively, the present dry film value of approximately 0.25 $\text{W m}^{-1} \text{K}^{-1}$ is higher than earlier through-plane measurements on commercial Nafion membranes. Khandelwal and Mench reported $0.16 \pm 0.03 \text{ W m}^{-1} \text{K}^{-1}$ near room temperature, decreasing to $0.13 \pm$

0.02 W m⁻¹ K⁻¹ at 65 °C [8]. Burheim et al. reported 0.177 ± 0.008 W m⁻¹ K⁻¹ for dry Nafion at 20 °C [6]. They used a steady state method with constant heat flux through the membrane. Bulk thermal conductivity was obtained from the slope of thermal resistance against measured membrane thickness, which also separated the contact resistance. At the dry condition, the result combined measurements on three samples of each of four membrane thicknesses. The quoted uncertainty was evaluated using analysis of variance and propagation of measured errors. The repeated measurements and the regression over several thicknesses explain the comparatively small quoted value. The present inversion gives a mean of 0.25 W m⁻¹ K⁻¹. Its largest propagated standard uncertainty for a fitted target is 0.0154 W m⁻¹ K⁻¹, or approximately 6.1%. The quoted Khandelwal–Mench uncertainties are approximately 19 and 15 percent, while the Burheim value is approximately 4.5 percent. Thus, the measurements agree on the characteristic low thermal conductivity scale of Nafion, but the present dry film value does not overlap the quoted uncertainty intervals of these earlier membrane measurements. A strict one-to-one comparison is not expected because the studies differ in sample preparation, thickness and morphology, mechanical loading, hydration protocol, and measurement geometry. In the present work, a nominally 32 μm, freshly deposited and cured film was measured continuously under vacuum without intentional ageing or degradation. The reported value specifically characterizes the controlled dry deposited film state investigated here. Molecular dynamics studies provide useful computational context but are not treated here as experimental benchmarks [12, 13].

The uncertainty performance is also consistent with a core strength of the 3ω method in film and low thermal conductivity measurements, where slope-based harmonic analysis can isolate thermal conductivity with high precision when boundary conditions are controlled [28]. In this thesis, substrate only glass validation remained below 2% relative uncertainty across the calibrated range. As an indicative benchmark, widely cited classical demonstrations report uncertainty on the order of 8% in thicker single-material studies [28]. This is not a strict one-to-one comparison because geometry and implementation differ, but it still supports the conclusion that the present platform reaches high precision for this measurement class.

Several literature reports show a weakly decreasing or weakly increasing $\kappa(T)$ trend for Nafion like systems. In the low thermal conductivity regime, such weak slopes are difficult to interpret robustly because absolute uncertainty floors can be comparable to the full reported trend span. For this reason, disagreement between studies does not necessarily imply contradictory physics. It can reflect differences in sample state, geometry, loading, hydration, and boundary conditions [6, 7, 8].

The temperature dependence reported for commercial Nafion membranes may therefore contain contributions from temperature dependent changes in sample state in addition to the intrinsic temperature dependence of the polymer. In general, the measured response can be regarded as $\kappa_{\text{measured}}(T) = \kappa[T, \mathcal{S}(T)]$, where $\mathcal{S}$ denotes hydration, void fraction, microstructure, and other state variables. This representation includes both intrinsic temperature dependence and temperature dependent changes in sample state. The defect sensitivity calculations in Section 4.2.3 demonstrate that changes in film composition and microstructure can produce measurable changes in the effective thermal conductivity. They do not establish that defects caused the lower thermal conductivities or temperature trends reported in earlier studies, but they provide a physically plausible mechanism by which sample history and state could contribute to the observed inter-study variation. The distinction is impor-

tant because the present film was freshly deposited and cured with the intention to preserve composition as much as possible, whereas pre-manufactured membranes necessarily have a different processing and handling history.

The advantage of the 3ω slope reduction used here is that, in the validated logarithmic frequency interval, the fitted slope isolates thermal conductivity as the dominant parameter [28]. Terms that mainly alter offsets or shift regime boundaries are strongly suppressed in the extracted slope. This was also confirmed in the FEM sensitivity check shown in Figures A.7 and A.8, where ρc variation shifted the frequency response while producing a smaller residual change in the conductivity obtained from the fitted mid-band slope.

Related platforms such as bidirectional chip-based 3ω sensing address complementary sample geometries and thermal thickness regimes [35]. They are highly useful in their intended sample classes, typically with larger lateral dimensions or different thermal thickness regimes. The present thesis addresses a different niche. It targets chemically sensitive polymer coatings deposited on 3ω sensor geometries, where direct analytical reduction is not sufficient and inverse finite element interpretation is required.

4.3.3 Thickness regimes and the intermediate film challenge

Geometric labels such as ultrathin, thin, and thick are not sufficient by themselves in 3ω analysis. The relevant classification is set by thermal length scales. The key quantity is thermal penetration depth in the 2ω temperature field

$$\delta(f) = \sqrt{\frac{\alpha}{4\pi f}}, \quad (4.5)$$

where f is the electrical drive frequency and α is thermal diffusivity. This is the 2ω penetration depth convention used throughout this thesis. The same film can behave as thermally thin or thermally thick depending on the selected frequency interval.

Two stack geometries define the interpretation path. In heater-film-substrate geometry, analytical reductions are practical mainly in limiting cases, either ultrathin films or quasi bulk thick layers. In film-heater-substrate geometry, which is the one used in this thesis for process compatibility reasons, the practical operating window for Nafion is often thermally intermediate. In this regime, neither thin-film nor bulk simplifications remain robust across the full band, so FEM based forward modeling with inverse extraction is the reliable route. This is the methodology deficit addressed by this work. This work provides a validated interpretation path for intermediate thickness polymer films in the real deposited film-heater-substrate stack [31, 32, 33, 34, 35].

Bidirectional platforms and the present methodology address complementary sample geometries and thermal thickness regimes. Bidirectional implementations are often demonstrated on coating layers that are comparatively thick in the thermal sense for the selected band [35]. The present Nafion dataset sits in a narrower intermediate regime for a polymer deposited on a sensor, where finite film thickness, top boundary effects, and heater geometry all contribute at comparable order.

4.3.4 Methodological contribution and transferability

The methodological contribution is the integration of three elements that must work together for reliable low κ film extraction. The first element is automation of bridge balancing

and dense frequency acquisition. This directly improves statistical quality of slope-based calibration and reduces operator-dependent variability [44]. The second element is strict thermal boundary control, which shortens stabilization time and keeps long run drift manageable. The third element is inverse finite element interpretation, which allows thermal conductivity estimation in coated multilayer geometries without assuming strict logarithmic linearity across the whole band.

A practical strength of this framework is the use of calibrated sensor chiplets before polymer deposition. Heater fabrication and electrical calibration are completed first, then the coating is applied and characterized. This decouples microfabrication constraints from polymer processing and makes chemically sensitive films measurable.

The composite study in Section 4.2.2 shows that modified Nafion compositions are resolvable across all three investigated contrast levels. The mean $V_{3\omega}$ separation increases from 1.9138 μV for the low-contrast branch to 5.2235 μV for the high-contrast branch, corresponding to mean resolvable filler fractions from 0.01076 to 0.00393.

The defect studies in Section 4.2.3 define the limits of that transferability. The gas-phase water-redistribution case and the vacuum-surrogate, air-, N_2 -, and O_2 -filled void scenarios remain resolvable at the measured uncertainty floor. H_2 -filled voids have a weaker mean resolvable fraction of 0.03104. The explicit skin model is not reliably identifiable: its thickness sweep is only marginally above the uncertainty floor, while its thermal conductivity sweep remains below it. These are predictive sensitivity results, the simulations show where the same platform can, and cannot, support future composition and degradation studies.

Chapter 5

CONCLUSIONS AND OUTLOOK

5.1 CONCLUSIONS

This thesis establishes and validates a novel advancement in 3ω thermal conductivity metrology for highly insulating polymer films: an integrated experimental and inverse-FEM methodology that resolves the real film–heater–substrate geometry instead of relying on a limiting analytical approximation.

The measurement platform achieved stable microvolt-level operation under controlled boundary conditions and vacuum, with dense automated frequency sweeps and explicit electrical correction. In substrate calibration on soda-lime glass, relative uncertainty remained below 2% across the calibrated range (Section 3.3). This demonstrates high-precision operation for this class of measurements.

The numerical component also reached its target. A forward finite element framework and an inverse estimation methodology were built and validated for polymer-on- 3ω -sensor geometries where direct analytical reduction is not sufficient. The solver chain, postprocessing chain, and inversion logic connect electrical excitation, thermal response, and extracted thermal conductivity in one consistent FEM platform. This enables coated multilayer interpretation without requiring strict global logarithmic linearity of the measured response. The validation chain includes the zeroth law of thermodynamics relaxation, mesh sensitivity, discrete residual and energy-balance checks, monotonic material response, and agreement with the Cahill solution and substrate experiment (Section 3.4 and Appendix A).

For dry depositable Nafion from 305.75 to 368.34 K, no temperature trend was resolvable within the propagated uncertainty. The 14 linear-fit target inversions have a mean thermal conductivity of $0.2500 \text{ W m}^{-1} \text{ K}^{-1}$ and span $0.2480\text{--}0.2518 \text{ W m}^{-1} \text{ K}^{-1}$. This result is physically plausible for the controlled dry state used in this thesis and provides a practical reference level for subsequent modified film studies (Chapter 4.1).

The composite feasibility study showed resolvable response separation for all three investigated contrast levels. Mean $V_{3\omega}$ separation increases from $1.9138 \mu\text{V}$ for the low-contrast case to $5.2235 \mu\text{V}$ for the high-contrast case (Section 4.2.2). The defect studies further defined the sensitivity boundary (Section 4.2.3). The gas-phase water-redistribution case and most gas-filled void scenarios are detectable at the measured uncertainty floor, whereas H_2 -filled voids have weaker concentration resolution and the investigated skin-property changes are not reliably identifiable. These simulations provide a predictive basis for selecting future experiments.

This work also enables a practical transfer route beyond the originating laboratory. The calibrated chiplet strategy means that laboratories interested in thermal conductivity of insulating polymers can use pre-fabricated and pre-calibrated sensors without requiring local cleanroom fabrication capability.

In practical terms, this provides a path toward transferable measurement and analysis protocols for depositable and curable polymers.

Taken together, these results meet the central thesis objective and constitute the principal novel contribution of this work. The developed methodology extends the practical reach of the 3ω method to intermediate thickness, highly insulating polymer films in real multilayer sensor geometries. It provides a validated and uncertainty-aware route from automated measurement to inverse thermal conductivity extraction, demonstrated on dry Nafion and directly transferable to modified Nafion, composite, and degradation studies.

The remaining limitations arise from heater geometry realization, film thickness metrology, temperature coefficient of resistance measurement, the selected thermal response frequency window, and model scope.

5.2 OUTLOOK

The most direct next step is to measure modified Nafion membranes with the validated setup and inverse finite element methodology developed in this thesis. The analysis toolset is already in place and can be used immediately for screening and comparison of candidate modified formulations under controlled conditions.

If these measurements confirm improved or otherwise targeted thermal conductivity behavior, the same materials can be advanced to fuel-cell-level testing in realistic operating environments. This creates a direct path from laboratory thermal characterization to application-level validation.

Hydration effects have already been widely explored in prior works [3, 11, 12, 73], and in practical operation hydration is constrained by the coupled operating window of temperature and water management in the cell. For this reason, the most useful and controllable design space is modification of the dry state response, which is the focus of this methodology.

A second direction is microstructure-aware catalyst layer study. The present framework is already suitable for layered systems with realistic geometry and can be extended toward catalyst-containing films where morphology and effective transport pathways vary with composition and processing.

A third direction is interlaboratory transfer of the calibrated chiplet methodology. This includes preparing standardized sensor batches, transfer protocols, and reference workflows so laboratories without cleanroom access can run comparable insulating polymer measurements. The same framework can support future round-robin studies for newly developed materials where cross-laboratory agreement is important for scientific reproducibility.

A fourth direction is expansion to a broader polymer and composite library. The calibrated chiplet plus post-deposition workflow provides a reusable route for chemically sensitive coatings that are incompatible with the lithography flow used in this work after deposition.

These future directions are technically enabled by the methodology developed here. Their execution depends on future project scope and available resources, but the experimental and numerical foundation required to start them is now in place.

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APPENDIX

A Numerical Validation Details

This appendix validates the FEM workflow in four stages. It first defines the periodic convergence criteria, then tests physical limiting cases and discrete conservation, quantifies mesh and property sensitivity, and finally compares the numerical response with analytical and experimental results.

A.1 Periodic convergence criteria

For a fixed time step, each convergence evaluation compares the current spatially averaged heater temperature, $\bar{T}_n$, with its value at the preceding evaluation. It also compares the standard deviation S_n of the heater temperature samples over the most recent electrical period with the value from the preceding evaluation:

$$d_{\text{mean}} = |\bar{T}_n - \bar{T}_{n-1}|, \quad d_S = |S_n - S_{n-1}|. \quad (\text{A.1})$$

The corresponding dynamic relative–absolute tolerances are

$$\varepsilon_{\text{mean}} = \max[\varepsilon_{\text{abs}}, r_{\text{mean}} |\bar{T}_n - T_{\text{bottom}}|], \quad \varepsilon_S = \max(\varepsilon_{\text{abs}}, r_S S_n). \quad (\text{A.2})$$

Convergence is accepted when both $d_{\text{mean}} < \varepsilon_{\text{mean}}$ and $d_S < \varepsilon_S$ hold for four consecutive evaluations, after the first electrical period and a minimum of 500 time steps. Evaluations are performed every 100 time steps. For the cases shown in Figures 3.25 and 3.26, the rough stage relative tolerances are $r_{\text{mean}} = r_S = 3 \times 10^{-3}$, with $\varepsilon_{\text{abs}} = 2 \times 10^{-4}$ K. The fine stage values are $r_{\text{mean}} = r_S = 7 \times 10^{-4}$ and $\varepsilon_{\text{abs}} = 10^{-5}$ K.

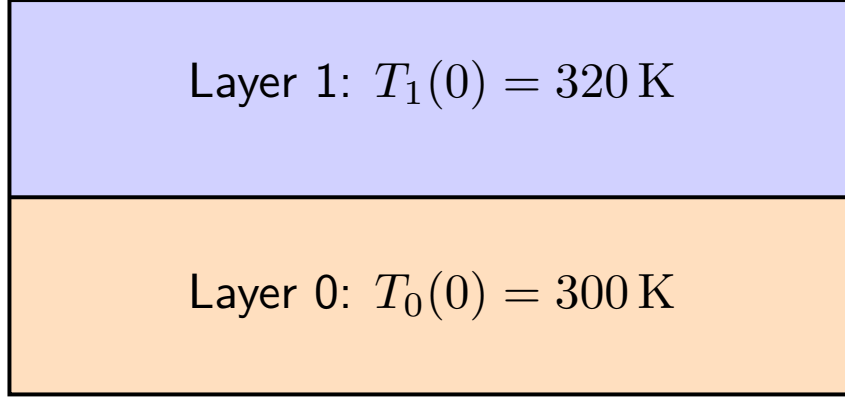
The first complete electrical period is not counted when assessing convergence. At the start of a run, successive temperature states can be nearly identical before the oscillatory response has developed. Excluding this initial period prevents that temporary similarity from being accepted as false convergence. Neither convergence nor the handoff from the rough to the fine stage can therefore be accepted during the first period.

The rough stage additionally has a handoff criterion after which the orchestrator transitions to the fine stage. Within a moving window of six evaluations, the signed changes in both $\bar{T}$ and S must reverse direction at least twice, after the first electrical period and a minimum of 500 time steps. When met, this criterion indicates that the transient has entered a bounded oscillatory regime, and the final rough temperature field is transferred to the fine stage. The fine stage then continues with a smaller time step and terminates using the combined relative and absolute convergence test above. Finally, $A_{2\omega}$ is fitted to the last five thermal cycles of the fine-stage response. Periodic convergence at a fixed time step therefore does not imply invariance of the oscillation amplitude under subsequent time-step refinement.

A.2 Physical limiting cases and numerical consistency

The zeroth law of thermodynamics test uses two identical, thermally isolated $1 \times 1 \text{ mm}^2$ layers initialized at 320 and 300 K, with $\kappa = 1 \text{ W m}^{-1}\text{K}^{-1}$, $\rho c = 2.175 \times 10^6 \text{ J m}^{-3}\text{K}^{-1}$, and Joule heating disabled. The transient calculation uses first-order elements and the $\theta = 0.5$ time-integration scheme. Equal thermal capacities give the expected equilibrium

temperature $T_{\text{eq}} = 310$ K. Figure A.1 shows that the FEM layer means follow the analytical relaxation and reach the same equilibrium.



(a) Two layers in perfect thermal contact at $t = 0$.

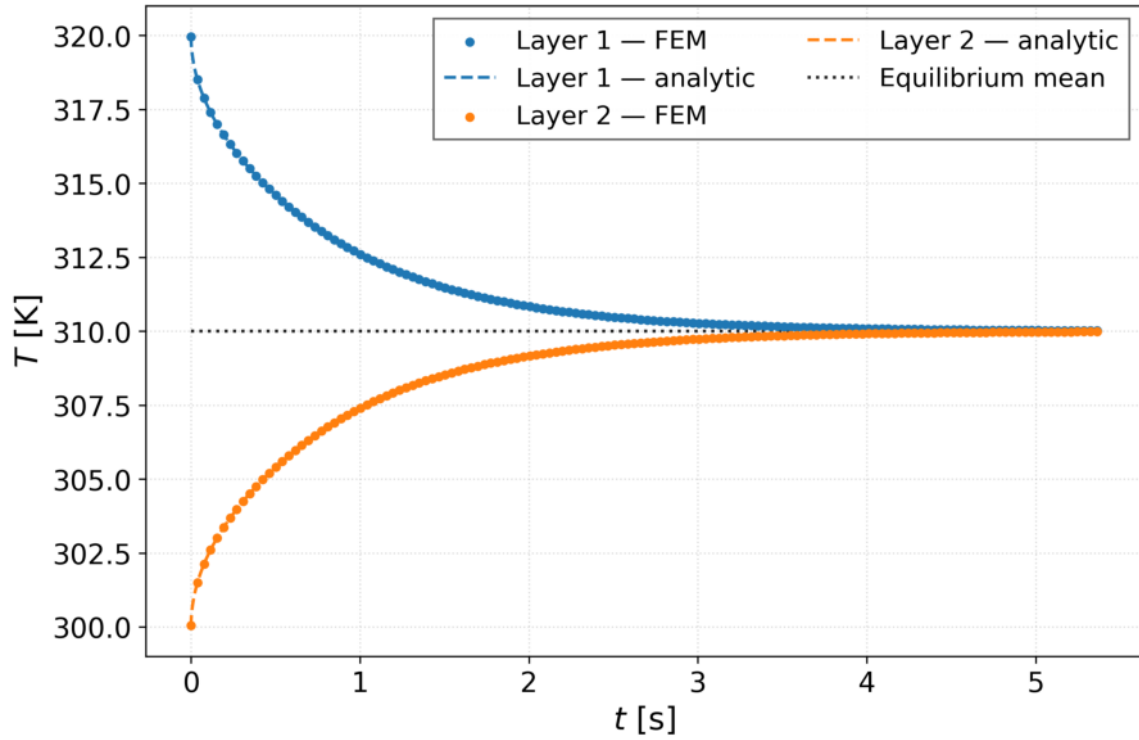


Figure A.1: Geometry and thermal relaxation of two initially unequal-temperature layers toward the common equilibrium temperature. FEM layer means are shown as points, the analytical solution as dashed curves, and the dotted line marks $T_{\text{eq}} = 310$ K.

Figure A.2 confirms the same result quantitatively. Integrating the governing heat equation, Eq. (3.16), over this adiabatic source-free domain shows that the thermal energy per unit out-of-plane length should be constant. The numerical diagnostic evaluates

$$E(t) = \int_{\mathcal{D}} \rho c T(x, y, t) dA, \quad d_E(t) = \frac{E(t) - E(0)}{E(0)}, \quad (\text{A.3})$$

using element areas and the volumetric heat capacity of each layer. The figure reports $10^6 d_E$ in parts per million. The layer-gap root-mean-square error (RMSE) is 1.03×10^{-3} K, the maximum absolute energy drift is 1.56 ppm, and the global mean changes by only -4.82×10^{-4} K. The upper trace in Figure A.2 shows the temperature gap decaying to zero with the analytical time dependence, while the lower trace remains at the parts per million level. Taken together, the two panels verify equilibration without spurious creation or loss of energy.

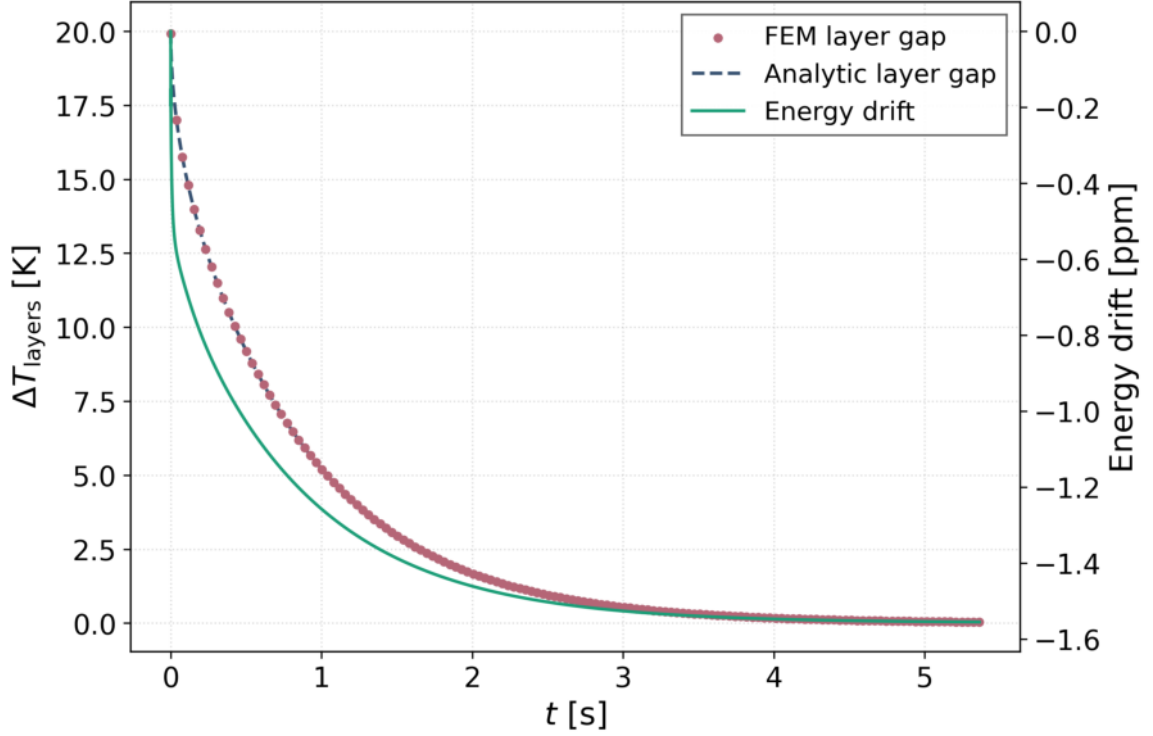


Figure A.2: Decay of the interlayer temperature difference compared with the analytical solution, together with the relative energy drift from Eq. (A.3) for the isolated numerical domain.

Figure A.3 shows the expected change in the peak lateral temperature field after adding the Nafion layer.

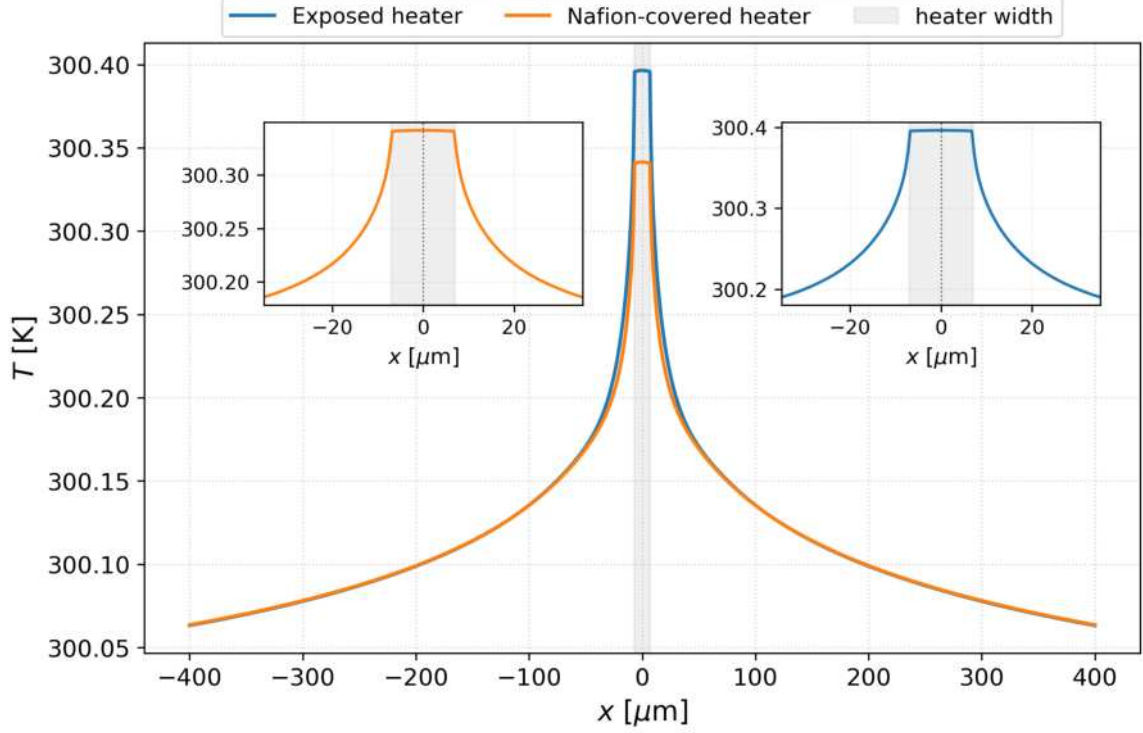
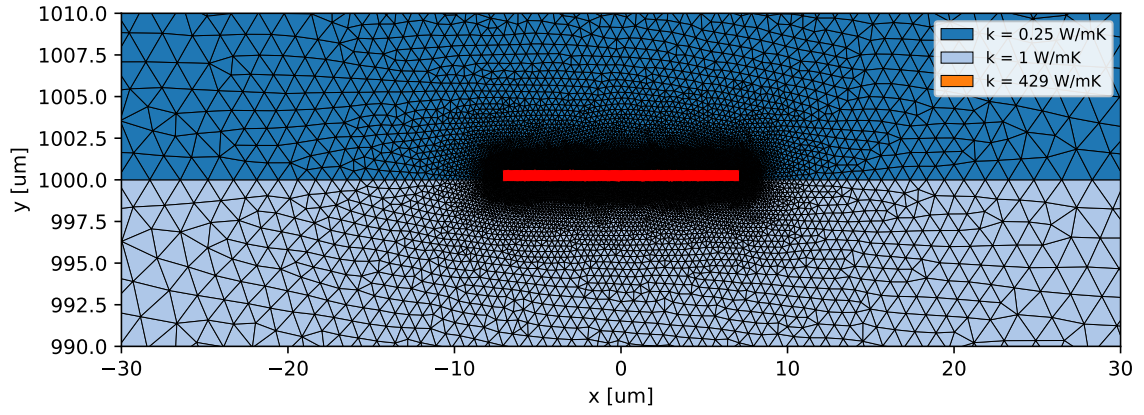


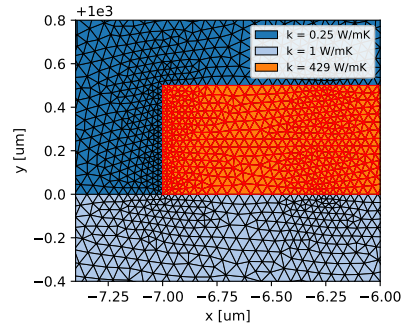
Figure A.3: Lateral temperature profiles for exposed and Nafion-covered $14\ \mu\text{m}$ heaters at the peak of their periodic responses. The insets are a zoomed-in view of the heater region. The exposed-heater profile is symmetric about the heater centerline because the modeled geometry, material properties, heat source, and lateral boundary conditions are symmetric.

A.3 Mesh and material property sensitivity

The conformal triangular mesh is refined at the heater, film, and material interfaces and coarsened away from the heated region (Figure A.4). The mesh factor $m = 1$ denotes the production mesh. It multiplies the baseline mesh density controls, so smaller and larger values request coarser and finer discretizations, respectively. The production configuration uses $n_x = 400$ and $n_y = 80$ as the baseline horizontal and vertical mesh controls before local refinement at the heater and interfaces.



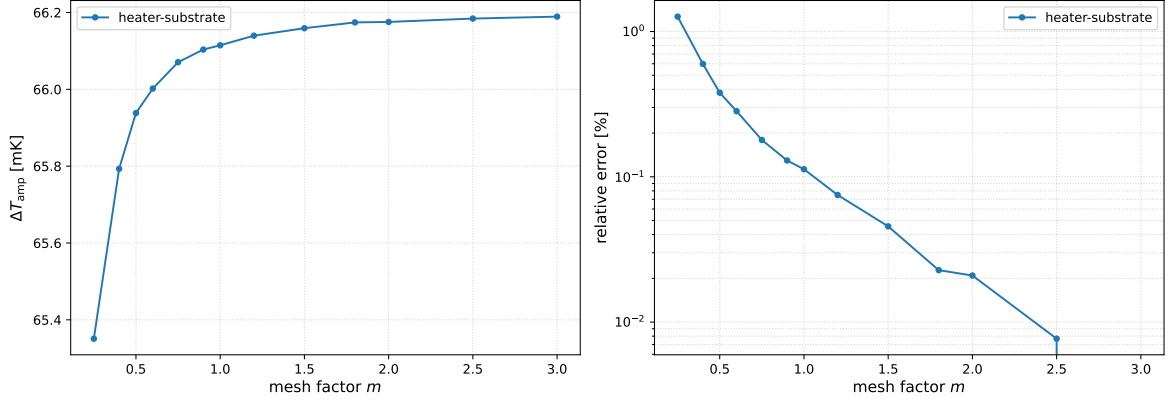
(a) Graded refinement around the heater and film.



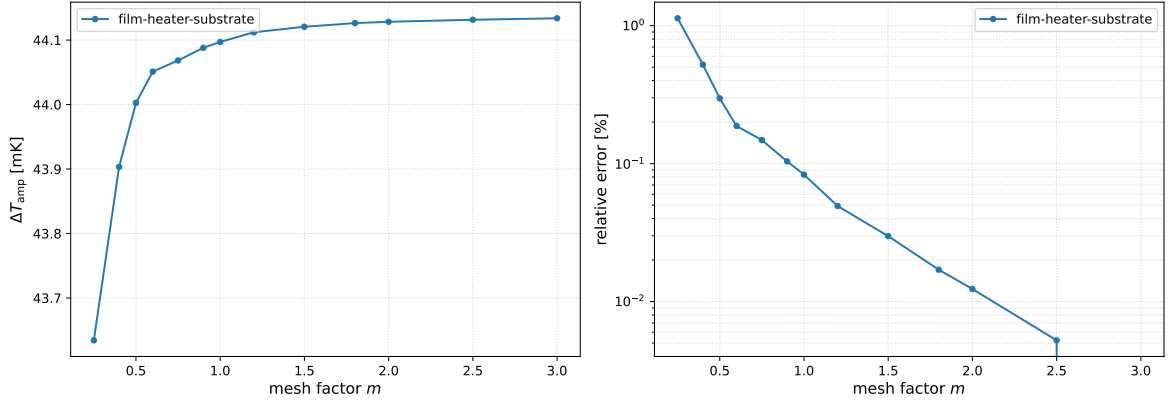
(b) Element continuity at the edge of the heater and across the material interfaces.

Figure A.4: Production film–heater–substrate mesh shown at the domain, heated-region, and interface scales.

Mesh sensitivity was tested at 500 Hz electrical excitation for $m = 0.25$ –3, using $m = 3$ as the reference (Figure A.5).



(a) Substrate-only stack.



(b) Film-heater-substrate stack.

Figure A.5: Mesh convergence results at 500 Hz electrical excitation for the substrate-only and film stacks. For each geometry, the left panel shows the heater temperature oscillation amplitude and the right panel shows its relative difference from the finest retained mesh, $m = 3$, as functions of the mesh factor.

At $m = 1$, the heater-amplitude differences are 0.113% for the substrate and 0.083% for the film stack, showing convergence to better than 0.2%. Table A.1 summarizes the remaining checks. The small layer-split difference, discrete residual, and power imbalance confirm consistent interface assembly, equation solution, and global energy balance.

Table A.1: Summary of numerical consistency checks obtained from the retained calculations.

Check	Comparison and observable	Largest difference
Mesh sensitivity	Production mesh $m = 1$ against the finest retained mesh $m = 3$, using the heater temperature oscillation amplitude	0.113%
Same property layer split	One homogeneous substrate region against 50 conformal regions with identical properties, using the heater temperature amplitude	0.138%
Discrete equation residual	Relative L^2 residual of the Crank–Nicolson temperature update	4.54×10^{-12}
Mean energy closure	Difference between the applied mean power and the assembled global power balance	0.013%
Oscillatory energy closure	Difference between the applied and balanced components at the temperature oscillation frequency	0.91%

With all material properties fixed, changing the bottom temperature from 300 to 350 K should shift only the absolute temperature level. The periodic responses in Figure A.6 differ by at most 0.0073%, confirming invariance to a constant temperature offset.

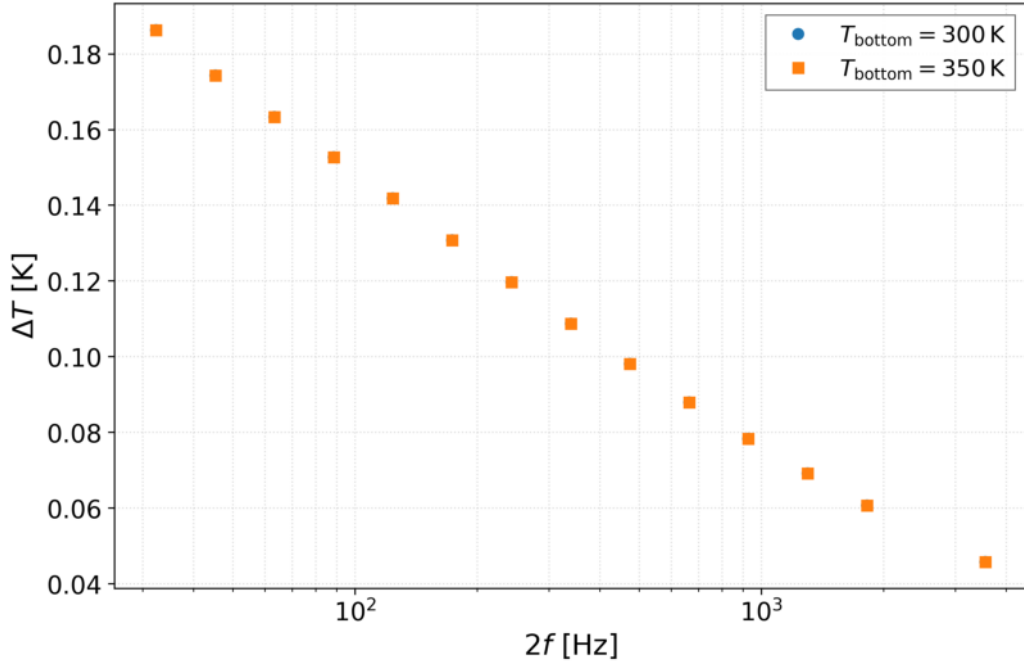


Figure A.6: Zeroth law of thermodynamics temperature offset test calculated with fixed bottom temperatures of 300 K and 350 K. The coincidence of the curves shows that a constant change in the absolute temperature reference does not alter the periodic temperature rise when the material properties are held fixed. The configuration parameters of the FEM model correspond to the experimental values from the measurement at 324.15K

The volumetric heat-capacity sensitivity check varies the substrate ρc at fixed thermal conductivity. As shown in Figure A.7, this shifts the frequency-dependent heater response

and the transition between thermal regimes. Figure A.8 shows the smaller residual variation of the thermal conductivity obtained from the logarithmic slope over the retained fit interval.

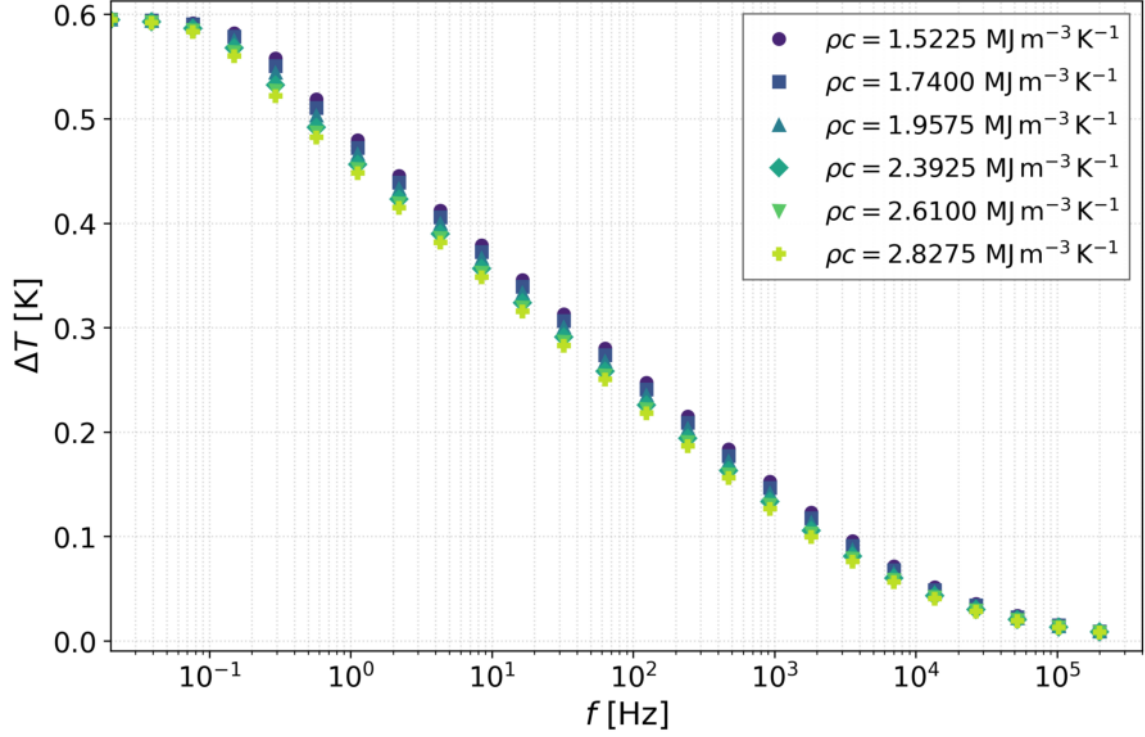


Figure A.7: FEM heater temperature response for six substrate volumetric heat capacities at fixed thermal conductivity.

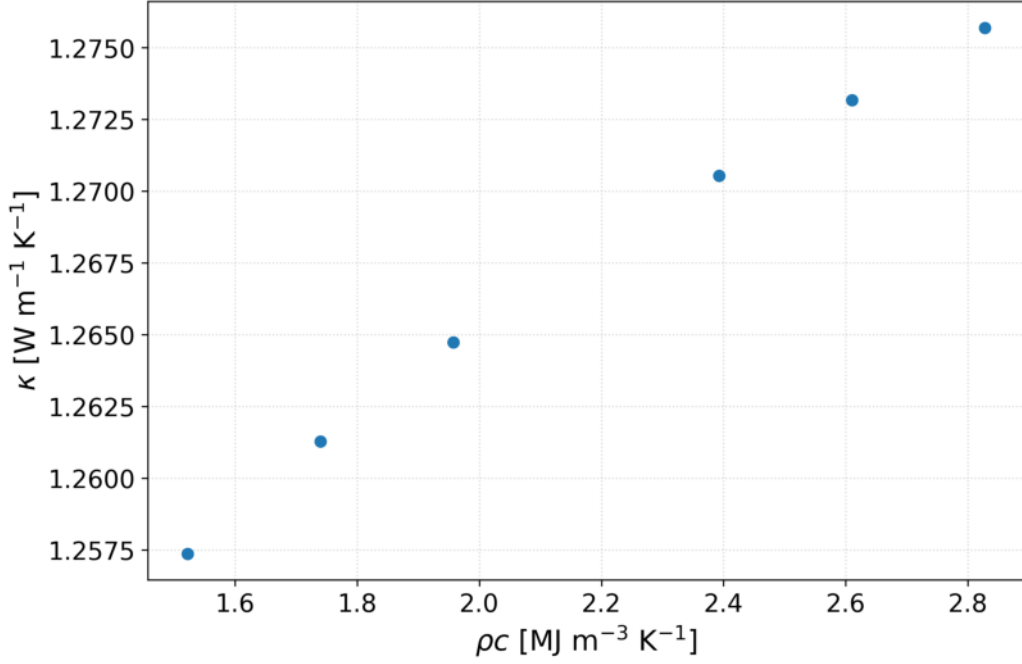


Figure A.8: Thermal conductivity obtained from the logarithmic slope for six substrate volumetric heat capacities. Slopes were fitted from 1 Hz to 1 kHz.

Across the tested range, ρc increases from 1.5225 to 2.8275 MJ m⁻³ K⁻¹, whereas the conductivity obtained from the fitted slope changes only from 1.257 to 1.276 W m⁻¹ K⁻¹. The full variation is approximately 1.45% of the mean extracted conductivity. A log-log fit to the six points gives the weak empirical scaling $\kappa_{\text{slope}} \propto (\rho c)^{0.023}$. Doubling ρc therefore changes the extracted conductivity by only about 1.6% over this range. Thus, although volumetric heat capacity visibly shifts the frequency response in Figure A.7, its effect on the conductivity obtained from the slope in Figure A.8 is small.

For each curve in Figures A.9 and A.10, the glass substrate conductivity is the measured value corresponding to the stated temperature. The film and all other configured properties are unchanged. Increasing substrate thermal conductivity reduces the temperature rise and makes the logarithmic-frequency slope less negative (Figure A.9). The same ordering is preserved after conversion to $V_{3\omega}$ (Figure A.10), validating the thermal and electrical reduction chain.

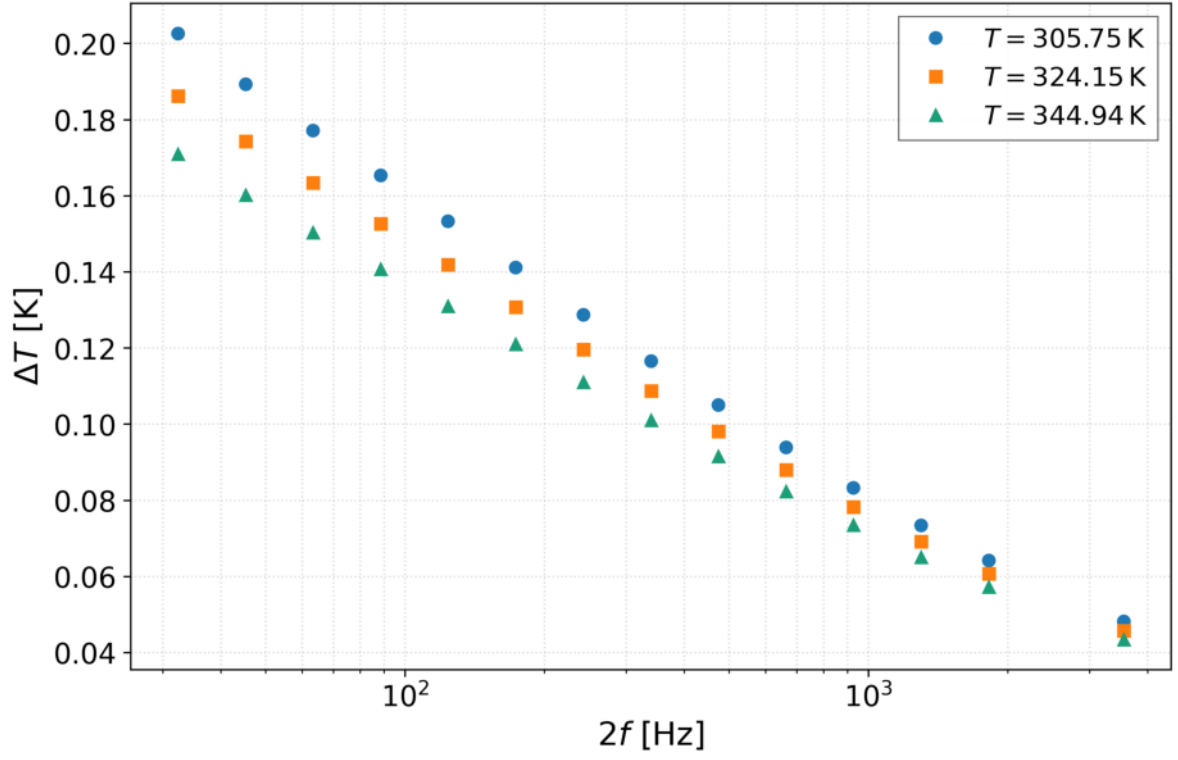


Figure A.9: Discrete FEM heater-temperature responses for the substrate sensitivity check, with model parameters configured to the experimental values measured at three different temperatures.

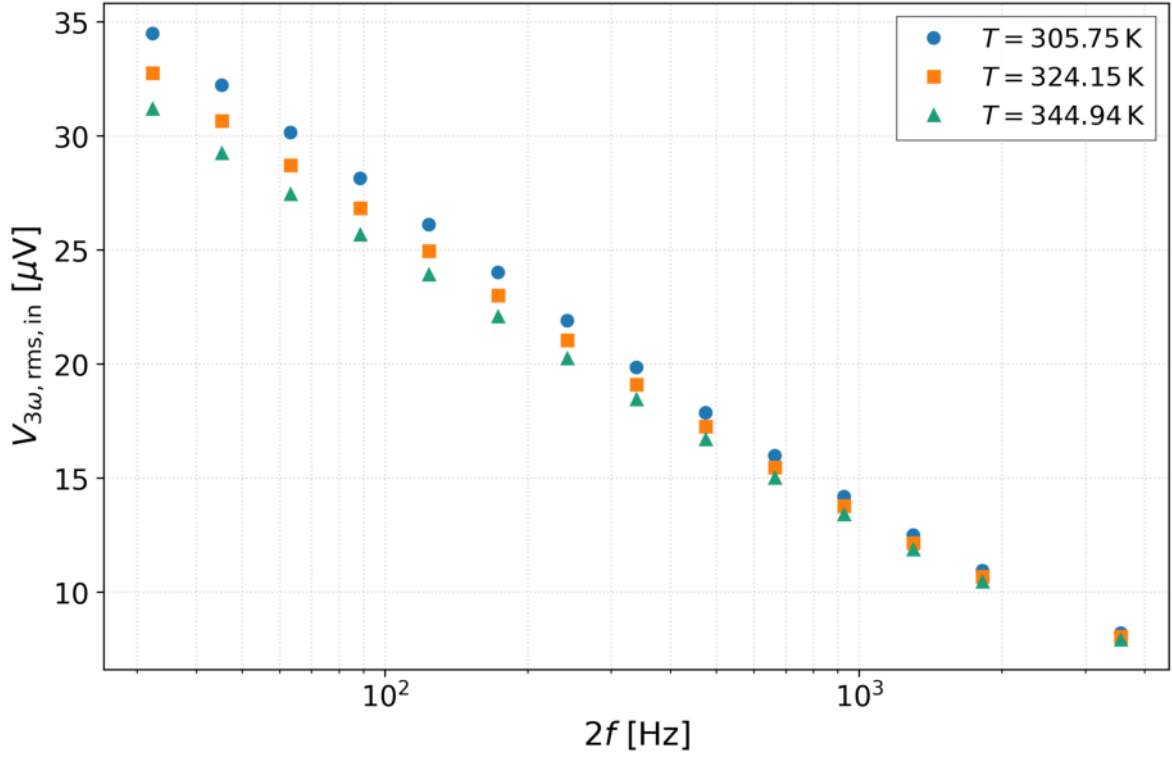


Figure A.10: Corresponding discrete $V_{3\omega}$ responses for the substrate sensitivity check at three temperatures.

Figure A.11 shows a monotonic response for film thermal conductivities from 0.05 to $0.50 \text{ W m}^{-1} \text{ K}^{-1}$ at both temperatures. A measured slope therefore maps to a unique thermal conductivity within the tested range.

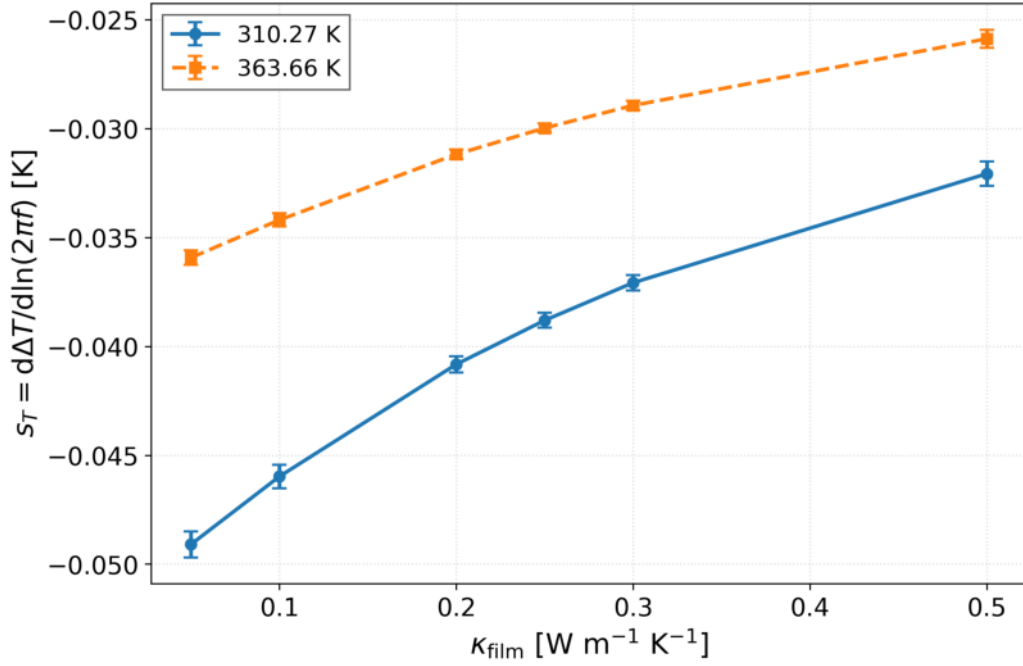


Figure A.11: Calculated logarithmic-frequency slope as a function of film thermal conductivity at two temperatures. The retained points form a monotonic forward map over the investigated interval.

The substrate-only FEM response was compared with the Cahill line-source solution for glass with $\kappa = 1.06 \text{ W m}^{-1} \text{K}^{-1}$ and heater widths of 1, 2, 3, 5, 6, 8, 13, 14, 22, 36, 60, and $100 \mu\text{m}$ [28]. Figures A.12–A.14 show the full series. Blue and green mark the Cahill and Kabaši linear-regime criteria, respectively [44].

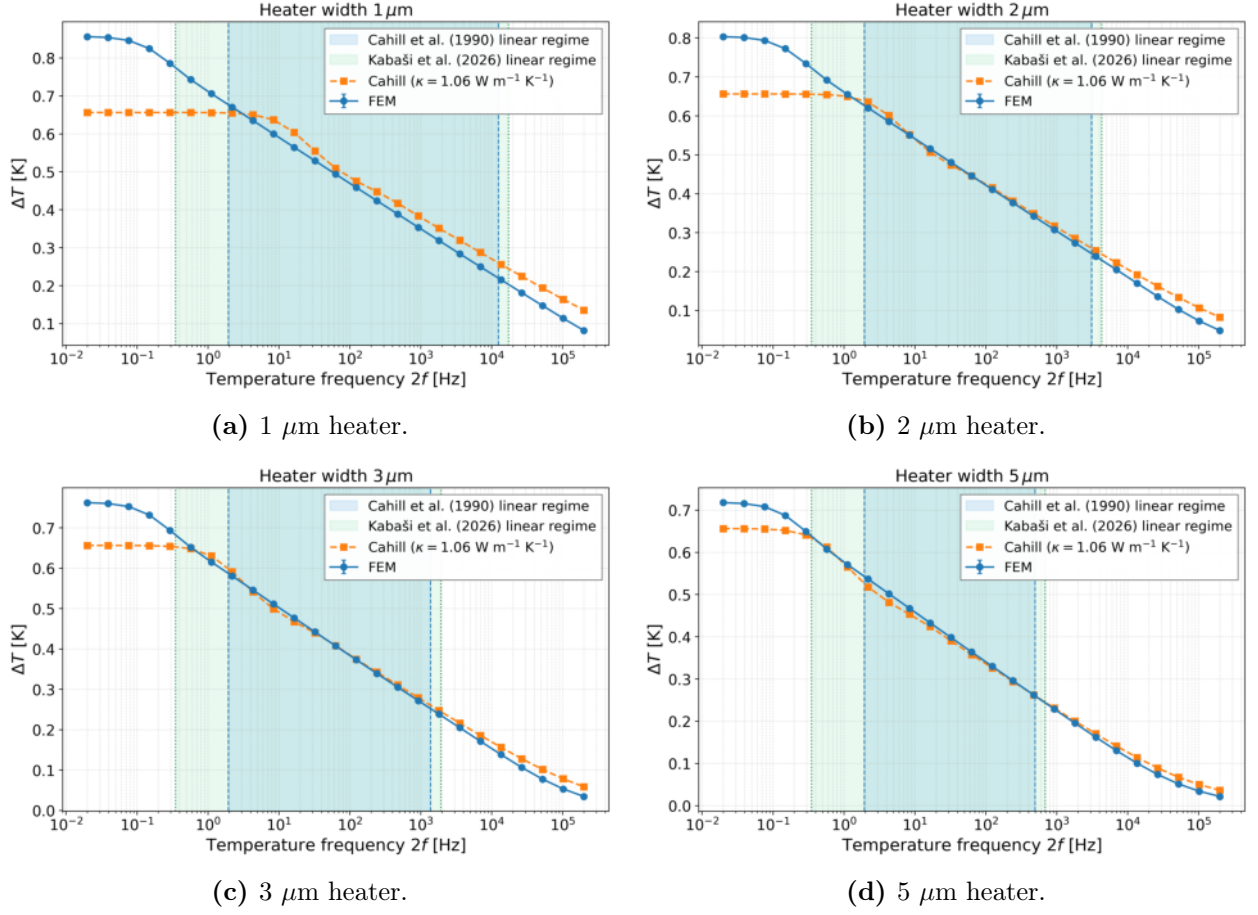


Figure A.12: Substrate-only finite-element and Cahill analytical temperature responses for heater widths from 1 to 5 μm . The blue dashed and green dotted ranges mark the Cahill and Kabaši linear-regime criteria, respectively.

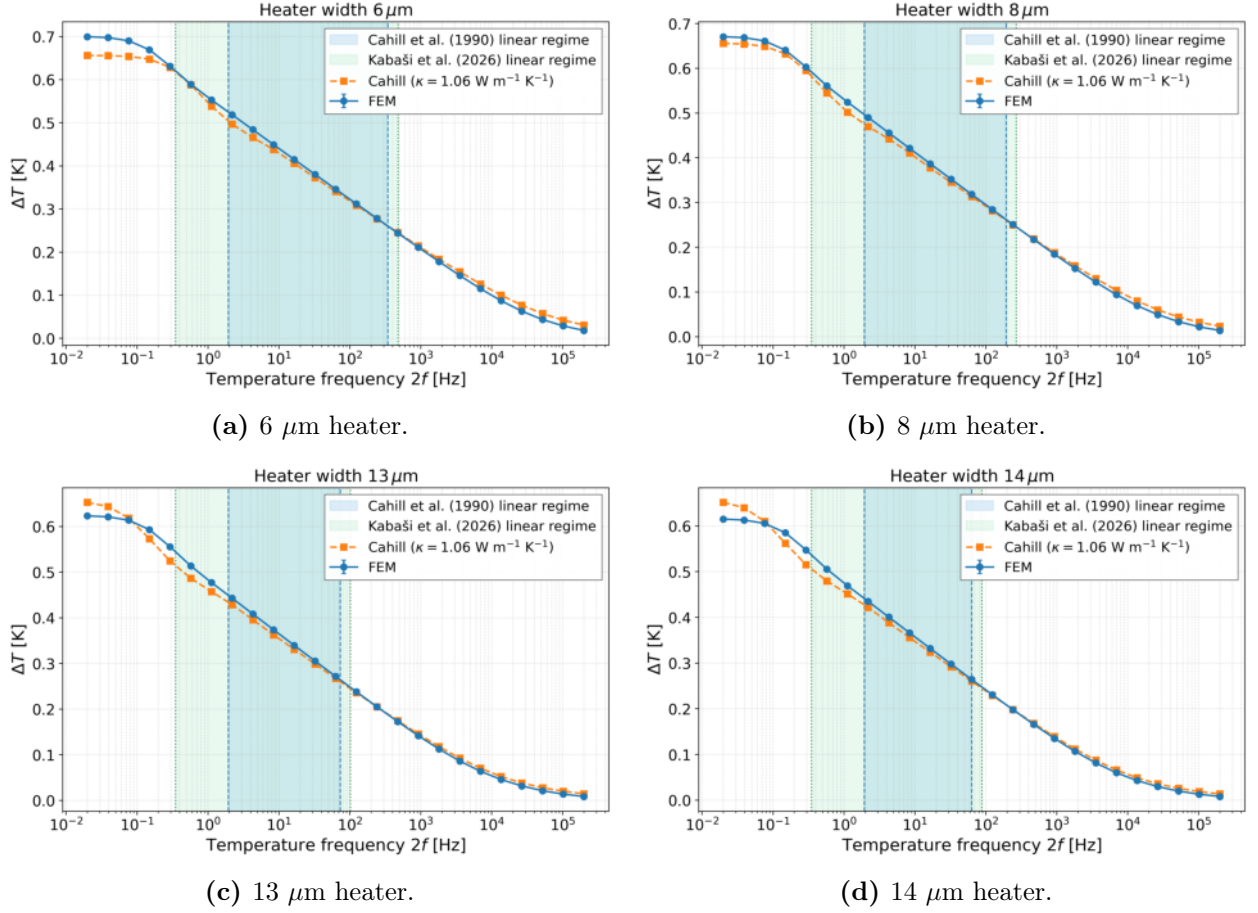


Figure A.13: Substrate-only finite-element and Cahill analytical temperature responses for heater widths from 6 to 14 μm , including the two widths used in the experimental workflow. The blue dashed and green dotted ranges mark the Cahill and Kabaši linear-regime criteria, respectively.

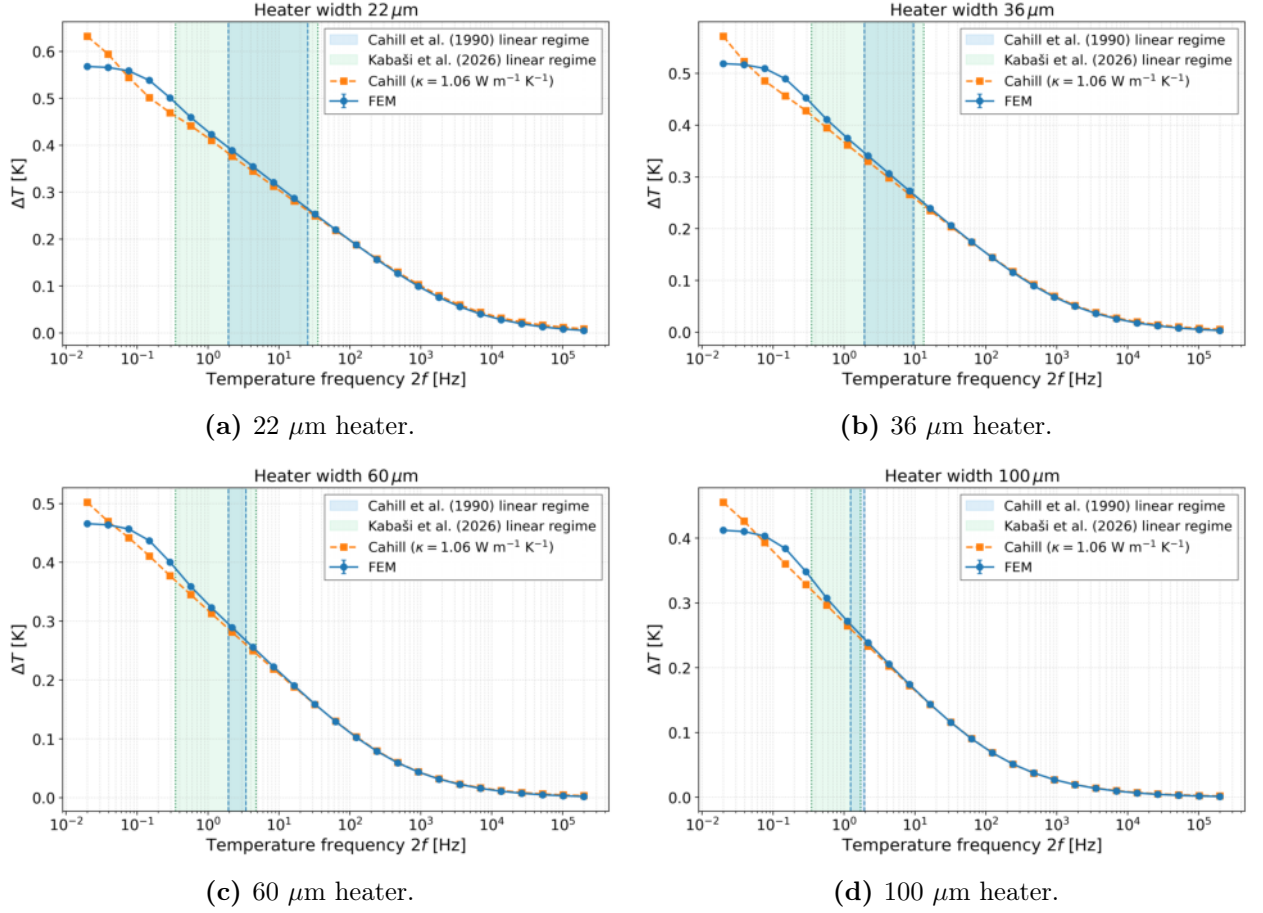


Figure A.14: Substrate-only finite-element and Cahill analytical temperature responses for heater widths from 22 to 100 μm . The blue dashed and green dotted ranges mark the Cahill and Kabaši linear-regime criteria, respectively.

A.4 Analytical and experimental comparisons

Differences outside the linear regime arise from finite substrate thickness at low frequency and finite heater geometry at high frequency. Agreement is close for most widths. The 1 μm case is most sensitive to heater thickness, area averaging, and mesh resolution. At this limiting width, the finite FEM heater occupies a small number of locally refined elements and retains a finite thickness, whereas the Cahill reference idealizes the heater as a line source with zero thickness. Those differences affect the near field most strongly for the narrowest heater and explain the larger deviation.

Agreement was quantified by the RMS relative deviation

$$\varepsilon_{\text{RMS}} = 100 \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{\Delta T_{\text{FEM},i} - \Delta T_{\text{Cahill},i}}{\Delta T_{\text{Cahill},i}} \right)^2}. \quad (\text{A.4})$$

The metric uses $N = 200$ logarithmically spaced points within the Cahill regime. Figure A.15 illustrates it for the most discrepant 1 μm case.

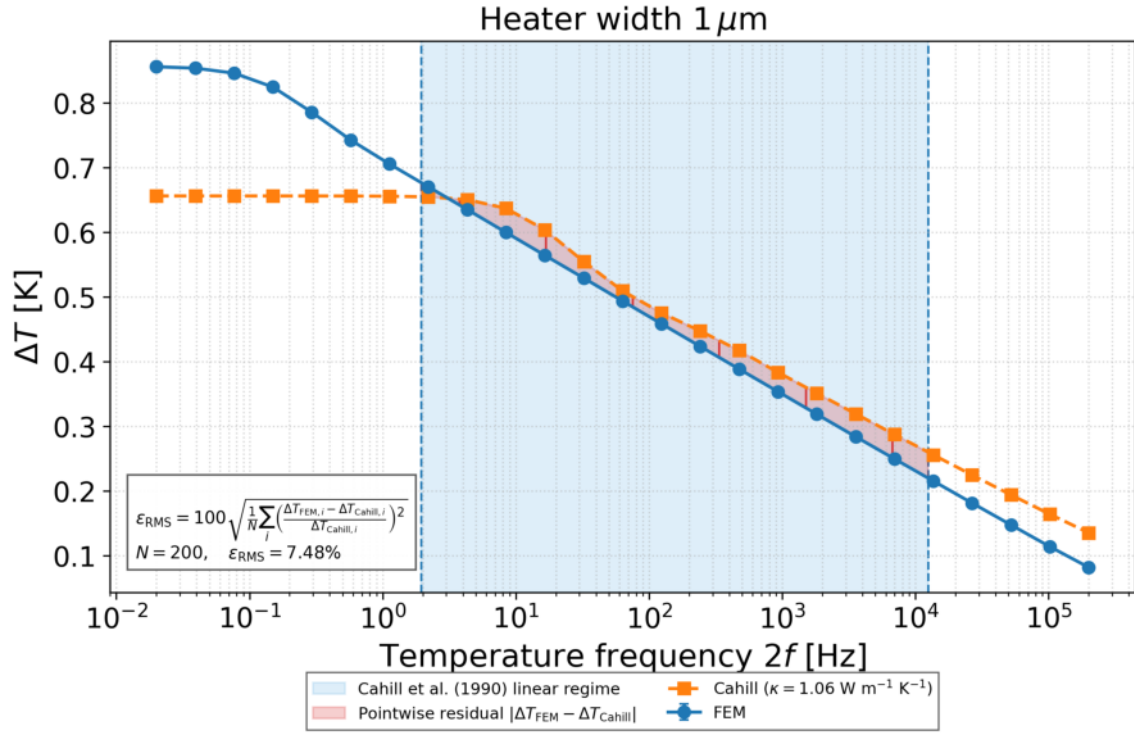


Figure A.15: Construction of the RMS relative-deviation metric for the $1\ \mu\text{m}$ heater. The red vertical segments and red shading show the pointwise absolute residual $|\Delta T_{\text{FEM}} - \Delta T_{\text{Cahill}}|$, evaluated on the common logarithmic frequency grid inside the Cahill linear regime.

Figure A.16 summarizes the result. The RMS difference is 1.5–3% for most widths and 7.48% for the $1\ \mu\text{m}$ limiting case. This confirms analytical agreement for the experimentally relevant heater widths.

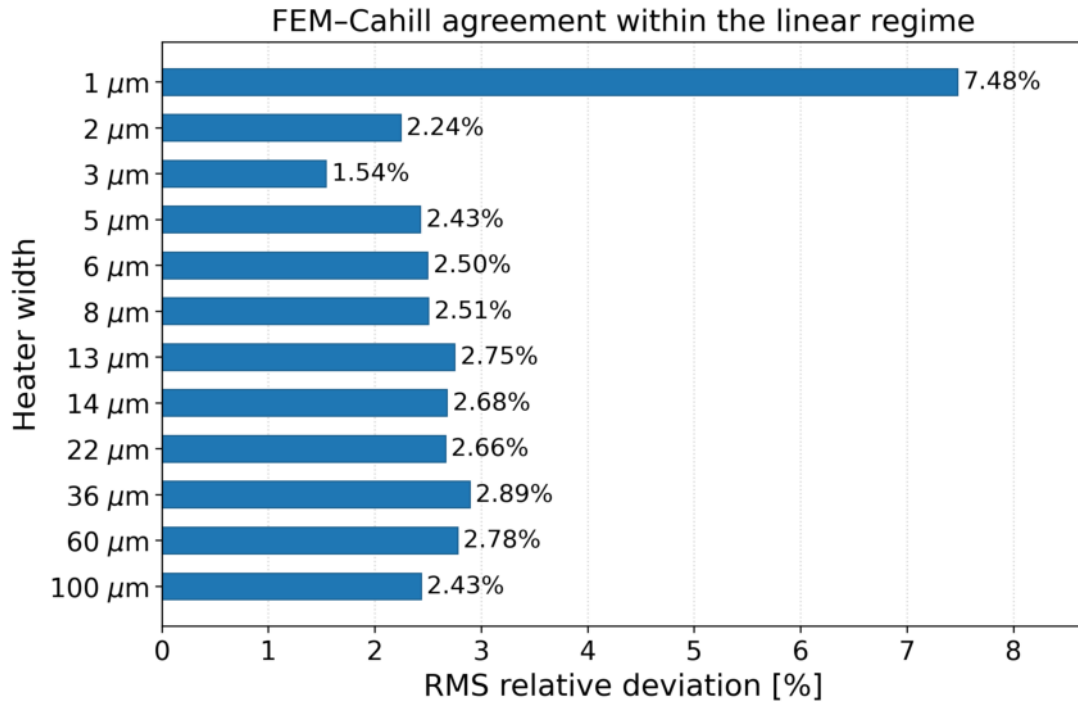


Figure A.16: RMS relative deviation between the finite-element and Cahill temperature responses within the Cahill linear regime for all investigated heater widths.

Finally, Figure A.17 shows that experiment, FEM, and the Cahill solution follow the same substrate response over the measured interval. This provides the direct experimental cross-check of the validated model.

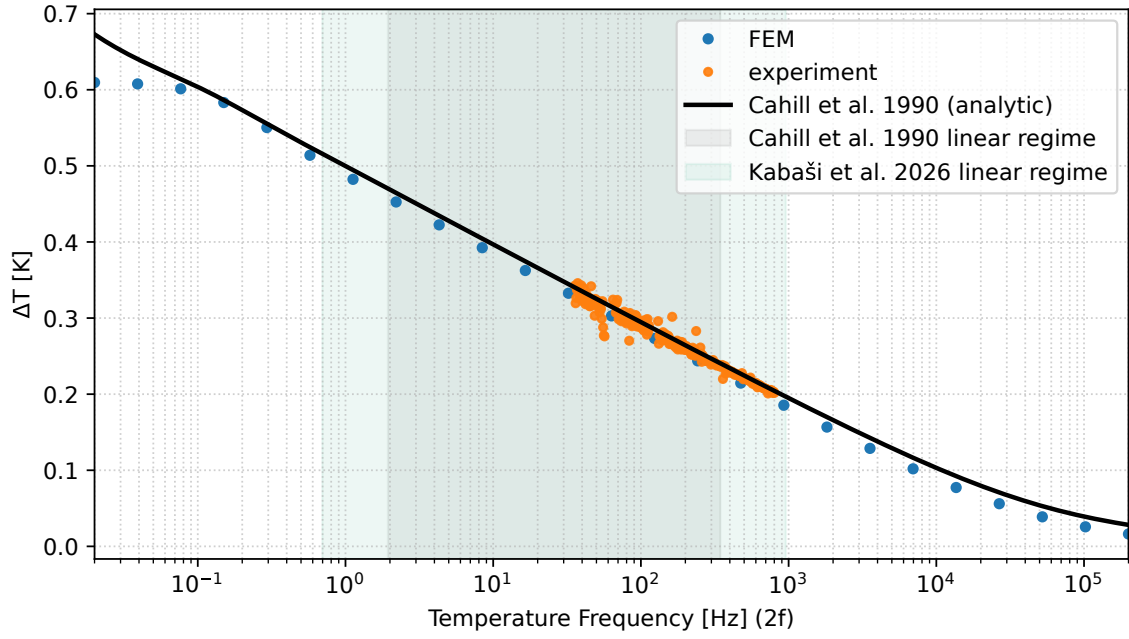


Figure A.17: Final substrate calibration cross-check between experiment, the substrate-only FEM response, and the analytical Cahill line-source solution. The frequency axis is the temperature-oscillation frequency $2f$.

Together, these checks show that the FEM package reproduces the zeroth law of thermodynamics, is numerically converged and energy consistent, and agrees with both the Cahill solution and the substrate experiment.

B Expanded Linear Frequency Range Derivation

This derivation was reported with the automated measurement system in [44]. The complete article is reproduced in Appendix D. It is included here separately so that the frequency-window criterion used throughout the thesis can be referenced directly.

The linear relationship between the amplitude of the third harmonic voltage $V_{3\omega}$ and the logarithm of twice the angular frequency $\ln(2\omega)$ is crucial for accurate determination of the thermal conductivity. This linearity is based on the assumption that the thermal waves generated by the heater penetrate the sample in a predictable way that depends on the frequency of the applied current and the thermal properties of the sample. The linearity between $V_{3\omega}$ and $\ln(2\omega)$ is valid if three conditions are met. The first is the assumption of a semi-infinite sample—it is thick enough that the thermal waves do not reach the backside of the sample during the measurement and do not reflect, $q^{-1} \ll t_{\text{sub}}$, where t_{sub} is the sample thickness. Furthermore, we consider the heat flow to be radial and $q^{-1} \gg b$, so that the heater can be approximated as an ideal line source. Finally, the heat capacity of the metal strip is negligible compared to the substrate. The geometry of the system is defined such that the z -direction represents the vertical axis, perpendicular to the surface of the substrate, with $z = 0$ at the interface between the heater and substrate. The x -direction represents the lateral axis, along the surface of the substrate and normal to the length of the heater strip. We can estimate these geometric empirical criteria based on the decay characteristics of exponential functions,

$$\Delta T(z, t) = \Delta T_0 e^{-zq} e^{i(\omega' t - zq')} . \quad (\text{B.1})$$

Eq. (B.1) is the general solution for the temperature oscillations in a semi-infinite solid assuming a 1-dimensional heat flow, where ΔT_0 is the amplitude of the temperature oscillations in the center of the heater, ω' is the characteristic decay frequency and q and q' are the characteristic wave vectors for the spatial decay and oscillations, respectively. The wave vector q is defined by equation (2.7). If we assume that the sample thickness is $3q^{-1}$, this leads to a reduction in the amplitude of the thermal oscillations at the bottom substrate boundary of $e^{-3} = 0.05$, which means that the amplitude is attenuated by 95%, so that the effects at the bottom edge are negligible and reflections or boundary conditions at the back contribute only minimally to the surface response. According to the equation (2.7), this results in the lower limit of the linear regime at $\omega_{\text{min}} = 9\alpha/(2t_{\text{sub}}^2)$, or $f_{\text{min}} = 9\alpha/(4\pi t_{\text{sub}}^2)$ in terms of frequency.

Let us consider the lateral heat flow and determine the upper frequency range in which these effects are negligible and the heat flow can actually be considered vertical and 1-dimensional. This simplification makes the mathematical modeling straightforward and the interpretation of the data reliable. We can approximate the temperature decay laterally from the heater as an exponential value $\Delta T(x) \propto e^{-xq}$. Let us define the maximum frequency as one corresponding to a thermal penetration depth of 3 half-widths, $q^{-1} = 3b$. The temperature drop at the lateral distance of 3 half-widths at this frequency is $\Delta T(3q^{-1}) = \Delta T_0 e^{-1} \approx 0.37 \Delta T_0$. In this case, the amplitude of the temperature oscillations decreases to 37% of its value in the center of the heater, which gives us the upper frequency limit of $\omega_{\text{max}} = \alpha/18b^2$ or $f_{\text{max}} = \alpha/36\pi b^2$ in terms of frequency.

From this we derive the theoretical linear frequency range:

$$\frac{9\alpha}{4\pi t_{\text{sub}}^2} \leq f_{\text{linear}} \leq \frac{\alpha}{36\pi b^2} . \quad (\text{B.2})$$

Consider a soda-lime glass substrate with a thickness of $1000\ \mu\text{m}$ on which a metal strip with a half-width of $3\ \mu\text{m}$ lies. The substrates are cut from a single soda-lime glass slide supplied by Marienfeld [53]. The relevant properties of soda-lime glass are [76]: $c_p = 0.87\ \text{J g}^{-1}\ \text{K}^{-1}$ for the specific heat capacity, $\rho = 2.5\ \text{g cm}^{-3}$ for the density and $\kappa = 1.06\ \text{W m}^{-1}\ \text{K}^{-1}$ for the thermal conductivity. If we substitute the values into the diffusivity relation $\alpha = \kappa/(\rho c_p)$, we get $\alpha = 4.9 \times 10^{-7}\ \text{m}^2\ \text{s}^{-1}$ for the diffusivity. Finally, we can assume the linear frequency range for this sample to be:

$$0.351\ \text{Hz} \leq f_{\text{linear}} \leq 481\ \text{Hz} . \quad (\text{B.3})$$

Thermal conductivity, specific heat capacity and mass density vary as functions of temperature, thus the thermal diffusivity also becomes temperature-dependent. Consequently, the calculated linear frequency range will shift slightly due to these variations. Thus, the expected linear response of the voltage of the third harmonic $V_{3\omega}$, with respect to the logarithm of the second harmonic, $\ln(2\omega)$, extends over three orders of magnitude as shown above. It is worth noting that the reported limits for the linear frequency range [48] are that the sample thickness is at least $5q^{-1}$ for the lower frequency limit, and the thermal penetration depth of five times the half-width of the heater for the upper limit. In our setup, the actual linear range is less restrictive than these conventionally imposed limits. The linearity criteria derived here are more representative of the experimental conditions specific to this measurement setup, and the conventionally measured frequencies still fall within this relaxed range, as discussed in [44]. In practice, however, both the lower and upper limits are higher. The heater acts as a linear or strip source, so the heat spreads in all directions. The presence of the surface at $z = 0$ limits the heat flow above the surface and "reflects" the heat back into the material. This causes the heat to penetrate deeper into the material in the z direction, while it spreads less in the x direction. By introducing the thermal mass of the copper to which the sample is attached, the underside of the sample goes from adiabatic to isothermal, further reducing lateral heat flow effects and allowing larger metal strip widths at frequencies suitable for measurement.

C Arduino 16-Bit PWM Control

The dynamically balanced Wheatstone bridge uses an Arduino Uno to control the LEDs of two CdS resistive optoisolators. The measurement system and balancing procedure are reported in [44], and the complete article is reproduced in Appendix D. The implementation below reproduces the 16-bit Timer1 approach used for fine resistance control, while making the serial parsing and output calls self-contained.

Timer1 is configured for fast PWM mode 14 with $ICR1 = 65535$ as the top value and no prescaling. This exposes the full 16-bit duty-cycle range on Arduino Uno pins 9 and 10. Pin 9 provides the secondary coarse setting, while pin 10 is updated by the automated bridge balancing routine. The host sends an integer from 0 to 65535 followed by a newline. The firmware clamps the received value to the valid 16-bit range before updating the PWM compare register.

```

1 #include <Arduino.h>
2
3 constexpr uint8_t kCoarsePwmPin = 9;    // Timer1 output A
4 constexpr uint8_t kBalancePwmPin = 10;  // Timer1 output B
5 constexpr uint16_t kPwmTop = 0xFFFF;
6
7 void setupPwm16() {
8     pinMode(kCoarsePwmPin, OUTPUT);
9     pinMode(kBalancePwmPin, OUTPUT);
10
11     // Timer1, mode 14: fast PWM, TOP = ICR1, non-inverting outputs.
12     TCCR1A = _BV(COM1A1) | _BV(COM1B1) | _BV(WGM11);
13     TCCR1B = _BV(WGM13) | _BV(WGM12) | _BV(CS10);
14     ICR1 = kPwmTop;
15 }
16
17 void analogWrite16(uint8_t pin, uint16_t value) {
18     if (pin == kCoarsePwmPin) {
19         OCR1A = value;
20     } else if (pin == kBalancePwmPin) {
21         OCR1B = value;
22     }
23 }
24
25 bool readDutyCycle(uint16_t &value) {
26     static uint32_t accumulator = 0;
27     static bool hasDigits = false;
28
29     while (Serial.available() > 0) {
30         const char incoming = static_cast<char>(Serial.read());
31
32         if (incoming >= '0' && incoming <= '9') {
33             accumulator = accumulator * 10UL
34                 + static_cast<uint8_t>(incoming - '0');
35             if (accumulator > kPwmTop) {
36                 accumulator = kPwmTop;
37             }
38             hasDigits = true;
39         } else if (incoming == '\n') {
40             if (hasDigits) {

```

```
41     value = static_cast<uint16_t>(accumulator);
42     accumulator = 0;
43     hasDigits = false;
44     return true;
45 }
46 } else if (incoming != '\r') {
47     // Reject malformed commands and wait for a new line.
48     accumulator = 0;
49     hasDigits = false;
50 }
51 }
52 return false;
53 }
54
55 void setup() {
56     Serial.begin(9600);
57     setupPwm16();
58
59     analogWrite16(kCoarsePwmPin, 45000);
60     analogWrite16(kBalancePwmPin, kPwmTop);
61 }
62
63 void loop() {
64     uint16_t requestedDutyCycle;
65     if (readDutyCycle(requestedDutyCycle)) {
66         analogWrite16(kBalancePwmPin, requestedDutyCycle);
67     }
68 }
```

Listing C.1: Arduino Uno firmware for 16-bit PWM control of the CdS resistive optoisolators.

During a measurement, the computer selects the duty-cycle value using the residual 1ω amplitude and phase criteria described in Section 3.1. The firmware only applies the requested 16-bit value. The instrument-control software performs the iterative balancing logic. This separation matches the architecture reported in [44].

D Published Article: Automated 3-Omega Thermal Conductivity Measurement System by Dynamically Balanced Wheatstone Bridge

The full published article corresponding to the main publication listed in this thesis is included below for non-commercial use in the dissertation. Reprinted from *Measurement*, Vol. 257, Anton Kabaši, Josipa Šćurla, and Ante Bilušić, “Automated 3-omega thermal conductivity measurement system by dynamically balanced Wheatstone bridge,” Article 118830, Copyright 2025 Elsevier. The article is included under Elsevier’s author reuse rights. The version of record is available at <https://doi.org/10.1016/j.measurement.2025.118830>.



Automated 3-omega thermal conductivity measurement system by dynamically balanced Wheatstone bridge

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ABSTRACT

We present the design and experimental validation of an automated 3-omega system for high-temperature thermal conductivity measurements, starting from room temperature. Unlike previous 3ω implementations, the system is fully automated: an Arduino-driven CdS optoisolator re-balances the Wheatstone bridge at every frequency, eliminating manual adjustment and enabling dense, stable sweeps. We introduce an algorithm to automatically minimize the 1ω harmonic voltage components from the input signal, thereby improving measurement precision and increasing the statistical significance of results—a challenge for earlier implementations of the technique. We developed a custom high-temperature insert to fit a commercial cylindrical tube furnace, ensuring precise temperature control and providing an isothermal environment in medium vacuum (0.1 Pa). The setup is designed to minimize radiative and convective contributions to thermal conductivity at high temperatures, an issue common in steady-state measurement. Experimental results were validated with measurements of a soda-lime glass sample using a silver strip fabricated by photolithography.

1. Introduction

The 3-omega (3ω) method has become a critical technique for measuring thermal conductivity in thin films and nanoscale materials. While the method was extensively developed and popularized by David G. Cahill in the late 1980s to 1990s [1–3], the roots of harmonic detection in thermal measurements can be traced back much earlier. In 1910, Corbino observed a third harmonic component in the voltage signal of an alternating current (AC) system, marking one of the earliest mentions of a concept that would later underpin the 3ω method [4].

Over the years, the 3ω method has been successfully applied to a broad range of material systems, including bulk materials [1,2,5,6], thin films [7–11], nanostructures [12,13] and nanolaminates [2,14].

By adjusting the measurement frequency, the thermal wavelength – and therefore the thermal penetration depth as defined by Cahill [2,7] – can be controlled. This relationship is expressed as:

$$q^{-1} = \sqrt{\frac{\alpha}{i2\omega}} \quad (1)$$

where q^{-1} is the thermal wavelength, $i = \sqrt{-1}$ is the imaginary unit, ω is the angular frequency and α is the thermal diffusivity of the material, calculated as:

$$\alpha = \frac{\kappa}{\rho c_p} \quad (2)$$

In this equation κ represents the thermal conductivity, ρ is the material's mass density, and c_p is the specific heat capacity.

1.1. 3ω method

Let us consider the metallic strip of resistance R , length L and width $2b$. The strip is applied on top of the measured sample, the geometry is depicted schematically in Fig. 1 (a). Since the strip is metallic, resistance varies linearly with temperature:

$$R = R_0 (1 + \beta \Delta T), \quad (3)$$

where R_0 is the strip resistance at a reference temperature, and β is the temperature coefficient of resistance (TCR). The metal strip functions as both a heater and a sensor when measuring thermal conductivity by 3ω method. Energizing it by an AC current with the frequency ω , $I(\omega) = I_0 \cos \omega t$, from the trigonometric identity $\cos^2(\omega t) \propto \cos(2\omega t)$ it follows that the sample and the strip undergo Joule heating $P = I^2 R$ with twice the frequency of the current (2ω).

The resulting temperature oscillations modulate the resistance of the strip and generate a voltage response that contains the frequency of the

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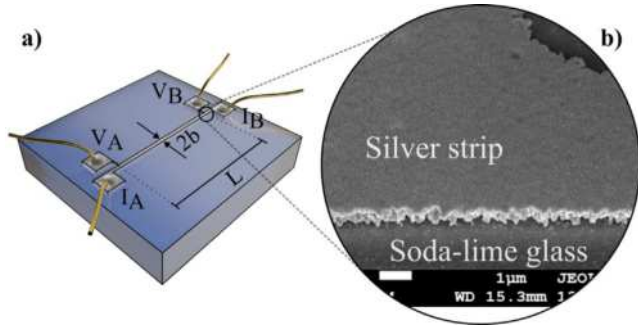


Fig. 1. (a) Schematic of the microscopic heater-sensor strip geometry. The strip serves as both a heater and temperature sensor in the 3ω thermal conductivity measurement. (b) SEM image of the fabricated silver strip, tilted at 45° , with the lower part of the sample raised toward the viewer. The white bar on the SEM image represents $1 \mu\text{m}$.

third harmonic (3ω):

$$V_{3\omega}(t) = \frac{1}{2} V_{rms} \beta |\Delta T| \cos(3\omega t + \phi). \quad (4)$$

V_{rms} is the root mean square voltage across the strip, while the amplitude and phase ϕ of this 3ω -voltage provide insights into the thermal conductivity of the material under study.

Cahill found the analytical solution to the thermal diffusion equation for the heater of finite width on an isotropic semi-infinite substrate in Fourier space k [2]:

$$\Delta T(k) = \frac{P_{RMS}}{\pi L} \int_0^\infty \frac{\sin^2(kb)}{(kb)^2 [\kappa \sqrt{k^2 + q^2}]} dk, \quad (5)$$

where P_{RMS} is the root mean square of the power generated by the strip. If we consider the material as semi-infinite and isotropic, and the heater geometry such that the thermal wavelength defined in Eq. (1) is much larger than the heater half-width b , $q^{-1} \gg b$, we can approximate the heater as a line source. In this case, the integral in Eq. (5) has an analytical solution, written explicitly in frequency space as a function of 2ω :

$$\Delta T(2\omega) = -\frac{P_{RMS}}{2\pi L \kappa} \left[\ln(2\omega) + \ln\left(\frac{b^2}{\alpha}\right) - 2\eta \right] - i \frac{P_{RMS}}{4\kappa}, \quad (6)$$

where η is an integration constant equal to 0.923 [8]. By substitution of Eq. (6) into Eq. (4) and considering $P_{RMS} = V_{rms}^2/R$ we arrive at the expression for the amplitude of the third harmonic voltage measurable by lock-in amplifier:

$$V_{3\omega} = -\frac{V_{rms}^3 \beta}{4\pi L \kappa R} \left[\ln(2\omega) + \ln\left(\frac{b^2}{\alpha}\right) - 2\eta \right] - i \frac{V_{rms}^3 \beta}{8L \kappa R}. \quad (7)$$

The real part is an equation of the line where the 3rd harmonic voltage is a function of $\ln(2\omega)$ and we calculate thermal conductivity κ as:

$$\kappa = \frac{V_{rms}^3 \beta}{4\pi L R s} \frac{1}{s}, \quad (8)$$

where s is the slope of the measured 3rd harmonic voltage. The first harmonic is primarily related to the electrical properties of the components, wires, and direct heating effects, and it does not carry the desired thermal information about the material under study.

Two methods are commonly used to suppress the first harmonic voltage and minimize its influence on the third harmonic measurement: the Wheatstone bridge [15] and the differential amplifier method [2, 6, 13, 16]. When the bridge is balanced, 1ω -voltage is minimized or completely canceled out because the voltage drops across the different arms of the bridge are equal in value and opposite in sign. This allows only higher harmonics to remain. The third harmonic is of particular interest because it corresponds to the temperature-dependent

change in resistance, which is directly related to the material's thermal conductivity, see Eqs. (7) and (8).

Earlier works by Cahill et al. [2] measured multiple frequency points during their experiments, however, for the calculation of substrate thermal conductivity, only two specific frequency points are typically utilized, and the thermal conductivity is then calculated. This methodology obscures potential frequency-dependent effects on other thermal properties, such as the heat capacity, which can vary with frequency. For instance, studies on thin dielectric films highlight that thermal transport properties depend significantly on frequency and material interfaces, affecting the measurement of properties like specific heat capacity [17].

As the frequency changes, the balance of the measurement circuit should theoretically remain constant, as only the real (resistive) component of the voltage is of interest. In practice, however, it depends on the impedance of the components and thus on frequency. This leads to fluctuations in the power dissipated by the resistive components including the strip resistance, destabilizing the measurement temporarily until thermal equilibrium is re-established. This holds even in materials with low TCR, such as chromel or constantan [18,19] utilized in modern electronics.

To address this issue, the automated setup balances the bridge at every measurement frequency. We observe that the first harmonic voltage changes significantly with frequency, up to two orders of magnitude above the 3rd harmonic voltage, requiring frequent rebalancing.

The automation of this process is key to acquiring a high number of data points across a range of frequencies. This improves statistical robustness and precision of the 3ω method, laying the groundwork for measurement of frequency-dependent thermal properties such as heat capacity explored in previous works [17] in more detail.

The primary aim of this work is to present and validate an automated 3-omega measurement system for high temperatures, utilizing a dynamically balanced Wheatstone bridge that enables increased measurement reliability, density, precision, and operational practicality compared to conventional manual bridge balancing methods. The key innovation is the integration of a real-time, frequency-by-frequency bridge-balancing algorithm that keeps the 1ω component below $10 \mu\text{V}$ without operator intervention, something not reported in earlier 3ω studies.

2. Materials and methods

2.1. Balancing the Wheatstone bridge

To our knowledge, this is the first 3ω setup to use a microcontroller-driven optoisolator for continuous bridge balancing. The custom-built resistive optoisolator was composed of a CdS-based photoresistor (LDR) that was attached to a red light-emitting diode (LED) with transparent adhesive. It was encased in black heat-shrink tubing, forming a high-precision variable resistance component within the Wheatstone bridge which Fig. 2 (a) depicts. The CdS-based optoisolator is located outside the heated measurement chamber, ensuring minimal temperature variation. Measurements were only recorded once the lock-in amplifier output was stable, effectively eliminating thermal drift. The resistance of the photoresistor was controlled by adjusting the brightness of the LED, which was controlled by a pulse-width modulated (PWM) signal from an Arduino Uno microcontroller. The algorithm continuously adjusted the PWM duty cycle to fine-tune the LED's intensity, thereby allowing precise control of the photoresistor's resistance and therefore balancing of the Wheatstone bridge. The measurement procedure is detailed below and depicted in Fig. 3.

Temperatures were selected from a set of nominal values. After thermal stability was achieved, the electronics were initialized. Initialization began by selecting the highest frequency from a predefined set. The lock-in amplifier then measured the phase; if its deviation from 90° exceeded 1% or 1ω voltage amplitude was over $10 \mu\text{V}$, the light

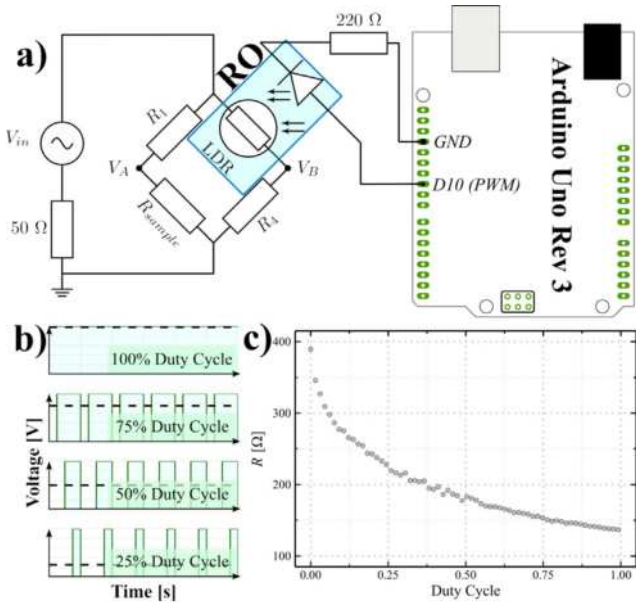


Fig. 2. (a) Automated Wheatstone bridge circuit for 3-omega thermal conductivity measurements based on a resistive optoisolator (RO). Light dependent resistor's (LDR) resistance controlled by LED light intensity via microcontroller pulse-width modulated (PWM) signal. The bridge compensates for resistance changes in wiring and electronics due to environment. (b) PWM signals used to control the LED in the optoisolator. The dashed lines represent the mean value of the output voltage in the range from 0 to 5 V. At 100% duty cycle the voltage is 5 V. (c) LDR based on CdS shows strong photoconductive effect at low light intensities, transitions to a more linear decrease as carrier saturation sets in.

intensity was adjusted via PWM with progressively finer steps until 90° was reached (ensuring effective filtering of the 1ω harmonic). Once phase was within 1% or 1ω voltage amplitude was within $10 \mu\text{V}$, the algorithm recorded the 1ω voltage, switched to the 3ω measurement, logged the data, then reverted to 1ω before moving on to the next frequency. The Arduino updated the PWM duty cycle according to the 1ω voltage read by the lock-in amplifier in a closed loop. The Stanford Research SR830 lock-in amplifier, operating in differential mode, measured the harmonic signals and also served as the sinusoidal voltage generator for the system. Fig. 2 (a) shows that the lock-in measured the differential voltage between bridge nodes V_A and V_B , not the voltage directly across the heater. The 3ω voltage was obtained by multiplying the measured differential signal with a correction factor based on known bridge resistances. This factor is only valid when the bridge is balanced and follows standard voltage divider analysis [20]. In the unbalanced case, this factor no longer applies, making the extracted 3ω voltage – and thus the thermal conductivity – unreliable. Stabilization of the Wheatstone bridge took less than 15 s per frequency. A single measurement at a particular frequency took up to 40 s including the time taken to dynamically balance the bridge. After each measurement frequency change, a wait time of 3 s was given for the lock-in amplifier to stabilize. It took 10 s each to measure the first and third harmonic. Measurement for a single temperature took, on average, 2 h, including thermal stabilization.

Arduino Uno served as the microcontroller for managing the resistive optoisolator within the Wheatstone bridge. The relationship between the photoresistor resistance and the duty cycle which corresponds to the normalized light intensity is shown in Fig. 2 (c).

For more detailed information on implementation of the 16-bit PWM output on Arduino, see Ref. [21].

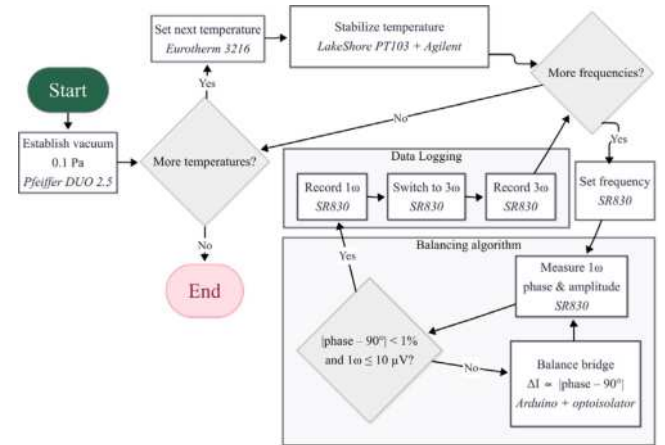


Fig. 3. Measurement procedure: Temperatures are chosen from a list of nominal temperatures, exact temperatures at the sample are measured using a calibrated platinum resistance thermometer. Once the system temperature stabilizes, the frequency sweep, bridge balancing and data logging starts. ΔI is the change in LED light-intensity which leads to resistance change in the photoresistor, implemented algorithmically as a variable resistance step $\Delta R \propto |\phi - 90^\circ|$. The algorithm continuously adjusts the resistance until the phase deviation falls below 1% of 90° and the 1st harmonic voltage is below $10 \mu\text{V}$.

2.2. Sample holder and temperature control

The custom sample holder was designed to slide in and out of the tube furnace and was equipped with four-wire coaxial electrical contacts connected to the sample, as well as four-wire contacts connected to a LakeShore PT103 thermometer. The sample contacts were achieved by Allectra miniature Kapton coaxial cables for high temperature, vacuum and radiation applications, 311-KAP50S-RAD, with $7 \times 0.07 \text{ mm}$ thick silver-plated copper stranded center wire, surrounded by a polyimide dielectric and a silver-plated copper braid as the outer conductor in a polyimide jacket. These cables were rated for operation up to approximately 250°C but we opted to limit our measurements to below 200°C to ensure the long-term reliability of the setup. All the electrical connections and Wheatstone bridge printed circuit board (PCB) were impedance-matched to 50 ohms to minimize electrical reflections. The thermometer contacts were made from four 99.99% pure platinum wires with a diameter of $102 \mu\text{m}$ passed through alumina six-wire tubing. This configuration ensured precise temperature measurement and minimized cross-talk and electrical noise.

Temperature control during thermal measurements was managed using a Carbolite Gero MTF 12/38/250 tube furnace with integrated Eurotherm 3216 temperature controller which offered a high level of precision in temperature regulation. The borosilicate tube inside the furnace allowed for arbitrary atmosphere during measurements, while vacuum generation was facilitated by a Pfeiffer Vacuum DUO 2.5 vacuum pump. This setup ensured that the sample remained in well-defined thermal and atmospheric conditions throughout the experimental procedures.

The silver strip utilized in these experiments was fabricated on a soda-lime glass substrate through the process of optical lithography to ensure dimensional precision. Silver was selected for its high TCR, which enhances the sensitivity of the strip to temperature-induced resistance changes [22].

The fabrication process began with a thorough cleaning of the soda-lime glass substrate to eliminate any contaminants. The substrate was ultrasonically cleaned in a mixture of isopropanol and acetone at a 3:8 volume ratio at room temperature. After ultrasonic cleaning, the substrate was dried using nitrogen gas to remove any remaining

solvents. Finally, the cleaned substrate was immediately placed into the sputtering chamber for further processing.

A 3-Ångström thick layer of chromium was sputtered onto the substrate to serve as an adhesion layer between the glass and the silver; the thickness of this layer was monitored using a piezoelectric sensor that detected changes in the resonant frequency of a quartz crystal. Following this, silver was sputtered onto the substrate and the thickness of the silver layer was subsequently confirmed using a 45° tilted scanning electron microscope (SEM) image (Fig. 1 b). A uniform layer of positive photoresist (AZ 1505), approximately 500 nanometers thick, was applied to the substrate using a spin coater. Since the 3ω method relies on the logarithmic slope of the temperature response and not on absolute heater power density, the film thickness does not enter the calculation of κ . Variations in thickness are thus irrelevant for uncertainty analysis.

The substrate was then exposed to UV light through a photomask using the EVG 610 Mask Alignment System, which defined the metal strip pattern. The photoresist was developed, removing the exposed photoresist and revealing the strip pattern. Finally, the unprotected silver was etched away using an iron(III) nitrate solution at room temperature, leaving the precise strip pattern on the glass substrate.

The fabricated sample was subsequently mounted onto the high-temperature insert copper plate, which serves as a sample holder, attached using EPO-TEK EJ2312, a 2-component room temperature curing conductive adhesive. Electrical contacts were made to the high-temperature insert sample head using nickel-plated copper wires, affixed to the four contact pads patterned on the strip with the same electrically conductive adhesive.

2.3. Measurement procedure and data analysis

Resistance of the metal strip was determined from the slope of the current–voltage (IU) curve measured using a Keysight B2901A Precision Source-Measure Unit. For each temperature, the source-measure unit supplied voltages in 10 steps (from -0.2 V to $+0.2\text{ V}$, measuring the resulting current at each step. Each IU point was formed as an average of 10 measurements, and the final resistance was calculated as $R = 1/\text{slope}$, where the slope was obtained from a linear fit of the IU data.

Temperature was measured using a Lakeshore PT-103 platinum resistance thermometer connected to an Agilent 34401 A multimeter. The four-wire resistance measurement method was employed to accurately determine the thermometer's resistance. A calibration curve, established using a second calibrated thermometer, was used to convert the resistance readings into temperature values.

TCR was calculated from the slope of the $R(T)$ curve using the Orthogonal Distance Regression (ODR) method included in the python SciPy library [23] based on the work by Boggs et al. [24]. This method accounts for errors in both resistance and temperature and the uncertainty in β was directly derived from the ODR fit. The ODR method minimizes the orthogonal distances between the data points and the fitted line, providing a more robust estimation of the uncertainty when errors exist in the independent variable.

The 3ω voltage was measured by passing an AC current through the strip at frequency ω . The heating effect causes temperature fluctuations at 2ω , which modulates the resistance of the strip, generating a voltage at 3ω . The Arduino-controlled Wheatstone bridge adjusted the resistance to minimize the 1ω harmonic, isolating the 3ω component for analysis. Thermal conductivity was calculated using Cahill's approximation for a semi-infinite cylindrical geometry of the heater, under the assumption that the heater length is significantly longer than the thermal penetration depth, as discussed by Cahill in the context of the diffusion equation solution [2].

Thermal conductivity was derived from the slope of the in-phase 3ω voltage as a function of the logarithm of the 2ω frequency according to Eq. (8).

Table 1

Dimensions and measured reference resistances R_0 and temperature coefficients of resistance β for the silver strip heater. Heater resistance was measured from room temperature to 453 K.

2b (μm)	6.0
L (mm)	3.0
t (nm)	500
Cooling	
R_0 (Ω)	4.4917 ± 0.0005
β ($\text{ppm}\cdot\text{K}^{-1}$)	2979.3 ± 1.0
Heating	
R_0 (Ω)	4.4808 ± 0.0004
β ($\text{ppm}\cdot\text{K}^{-1}$)	3027.3 ± 1.4

2.4. Uncertainty analysis

To determine the uncertainty in the thermal conductivity, we propagated the uncertainties in the measured quantities – the initial voltage $\sigma_{V_{rms}}$, the temperature coefficient of resistance σ_β , the resistance of the heater σ_R and the slope of the measured voltage σ_s . For any derived quantity $f(x_1, x_2, \dots, x_n)$ the uncertainty in f , denoted σ_f , is given by the propagation of uncertainties in the independent variables $x_1, x_2, \dots, x_n$, each with its own uncertainty σ_{x_i} according to:

$$\sigma_f^2 = \sum \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma_{x_i}^2. \quad (9)$$

In the case of thermal conductivity κ the error propagation is thus given by:

$$\sigma_\kappa = \kappa \cdot \sqrt{\left(\frac{3\sigma_{V_{rms}}}{V_{rms}} \right)^2 + \left(\frac{\sigma_\beta}{\beta} \right)^2 + \left(\frac{\sigma_R}{R} \right)^2 + \left(\frac{\sigma_s}{s} \right)^2}. \quad (10)$$

Mask-defined heater length (3.000 mm) carried a $0.8\text{ }\mu\text{m}$ tolerance ($\Delta L/L = 0.027\%$). Propagating this term modifies the combined uncertainty only in the third decimal place, so it was omitted from the calculation.

We found that, after propagating all independent variable errors, the relative uncertainty in each κ measurement did not exceed 2%.

3. Results

The automated experimental setup was validated using soda-lime glass substrate with a $6\text{ }\mu\text{m}$ wide sputtered silver strip heater. Dimensions, measured reference resistance R_0 and TCR of the strip are listed in Table 1.

Fig. 4(a) compares the conventional and automated approaches. In the conventional approach, the bridge is balanced at the midpoint of the frequency sweep (in this case, at the geometric mean of the frequency interval between 100 Hz and 800 Hz, i.e. at 283 Hz). However, the impedances drift due to temperature changes in the electronic circuits. Since the Wheatstone bridge is very sensitive to phase shifts and resistance drift, voltage is generally not balanced over the whole frequency interval and the third harmonic voltage cannot be determined correctly. In contrast, the automatically balanced setup used in this study allows for arbitrary accuracy, which in this case is set to $10\text{ }\mu\text{V}$ or less, to provide comparable measurement times between conventional and automated measurement. The comparison of the first harmonic voltages balanced in both approaches (Fig. 4(a)) clearly shows the difference in the resulting balance of the 1ω voltage. The frequency points during the measurement were selected logarithmically to obtain even distribution of data.

We found that the TCR depends strongly on strip geometry: when the strip heater-thermometer thickness approaches the nanometer scale,

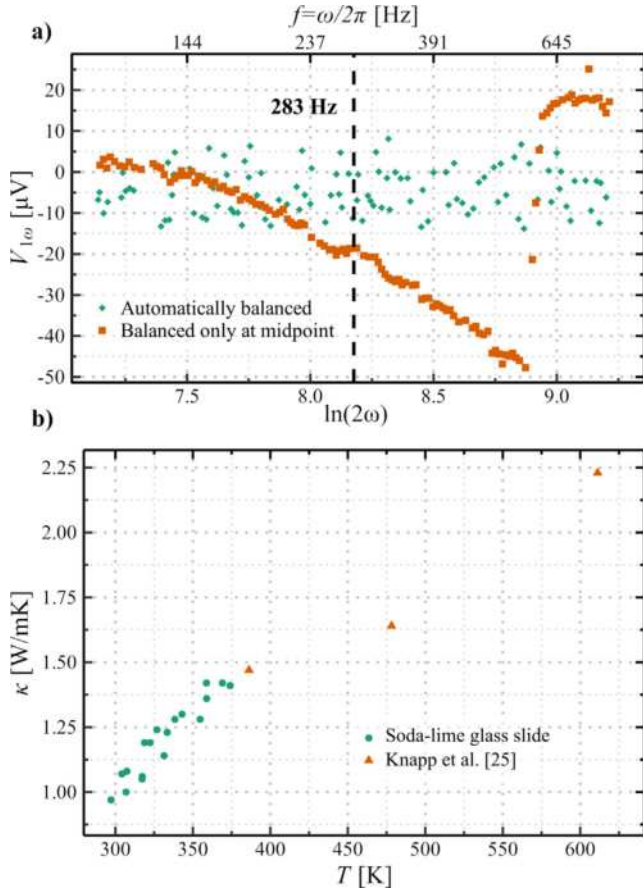


Fig. 4. (a) First harmonic voltage across the Wheatstone bridge balanced automatically vs only at midpoint of the measured frequency interval (conventional approach). (b) Thermal conductivity of soda-lime glass from room temperature to 375 K. The trend is well aligned with reference data at high temperatures [25] and agrees with supplier measured values at room temperature [26].

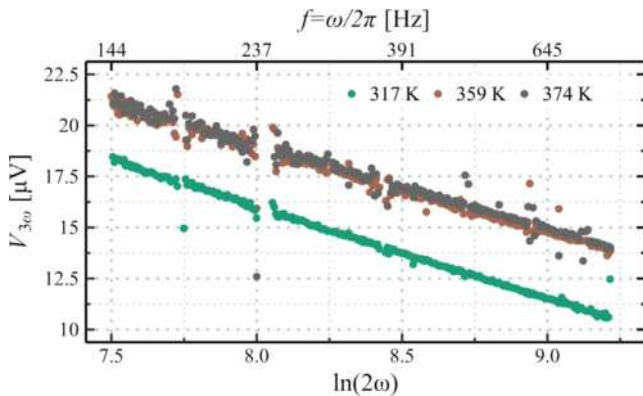


Fig. 5. Measured amplitudes of third harmonic voltage $V_{3\omega}$ vs. $\ln(2\omega)$ at 317, 359, and 374 K (logarithmically spaced frequencies).

the TCR diverges from that of bulk silver. After repeated thermal cycling, the strip's electrical resistance remained stable (Table 1), providing a reliable temperature-resistance calibration for the silver heater-thermometer.

Fig. 5 demonstrates a clear linear relationship between the 3ω voltage and the natural logarithm of 2ω , consistent with theoretical predictions by Cahill [2].

Fig. 4 (b) displays the thermal conductivity of soda-lime glass measured from room temperature up to 375 K. The curve matches supplier data at room temperature [26] and follows the high-temperature trend reported by Knapp [25]. All points were acquired over two weeks in a deliberately non-sequential temperature order to preclude artifacts.

4. Discussion

The in-phase 3ω voltage shown in Fig. 5 obeys $\Re\{V_{3\omega}\} \propto \ln(2\omega)$ from 0.35 Hz and above 800 Hz using $f_{\min} = 9\alpha/(4\pi t^2)$ and $f_{\max} = \alpha/(36\pi b^2)$ (refer to Appendix A). This extended linearity stems from differences between the actual thermal diffusivity, specific heat, and density of our soda-lime glass sample and the literature values used in the derivation, as well as from our specific setup geometry and boundary conditions. These findings suggest that sample-specific material properties and measurement configuration shift and broaden the valid 3ω regime beyond the classical limits introduced by Cahill.

Accurately knowing how much heat is supplied to the sample is essential for precise thermal-conductivity measurements. Radiative losses in 3ω measurements have been analyzed in detail by Cahill [2], who showed they scale as $\epsilon T^3 b/\kappa$, where ϵ is the emissivity. Under our experimental conditions – comparable to those studied in that work – radiative losses are negligible, remaining well below 2% even at 1000 K. At elevated temperatures, radiative losses become non-negligible and complicate that determination. The temperature at which radiation dominates depends on the material and its geometry, but in most setups corrections are required once the specimen approaches 1000 K. Convective heat losses are negligible when applying the method, as previously established [27] and thus do not significantly impact the measured thermal conductivity values presented here.

Recent battery calorimetry studies on centimetre-scale cells operated at ambient pressure carefully model coupled conduction, convection and radiation, often with anisotropic media and complex boundary conditions [28–31]. By contrast, our 3ω heater is microscale, the experiment is performed in medium vacuum ($\sim 0.1 \text{ Pa}$), and the AC analysis localizes the thermal field within the substrate, so the dominant loss channels highlighted in those studies are strongly suppressed here. Consistent with the standard 3ω scaling arguments (e.g. Cahill [2]), the fractional loss remains negligible across our frequency and temperature window, justifying the use of the conventional Cahill reduction without introducing extra loss parameters. The detailed coupled-loss strategies developed for batteries, however, become directly relevant for future extensions of the methodology to higher temperatures, ambient-pressure operation, very low- κ or very thick substrates and heater geometries outside the strict Cahill regime.

The Wheatstone bridge's adjustable leg is a light-controlled resistive optoisolator whose resistance is set by an Arduino-driven LED (see Section 2.1). When the bridge was balanced, the first harmonic of the electrical potential drop across the bridge was typically reduced by two orders of magnitude (e.g. from 100 – 500 μV to below 10 μV). Bridge balancing enables the detection of the third harmonic of the electrical voltage, Eq. (4), whose typical value is in the order of 10 μV as Fig. 5 illustrates. The automatic bridge balancing used in this study was limited by the resistance change of the photoresistor with respect to the duty cycle of the diode (Fig. 2 (c)).

The effectiveness of the bridge balancing depends on its resistances. Since the strip resistance changes with temperature, there is a possibility that at some temperatures the bridge cannot be balanced. For that purpose the corresponding electric circuit is flexible and additional resistors can be added.

Finally, the thermal conductivity is calculated from the slope of the curve $V_{3\omega}$ against $\ln(2\omega)$ in the linear range (Eqs. (7) and (8)).

For a metal strip sputtered directly onto glass the metal-substrate boundary adds only a constant offset that cancels in the slope method [2], so interfacial resistance does not affect κ .

The rationality of the extracted results is supported by several internal consistency checks: the observed linear dependence $V_{3\omega} \propto \ln(2\omega)$ confirms the validity of the underlying thermal model, the extracted thermal conductivity matches vendor and literature values for soda-lime glass within uncertainty, and the heater resistance remains unchanged after full thermal cycling, indicating the integrity of the microstructure throughout the measurement.

An earlier study by Jaber et al. [32] investigated geometric non-idealities in the heater design. They showed that narrower heaters produce larger temperature rises in the strip due to less efficient heat diffusion into the substrate thereby enhancing sensitivity in thermal conductivity measurements. In our work, the strip's aspect ratio $L/2b = 500$ (Table 1) meets the analytical model conditions and delivers precise thermal conductivity values.

While the 3ω method itself is routinely applied to metals, semiconductors, ceramics, and polymers (see Introduction), the present study intentionally validates the automation loop on a single insulating glass. Extending the same protocol to additional low- κ materials is left for future studies.

5. Conclusion

This work presents a novel instrumentation advancement for 3-omega thermal conductivity measurements, introducing an automated Wheatstone bridge with real-time pulse-width modulated balancing built around the Arduino microcontroller which controls a resistive optoisolator algorithmically. This approach eliminates errors from thermal drift, enables arbitrary nullification of the first harmonic voltage and significantly improves the precision and reproducibility of third harmonic voltage extraction. Although the present demonstration is limited to 375 K by the Kapton wiring, the automation strategy itself is temperature-agnostic - it is extendable to cryogenic and higher temperature systems.

The requirement for the largest possible ratio between the length and width of the heater strip must be met in order to apply the Cahill model for calculation for thermal conductivity. This novel, robust and reliable method allows for measurement of a variety of materials over a wide temperature range. Its usefulness extends to fields such as energy engineering and materials science, where a thorough understanding of heat transfer in nano- and micro-scale is essential.

CRedit authorship contribution statement

Anton Kabašić: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Josipa Šćurla:** Writing – review & editing, Software, Resources, Conceptualization. **Ante Bilušić:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Expanded linear frequency range derivation

The linear relationship between the amplitude of the third harmonic voltage $V_{3\omega}$ and the logarithm of twice the angular frequency $\ln(2\omega)$ is crucial for accurate determination of the thermal conductivity. This linearity is based on the assumption that the thermal waves generated by the heater penetrate the sample in a predictable way that depends on the frequency of the applied current and the thermal properties of the sample. The linearity between $V_{3\omega}$ and $\ln(2\omega)$ is valid if three conditions are met. The first is the assumption of a semi-infinite sample — it is thick enough that the thermal waves do not reach the backside of the sample during the measurement and do not reflect, $q^{-1} \ll t$ where t is the sample thickness. Furthermore, we consider the heat flow to be radial and $q^{-1} \gg b$, so that the heater can be approximated as an ideal line source. Finally, the heat capacity of the metal strip is negligible compared to the substrate. The geometry of the system is defined such that the z -direction represents the vertical axis, perpendicular to the surface of the substrate, with $z = 0$ at the interface between the heater and substrate. The x -direction represents the lateral axis, along the surface of the substrate and normal to the length of the heater strip. We can estimate these geometric empirical criteria based on the decay characteristics of exponential functions,

$$\Delta T(z, t) = \Delta T_0 e^{-zq} e^{i(\omega' t - zq')} \quad (\text{A.1})$$

Eq. (A.1) is the general solution for the temperature oscillations in a semi-infinite solid assuming a 1-dimensional heat flow, where ΔT_0 is the amplitude of the temperature oscillations in the center of the heater, ω' is the characteristic decay frequency and q and q' are the characteristic wave vectors for the spatial decay and oscillations, respectively. The wave vector q is defined by Eq. (1). If we assume that the sample thickness is $3q^{-1}$, this leads to a reduction in the amplitude of the thermal oscillations at the bottom substrate boundary of $e^{-3} = 0.05$, which means that the amplitude is attenuated by 95%, so that the effects at the bottom edge are negligible and reflections or boundary conditions at the back contribute only minimally to the surface response. According to Eq. (1), this results in the lower limit of the linear regime at $\omega_{\min} = 9\alpha/2t^2$, or $f_{\min} = 9\alpha/4\pi t^2$ in terms of frequency.

Let us consider the lateral heat flow and determine the upper frequency range in which these effects are negligible and the heat flow can actually be considered vertical and 1-dimensional. This simplification makes the mathematical modeling straightforward and the interpretation of the data reliable. We can approximate the temperature decay laterally from the heater as an exponential value $\Delta T(x) \propto e^{-xq}$. Let us define the maximum frequency as one corresponding to a thermal penetration depth of 3 half-widths, $q^{-1} = 3b$. The temperature drop at the lateral distance of 3 half-widths at this frequency is $\Delta T(3q^{-1}) = \Delta T_0 e^{-1} \approx 0.37 \Delta T_0$. In this case, the amplitude of the temperature oscillations decreases to 37% of its value in the center of the heater, which gives us the upper frequency limit of $\omega_{\max} = \alpha/18b^2$ or $f_{\max} = \alpha/36\pi b^2$ in terms of frequency.

From this we derive the theoretical linear frequency range:

$$\frac{9\alpha}{4\pi t^2} \leq f_{\text{linear}} \leq \frac{\alpha}{36\pi b^2} \quad (\text{A.2})$$

Consider a soda lime glass substrate with a thickness of 1000 μm on which a metal strip with a half-width of 3 μm lies. The substrates are cut from a single soda-lime glass slide supplied by Marienfeld [26]. The relevant properties of soda-lime glass are [33]: $c_p = 0.87 \text{ J g}^{-1} \text{ K}^{-1}$ for the specific heat capacity, $\rho = 2.5 \text{ g cm}^{-3}$ for the density and $\kappa = 1.06 \text{ W m}^{-1} \text{ K}^{-1}$ for the thermal conductivity. If we substitute the values into Eq. (2), we get $\alpha = 4.9 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ for the diffusivity.

Finally, we can assume the linear frequency range for this sample to be:

$$0.351 \text{ Hz} \leq f_{\text{linear}} \leq 481 \text{ Hz}.$$

Thermal conductivity, specific heat capacity and mass density vary as functions of temperature, thus the thermal diffusivity also becomes temperature-dependent. Consequently, the calculated linear frequency range will shift slightly due to these variations. Thus, the expected linear response of the voltage of the third harmonic $V_{3\omega}$, with respect to the logarithm of the second harmonic, $\ln(2\omega)$, extends over three orders of magnitude as shown above. It is worth noting that the reported limits for the linear frequency range [5] are that the sample thickness is at least $5q^{-1}$ for the lower frequency limit, and the thermal penetration depth of five times the half-width of the heater for the upper limit. In our setup, the actual linear range is less restrictive than these conventionally imposed limits. The linearity criteria derived here are more representative of the experimental conditions specific to this measurement setup, and the conventionally measured frequencies still fall within this relaxed range. In practice, however, both the lower and upper limits are higher. The heater acts as a linear or strip source, so the heat spreads in all directions. The presence of the surface at $z = 0$ limits the heat flow above the surface and “reflects” the heat back into the material. This causes the heat to penetrate deeper into the material in the z direction, while it spreads less in the x direction. By introducing the thermal mass of the copper to which the sample is attached, the underside of the sample goes from adiabatic to isothermal, further reducing lateral heat flow effects and allowing larger metal strip widths at frequencies suitable for measurement.

Appendix B. Arduino code to enable 16-bit resolution PWM output and software control of the photoresistor resistance via serial

```
void setup() {
  Serial.begin(9600);
  setupPWM16();

  pinMode(9, OUTPUT);
  pinMode(10, OUTPUT);

  analogWrite16(9,45000); // First optoisolator,
    manual adjustment
  analogWrite(10,65535); // Second optoisolator,
    automated adjustment
}

uint16_t icr = 0xffff;

unsigned int integerValue = 0; // Max value is 65535
char incomingByte;
unsigned int setLDR = 0; // LDR = light dependent resistance

void loop() {
  // reads 0 to 65535 from serial port
  //corresponding to 0 to 5V or 0 to 20mA
  if (Serial.available() > 0) {
    // something came across serial

    integerValue = 0; // throw away previous integerValue
    // Arduino receives the integer over serial byte by byte
    while (1) { // force into a loop until 'n' is received
      incomingByte = Serial.read();
      // exit the while(1), we're done receiving
      if (incomingByte == '\n') break;
      // if no characters are in the buffer read() returns -1
      if (incomingByte == -1) continue;

      // shift left 1 decimal place
      // convert incoming ASCII to integer
      integerValue = integerValue * 10 + (incomingByte - 48);
      delay(2);
    }
    setLDR=integerValue;
  }
}
```

```
    analogWrite16(10, setLDR); // set resistance
  }
}

void setupPWM16() {
  DDRB |= _BV(PB1) | _BV(PB2); // set pins as outputs
  TCCR1A = _BV(COM1A1) | _BV(COM1B1) // non-inverting PWM
    | _BV(WGM11); // mode 14: fast PWM, TOP=ICR1
  TCCR1B = _BV(WGM13) | _BV(WGM12)
    | _BV(CS10); //prescaler 1
  ICR1 = icr; // TOP counter value (freeing OCR1A
}

// 16-bit version of analogWrite().
Set up only on pins 9 and 10.
void analogWrite16(uint8_t pin, uint16_t val) {
  switch (pin) {
    case 9: OCR1A = val; break;
    case 10: OCR1B = val; break;
  }
}
```

Data availability

Data will be made available on request.

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LIST OF PUBLICATIONS

Publication related to the thesis

- Kabaši, A., Šćurla, J., and Bilušić, A., “Automated 3ω thermal conductivity measurement system by dynamically balanced Wheatstone bridge,” *Measurement*, vol. 257, 118830, 2026. DOI: [10.1016/j.measurement.2025.118830](https://doi.org/10.1016/j.measurement.2025.118830). The article is reproduced in Appendix D.

Other publications

- Bunčić, N., Kabaši, A., Čakarić, T., and Bilušić, A., “Prototyping of a high frequency phased array ultrasound transducer on a piezoelectric thick film,” *Informacije MIDE*M, vol. 49, no. 1, pp. 3–9, 2019. DOI: [10.33180/InfMIDEM2019.101](https://doi.org/10.33180/InfMIDEM2019.101).
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