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On the local constitutive convolution and graph theoretical representations of thermodynamic processes

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ABSTRACT

A thermodynamic processes can be represented as either a local constitutive relationship or as a directed graph network. It is demonstrated that only the local constitutive equations yield, for all cases considered, the correct values for the physical properties of the materials under test, whereas the directed graph network representations are unreliable. This is because the directed graph network representations can be ill posed and likely to lead to erroneous values for the transport coefficients. The local constitutive equations allow the measurement of the linear and nonlinear transport properties under dynamical conditions. The response function values are estimated directly from the time series data of the physical observables and the area under the response function is equal to the equilibrium transport coefficient value. The nonlinear temporal form of the multidimensional convolution representation is also given and used to estimate the linear and nonlinear thermal transport coefficients of materials with low thermal conductivities. The nonlinear analysis shows that the one dimensional thermal conductive transport is linear within the experimental uncertainties for a range of material types whose conductivity spans three orders of magnitude.

Introduction

A local thermodynamic system which is embedded in an open environment experiences a set of thermodynamic potentials, whose gradients cause the exchange of carriers between the local system and the environment. These are called the thermodynamic forces and fluxes respectively. In the majority of thermodynamic systems found in nature, the relationships between the physical observables are multivariate complex and often nonlinear.

In this work thermodynamic systems are initially considered to be linear transport processes. Two alternative hypotheses exist for the representation of thermodynamic transport, local constitutive and directed graph network. These two hypotheses were tested for the most simple thermodynamic case of one dimensional thermal conductive transport in a homogeneous sourceless solid. Both representations were able to accurately characterise the observed behaviour. However, only the local constitutive representation was consistently able to determine accurate values for the thermal conductivity of a wide range of solid materials.

An engineering test facility was used to measure the one dimensional thermal conductivity of a range of solid homogeneous materials. The experiments were performed under dynamical meteorological boundary conditions. The time series data for both sets of boundary conditions was analysed by two representations and compared to the ratio of mean's method and published data. This enabled the direct comparisons to be made between the two representations. Time series representations for linear and nonlinear local constitutive relations are given together with the moment hierarchy method of solution [1]. This allows the linearity of one dimensional thermal conduction to be quantitatively examined.

Representations of the thermodynamic process

The two representations used are:

1. the local constitutive, or dynamic Onsager, representation, where the local one dimensional heat flux in the solid material is assumed to be related to the historical temperature gradients.
2. the graph network, or Peusner, representation, where the heat flux and temperature gradient in one region is related to the historical heat flux and temperature gradient values in another region of the solid.

The moment hierarchy method [1] is used to calculate the coefficients for each of these representations.

The local constitutive representation

An observed thermodynamic flux can be characterised in terms of the observed thermodynamic forces and observed properties of the medium. The equilibrium constants of proportionality are called the transport coefficients and represent the gains of the independent variable to the dependent variables. It is usually assumed that the thermodynamic fluxes, $\{J_k(t)\}$, depend on the set of thermodynamic forces, $\{F_i(t)\}$, and that each of the thermodynamic flux can be written as a multidimensional function of the forces, with

$$J_k(t) = J_k(F_1, \dots, F_A) \quad (1)$$

The linear equilibrium transport properties can be described by the irreversible thermodynamic equations of Onsager [2,3]. The linear constitutive equations relate the independent thermodynamic fluxes, $\{J_k(t)\}$, in terms of their conjugate thermodynamic forces, $\{F_i(t)\}$, and a set of linear equilibrium Onsager coefficients, L_{ik} , with

$$J_k(t) = \sum_i L_{ik} F_i(t) \quad (2)$$

The Onsager formalism can be extended to the equilibrium nonlinear case [4,5] by suitably truncating an ascending order of a multidimensional Taylor's series expansion with

$$J_k(t) = \sum_i L_{ik} F_i(t) + \frac{1}{2!} \sum_i \sum_j L_{ijk} F_i(t) F_j(t) + \dots \quad (3)$$

where the transport coefficients are given by

$$L_{ik} = \left(\frac{\partial J_k}{\partial F_i} \right)_0 \quad \text{and} \quad L_{ijk} = \left(\frac{\partial^2 J_k}{\partial F_i \partial F_j} \right)_0$$

In both the linear and the nonlinear cases the transport coefficients are difficult to determine experimentally. In addition, they do not provide any information about the dynamics of the process and, as expected, their values cannot be derived from purely theoretical grounds. Indeed, although Onsager's theory [2,3] is based on Einstein's analysis of the statistical fluctuations of Brownian motion [6,7] there are examples of Onsager's reciprocities which hold far from equilibrium and there are many examples where the reciprocities do not hold, even in equilibrium [8].

The most simple case to study is the one dimensional heat conduction experiment. The Fourier law relates the heat flux at a given point in a one dimensional solid to the local temperature gradient at the same point. In the linear approximation the heat flux is proportional to the local temperature gradient, with the constant of proportionality being called the thermal conductivity. The thermal conductivity has a minus sign as the heat flux will flow against the temperature gradient, with

$$J_k(x, t) = -\kappa \nabla T_k(x, t) \quad (4)$$

A heat flux flowing in one part of a solid will change the local temperature and temperature gradient. In the Fourier law approximation, this change of temperature will be felt instantaneously at every field point in the solid, no matter how remote. This property of infinite propagation is unphysical and the above form of the Fourier law provides only an approximation to the actual laws which govern the thermal transport in solids. Cattaneo [9] was the first to explicitly modify the Fourier equation in order to correct for this problem, writing

$$\tau \frac{\partial J_k(x, t)}{\partial t} = -\kappa J_k(x, t) - \kappa^2 \nabla T(x, t) \quad (5)$$

where τ is the relaxation time of the process and where κ is the conductivity of the solid.

Gurtin and Pipkin [10] developed a realistic field theory for heat conduction using constitutive assumptions that lead to finite propagation speeds. Their field theory is based on a Volterra functional expansion with the discrete linearised constitutive equation for the heat flux in terms of the local temperature gradient being

$$J_k(x, t) = \sum_{\sigma=0}^t L_{J_k \nabla T}(t - \sigma) \nabla T(x, \sigma) d\sigma \quad (6)$$

where $L_{J_k \nabla T}(\sigma)$ is the first order Volterra kernel function.

Chen and Nunziato [11] used the second law of thermodynamics to show that the thermal conductivity must be positive definite with

$$\kappa = \sum_{\sigma=0}^t L_{J_k \nabla T}(\sigma) > 0 \quad (7)$$

where κ is the thermal conductivity of the solid.

The nonlinear nonequilibrium behaviour of a macroscopic thermodynamic process can be described as a functional expansion of physically observable causal time series quantities. The kernel functions of the convolution expansion represent the dynamic nonlinear transport coefficients [12]. The integral of the kernel function values yields the equilibrium gain between the observables [1] and are equivalent to the ascending kinetic of Burnett coefficients of nonlinear equilibrium thermodynamics.

For example, if there is only a single thermodynamic force, $\{F_1(t)\}$, acting and the properties of the medium are constant and if the process possesses a finite memory of duration μ , then a single component of a thermodynamic flux, $\{J_k(t)\}$, can be written as a discrete Volterra functional expansion with

$$J_k(t) = \sum_{n=1}^N \frac{1}{n!} \sum_{\sigma_1=0}^{\mu} \dots \sum_{\sigma_n=0}^{\mu} L_{J_k F_1^n}(\sigma_1, \dots, \sigma_n) \prod_{i=1}^n F_1(t - \sigma_i) \quad (8)$$

where N is the order of the system, where t denote time and where the σ_i 's denotes time delay with respect to the time t and where the kernel function values, $L_{J_k F_1^n}(\sigma_1, \dots, \sigma_n)$, characterise the behaviour of the process.

The kernel function values, $L_{J_k F_1^n}(\sigma_1, \dots, \sigma_n)$, represent the temporal response of the flux, $\{J_k(t)\}$, to the thermodynamic force, $\{F_1(t)\}$, are can be defined as the dynamic kinetic coefficients. Integrating these response functions yields the linear and nonlinear gain between the dependent and independent variables [1], with

$$L_{J_k F_1^n}^*(n) = \sum_{\sigma_1=0}^{\mu} \dots \sum_{\sigma_n=0}^{\mu} L_{J_k F_1^n}(\sigma_1, \dots, \sigma_n) \quad (9)$$

which are equivalent to the higher order kinetic or Burnett transport coefficients.

Equation (8) provides a local multidimensional convolution representation of the constitutive relationship between the thermodynamic flux, $\{J_k(t)\}$, and the local thermodynamic force, $\{F_l(t)\}$. The dynamic and equilibrium values of the transport coefficients can be estimated from the data in order to characterise the properties of the experimental data. Alternatively the formalism can be used for theoretical investigations, where the form of the kernel functions is chosen and the thermodynamic behaviour determined for specific cases. The single input temporal formalism given above can be generalised to the multivariate case.

The directed graph network representation

An alternative description is to characterise the relationship between subsystems within the thermodynamic environment by directed graph networks. The most simple thermostatic network case to examine is the relationship between the heat flux and the temperature field measured on each side of a plane parallel homogeneous slab.

Recently Peusner [13,14,15,16], has developed the thermostatic directed graph network formalism for the multiple thermal subsystem case. In that work the elements of the transfer matrices are assumed to be equal to the partial derivatives of the thermodynamic equations of state when equilibrium conditions prevail, with several thermodynamic variables being assumed to be held at constant values.

Peusner used elements of linear topology and graph theory to develop a directed graph network representation of thermostatic systems. That approach is in direct analogy to the network and graph theoretical methods developed for linear electrical circuits. Kirchhoff's law's are used to obtain a suitable, but not unique [15], set of equations to describe the thermal flows.

Peusner considers a variety of network forms, in particular vector of thermodynamic fluxes in terms of the vector of thermodynamic forces with

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = \begin{bmatrix} G_{J_1 F_1} & G_{J_1 F_2} \\ G_{J_2 F_1} & G_{J_2 F_2} \end{bmatrix} \begin{bmatrix} F_1 \\ F_2 \end{bmatrix} \quad (12)$$

and hybrid forms relating the thermodynamic force and flux at each port, with

$$\begin{bmatrix} J_1 \\ F_1 \end{bmatrix} = \begin{bmatrix} H_{J_1 J_2} & H_{J_1 F_2} \\ H_{F_1 J_2} & H_{F_1 F_2} \end{bmatrix} \begin{bmatrix} J_2 \\ F_2 \end{bmatrix} \quad (13)$$

Linear temporal response function estimation

The dynamic form of the local constitutive representation is considered to be a linear convolution equation which describes the one dimensional heat conduction in an isotropic solid which contains no sources of heat. It is assumed that the heat flux observed can be expressed as a convolution between the observed heat flux, $\{J_k(t)\}$, the local temperature gradient, $\{\nabla T(t)\}$, and the linear temporal response function, $L_{J_k \nabla T}(\sigma_1)$. In this example it is assumed that the process is linear and time invariant, and that the local heat flux and temperature gradient provide a complete description of the heat transport process. For a discrete process which possesses a finite memory of duration μ , the convolution can be expressed as

$$J_k(t) = \sum_{\sigma_1=0}^{\mu} L_{J_k \nabla T}(\sigma_1) \nabla T(t - \sigma_1) \quad (14)$$

where σ_1 denotes lag and where μ is the finite memory of the conductive process in the system. This is a scalar equation and assumes that the heat flux has only one variable, the temperature gradient, which is the force which drives the heat flux. The response function, $L_{J_k \nabla T}(\sigma_1)$, is related to the equilibrium thermal conductivity, κ_1 , with

$$\kappa_1 = \sum_{\sigma_1=0}^{\mu} L_{J_k \nabla T}(\sigma_1) \quad (15)$$

As it stands, equation (14) is ill posed, in the sense that there are too many unknown coefficients. In addition, equation it is ill conditioned because it has dependent and independent variables that are stochastic functions of time. By operating on equation (14) with the averaging operator $\langle \nabla T(t - \tau_1) * \rangle$ a tractable set of $(\mu+1)$ equations with well behaved coefficients is obtained which can be solved for the response function values. Explicitly the moment hierarchy is

$$M_{\nabla T J_k}(\tau_1) = \sum_{\sigma_1=0}^{\mu} L_{J_k \nabla T}(\sigma_1) M_{\nabla T \nabla T}(\tau_1, \sigma_1) \quad (16)$$

where $0 \leq \tau_1 \leq \mu$, where the cross and auto moments between the observed heat flux, $\{J_k(t)\}$,

and the temperature gradient, $\{\nabla T(t)\}$ are defined as $M_{\nabla T J_k}(\tau_1) = \sum_{t=0}^N \nabla T(t - \tau) J_k(t)$ and

$M_{\nabla T \nabla T}(\tau_1, \sigma_1) = \sum_{t=0}^N \nabla T(t - \tau) \nabla T(t - \sigma)$ respectively, and where N is the length of the data

sample. Equation (16) can be seen to be a linear algebra expression $\underline{c} = \underline{a}\underline{h}$, where \underline{a} is the auto moment matrix, \underline{c} is the cross moment vector and \underline{h} is the vector of response function values [1].

In the Peusner thermostatic network representation of a conducting slab of material both surfaces can simultaneously experience unsteady heat flux and temperature gradient conditions. If this case, then the network thermostatic equation for the heat flux at one surface, $\{J_1(t)\}$, can be related, by a superposition of convolution equations, to the temperature gradient, $\{\nabla T_2(t)\}$, and the local heat flux, $\{J_2(t)\}$, at the opposite boundary.

The network equation connecting the two external surface regions is given by the convolution equation

$$\begin{vmatrix} J_1(t) \\ \nabla T_1(t) \end{vmatrix} = \begin{vmatrix} H_{J_1 J_2}(\sigma_1) & H_{J_1 \nabla T_2}(\sigma_1) \\ H_{\nabla T_1 J_2}(\sigma_1) & H_{\nabla T_1 \nabla T_2}(\sigma_1) \end{vmatrix} \begin{vmatrix} J_2(t - \sigma_1) \\ \nabla T_2(t - \sigma_1) \end{vmatrix} \quad (17)$$

The equation for the heat flux is explicitly given by the superposition of two linear convolution terms with

$$J_1(t) = \sum_{\sigma_1=0}^{\mu} H_{J_1 J_2}(\sigma_1) J_2(t - \sigma_1) + \sum_{\sigma_1=0}^{\mu} H_{J_1 \nabla T_2}(\sigma_1) \nabla T_2(t - \sigma_1) \quad (18)$$

and the equilibrium thermal conductivity, κ_2 , and the heat flux gain, ψ_2 , for the network representation will be given by

$$\kappa_2 = \sum_{\sigma_1=0}^{\mu} H_{J_1 \nabla T_2}(\sigma_1) \text{ and } \psi_2 = \sum_{\sigma_1=0}^{\mu} H_{J_1 J_2}(\sigma_1) \quad (19)$$

The moment hierarchy in this case are given by the simultaneous equations

$$M_{\nabla T_2 J_1}(\tau_1) = \sum_{\sigma_1=0}^{\mu} H_{J_1 J_2}(\sigma_1) M_{\nabla T_2 J_2}(\tau_1, \sigma_1) + \sum_{\sigma_1=0}^{\mu} H_{J_1 \nabla T_2}(\sigma_1) M_{\nabla T_2 \nabla T_2}(\tau_1, \sigma_1) \quad (20)$$

and

$$M_{J_2 J_1}(\tau_1) = \sum_{\sigma_1=0}^{\mu} H_{J_1 J_2}(\sigma_1) M_{J_2 J_2}(\tau_1, \sigma_1) + \sum_{\sigma_1=0}^{\mu} H_{J_1 \nabla T_2}(\sigma_1) M_{J_2 \nabla T_2}(\tau_1, \sigma_1) \quad (21)$$

For both representations, the response function values obtained using the time series techniques can then be used to provide a prediction of the local heat flux, $\{J_p(t)\}$, field which may be compared with the measured heat flux, $\{J_1(t)\}$. This provides a sensitive measure of the quality of the response function characterisation of the thermal transport process, both for the region of data which were used to estimate the response function values and for regions of data that were not used in the estimation process. 10

Experimental facility for low thermal conductivity solid materials

The experimental arrangement shown in figure 1 was designed to measure the thermal conductivity of a range of material types. Different sized samples were required to measure the thermal conductivity, the dimensions for each material type were determined using a two dimensional finite element model was used. This allowed an optimisation of sample size and establishing the best positions of the sensors.

Essentially the rig consists of a copper heat pipe to a cold temperature bath which is controlled and another copper heat pipe to atmospheric conditions which gives a damped stochastic heat flux at the surface of the sample under test. The cold bath is an enclosed copper heat exchanger that has cold water pumped through it. The absolute temperatures are measured with Platinum resistance thermometers and the heat fluxes are measured with thermopiles. The cold bath is an enclosed copper heat exchanger that has cold water pumped through it. The cooling of the water is achieved by using a commercial water chiller. The water is re-circulated through the chiller. The water temperature is fixed at 10.0 ± 0.02 °K. The temperature and heat flux are measured at positions above and below the as shown in figure 1. The test section is surrounded by loose vermiculite insulation. The insulation is contained within a 500 mm square enclosure.

The readings are taken every ten seconds over an eleven hour period, the time interval for data collection being determined by the response time of the sensors used. The experiments take place at the same time of night to minimise external interference. During the test period 4,000 sets of measurements are taken. Of these 4000 points, some 2000 are used to estimate the response function values of the process and the remaining 2000 points are used to compare with the values of the heat flux predicted using the estimated response function values

Linear analysis of the thermal conductivity data

The thermal conductivity of each sample was determined using the two representations. These conductivity values estimated using the field theoretical and the thermostatic network representations were compared with the values obtained from the literature.

These estimated values were used to predict the future behaviour of the heat flux at the surface of the sample. These predicted heat flux values are then compared with the actual observed values. The response function values obtained using the time series techniques can then be used to provide a prediction of the local heat flux, $\{J_p(t)\}$, field which may be compared with the measured heat flux, $\{J_1(t)\}$, which were not used to estimate the transport coefficients. This provides a sensitive measure of the quality of the response function characterisation of the thermal transport process, both for the region of data which were used to estimate the response function values and for other data sets which were not used in the estimation process. The accuracy of the modelling ability was determined by dividing the mean difference between actual, $\{J_1(t)\}$, and predicted, $\{J_p(t)\}$, time series sequences by the variance between them, that is, the students t-test is used for the test statistic.

In all cases the values of the test statistics for the differences between the measured, $\{J_k(t)\}$, and predicted, $\{J_p(t)\}$, output heat flux for both modelled and predicted data lay well within the acceptance region of the univariate Students t-test statistic. Thus each of the representations accurately quantifies the observed behaviour of the heat flux.

The important thing is to determine which of the two representations yielded physically meaningful and consistent values for the transport coefficients.

The values of the estimated one dimensional thermal conductivity from sample material spanning three orders of magnitude are presented in table 1. Each column contains the values from the analysis of a single sample of time series data from a single sample of the material. The experimental uncertainties given are dominated by the calibration accuracy of the heat flux mats.

Table 1: Estimated thermal conductivities of a range of materials

	local constitutive	directed graph network		Literature value
	κ_1 W /m °K	κ_2 W /m °K	Ψ_2 flux gain	W /m °K
stainless	12.2	12.2	0.0013	14.0
steel	± 0.11	± 0.17	± 0.0011	± 0.07
glass	0.827	0.078	1.007	1.00
	± 0.0	± 0.02	± 0.023	± 0.05
glass reinforced polyester	0.191	0.056	0.356	0.23
	± 0.020	± 0.009	± 0.05	± 0.03
cork	0.050	0.047	0.95	0.050
	± 0.005	± 0.005	± 0.10	± 0.006

The values of the estimated one dimensional thermal conductivity from four different samples of stainless steel are presented in tables 2 and 3. Each column contains the values from the analysis of a single sample of 400 points of time series data from a single sample of the material.

Table 2: Estimated thermal conductivity of four different samples of glass

	local constitutive	directed graph network		Literature value
Glass sample No.	κ_1 W/m °K	κ_2 W/m °K	Ψ_2 flux gain	W/m °K
1	0.827 ± 0.04	0.064 ± 0.010	0.949 ± 0.05	1.0 ± 0.05
2	0.611 ± 0.04	0.783 ± 0.08	-0.324 ± 0.05	1.0 ± 0.05
3	0.653 ± 0.05	0.668 ± 0.08	0.002 ± 0.001	1.00 ± 0.05
4	0.720 ± 0.04	0.122 ± 0.04	0.706 ± 0.04	1.00 ± 0.05

The values of the estimated one dimensional thermal conductivity from four different samples of cork are presented in table 3.

Table 3: Estimated thermal conductivity of four different samples of cork

	local constitutive	directed graph network		Literature value
cork sample No.	κ_1 W /m °K	κ_2 W /m °K	Ψ_2 flux gain	W /m °K
1	0.050 ± 0.005	0.047 ± 0.005	0.95 ± 0.10	0.050 ± 0.006
2	0.050 ± 0.005	0.039 ± 0.006	0.382 ± 0.05	0.050 ± 0.006
3	0.050 ± 0.005	0.0437 ± 0.006	0.135 ± 0.20	0.050 ± 0.006
4	0.050 ± 0.005	0.007 ± 0.002	1.218 ± 0.10	0.050 ± 0.006

It is clear that the local constitutive representation gives correct, accurate and consistent values for the conductivities over the whole range of materials considered. In contrast, whilst the directed graph network representation does give some correct and accurate conductivities for some materials, it is neither consistent nor accurate for the one dimensional thermal conductivity problem. The reason that the directed graph network representations are not consistent in this case and fail to give the correct answers for the thermal transport coefficients can be seen from the basic formulation of the problem, in that it is assumed the functional relationship is of the form

$$J_2(t) = f(J_1, \nabla T_1, t)$$

As the heat flow is approximately one dimensional through the slab of material then $J_2(t) \approx J_1(t)$ and the equation is ill posed, as it can be written as

$$J_2(t) \approx J_2(t) + \delta(J_1, \nabla T_1, t) .$$

With hindsight this might seem self evident; however, there are a number of widely used calculation procedures' that use the directed graph network representation for the one dimensional flow problem. Obviously for higher dimensional flows each case will need to be examined in detail before a given representation is used.

Nonlinear local constitutive relationships

Consider representing a thermodynamic observable, for example a flux, $\{J_k(t)\}$, in terms of the local temperature gradient, $\{F_k(t)\}$. The flux, $\{J_k(t)\}$, can be represented as a multidimensional convolution expansion in terms of the thermodynamic force, $\{F_k(t)\}$, which in discrete form is given by

$$J_k(t) = \sum_{n=1}^N \frac{1}{n!} \sum_{\sigma_1=0}^{\mu} \dots \sum_{\sigma_n=0}^{\mu} L_{J_k F^n}(\sigma_1, \dots, \sigma_n) \prod_{i=1}^n F_k(t - \sigma_i) \quad (31)$$

where σ_i denotes time delay, and where the quadratic approximation used in the present work is given by

$$J_k(t) = \sum_{\sigma_1=0}^{\mu} L_{J_k F}(\sigma_1) F_k(t - \sigma_1) + \sum_{\sigma_1=0}^{\mu} \sum_{\sigma_2=0}^{\mu} L_{J_k F^2}(\sigma_1, \sigma_2) F_k(t - \sigma_1) F_k(t - \sigma_2)$$

The estimated response values $L_{J_k F^n}(\sigma_1, \dots, \sigma_n)$ characterise the heat flux in terms of the thermodynamic force acting. In order to solve the propagation problem there is a need to generate a sufficient set of simultaneous equations whose number is equal to the total number of unknown response values. In this case the moment hierarchy is given by [1,12]

$$\langle \prod_{j=1}^m F_k(t - \tau_j) J_k(t) \rangle = \sum_{n=1}^N \frac{1}{n!} \sum_{\sigma_1=0}^{\mu} \dots \sum_{\sigma_n=0}^{\mu} L_{J_k F^n}(\sigma_1, \dots, \sigma_n) \langle \prod_{j=1}^m F_k(t - \tau_j) \prod_{i=1}^n F_k(t - \sigma_i) \rangle \quad (32)$$

where $\langle * \rangle$ denotes the averaging operation and this multivariate moment hierarchy is solved by standard matrix methods.

The above formulation is general and can be applied to a wide range of situations. Equation (31) is used below to analyse the thermal conduction process in a solid to indicate if conduction is a linear or a nonlinear process.

Nonlinear analysis of the thermal conductivity data

The thermal conductivity of each sample was determined using linear and nonlinear forms of the local constitutive representation. These estimated values of the response functions are then used to predict the future behaviour of the heat flux at the surface of the sample. These predicted heat flux values are then compared with the actual observed values.

The values of the estimated thermal transport coefficients under equilibrium conditions are presented in table 4.

Table 4: Linear and nonlinear transport coefficients under equilibrium conditions

	Linear analysis κ_1 W/ m °K	Nonlinear analysis linear coeff κ_1 W/ m °K	Nonlinear analysis quadratic coeff κ_2 W / °K ²
stainless steel 1	12.20 ± 0.5	13.05 ± 0.7	-0.004 ± 0.002
stainless steel 2	12.20 ± 0.5	12.17 ± 0.67	-0.031 ± 0.010
glass 1	0.827 ± 0.04	1.06 ± 0.10	0.03 ± 0.010
glass 2	0.827 ± 0.04	1.06 ± 0.10	0.03 ± 0.010
glass reinforced polyester	0.191 ± 0.02	0.0952 ± 0.012	0.00015 ± 0.00002
glass reinforced polyester	0.190 ± 0.02	0.0954 ± 0.012	0.00014 ± 0.00002
cork	0.050 ± 0.005	0.100 ± 0.09	-0.004 ± 0.001
cork	0.050 ± 0.005	0.101 ± 0.09	-0.003 ± 0.0008

It is clear from table 4 that the one dimensional thermal conduction is linear in solid materials over a range of three orders of magnitude of thermal conductivity. The magnitude of the nonlinear component seems to increase as the value of thermal conductivity decreases, but at present no clear inferences can be made about this nor to the existence of any nonlinear mathematical relationship.

Conclusions

In this work the thermal transport conductivity for a range of different materials has been determined using the local constitutive and directed graph network representations. Thus two alternative hypotheses exist for the representation of thermodynamic transport, local constitutive and directed graph network. These hypotheses were tested for the most simple thermodynamic case of one dimensional thermal conductive transport in a homogeneous sourceless solid. Both representations were able to accurately characterise the observed behaviour. However, only the local constitutive representation gave consistent and accurate values for the materials examined. Although the directed graph network and the representation could produce accurate thermal transport coefficient values for some cases, it was shown not to be consistent because the representation is ill posed. For this reason, designs based on the directed graph network representation are not likely to accurately represent the actual thermodynamic performance for one dimensional flow situations.

The nature of one dimensional thermal conduction was then considered. Linear and mixed linear and nonlinear local constitutive representations were used to characterise the conduction process in a range of sample materials. The results of the nonlinear analysis of the one dimensional thermal conduction data show that the process is linear, within the experimental uncertainties, for materials which span three orders of magnitude of thermal conductivity.

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References

- [1] Irving A D, Stochastic Sensitivity Analysis, Applied Mathematical Modelling, Vol. 16, January, 1992, p 3-15.
- [2] Onsager L, Reciprocal relations in irrervisible processes, I, Phys. Rev., Vol. 37, 1931, p 405.
- [3] Onsager L, Reciprocal relations in irrervisible processes, II, Phys. Rev., Vol. 38, 1931, p 2665.
- [4] Callen H B, Thermodynamics, John Wiley, New York, 1960.
- [5] Evans D J and Morris G P, Statistical mechanics of nonequilibrium liquids, Academic Press, 1990.
- [6] Einstein A, Investigation on the theory of Brownian movement, Dover Publications, New York, 1960.
- [7] Onsager L and Machlup S, Fluctuations and irreversible processes, Phys. Rev., 91, 1953, p1505.
- [8] Miller D, On the experimental verification of the Onsager reciprocal relation, in Transport Phenomena in Fluids, ed. Hanley H, M. Dekker, New York, 1969.
- [9] Cattaneo C, Sulla conduzione de calore, Atti. del Semin. Mat. e. Fis. Univ., Modena, 3, 1948, p 3.

- [10] Gurtin M E and Pipkin A C, A general theory of heat conduction with finite speed waves, Arch. Ration. Mech. Anal, 31, 1968, p 113.
- [11] Chen P and Nunziato J, Thermodynamic restrictions on the relaxation functions of the theory of heat conduction with finite speed waves, Z. Angew. Math. Phys., 25, 1974, p 791.
- [12] Irving A D, Dewson T, Hong G and Cunliffe N, Non-linear Response function Estimation I: Mixed Order Case, RAL report RAL-91-067, 1991; also submitted to Applied Mathematical Modelling, 1993.
- [13] Peusner L, Network thermostatics, J. Chem. Phys., Vol. 83, No. 3, 1985, p 1276-1291.
- [14] Peusner L, A network thermostatic approach to Hill and King-Altman reaction diffusion kinetics, J. Chem. Phys., Vol. 83, No. 11, 1985, p 5559.
- [15] Peusner L, Global reaction: Diffusion coupling and reciprocity in linear asymmetric kinetic networks, J. Chem. Phys., Vol. 77, No. 11, 1982, p 5500.
- [16] Peusner L, Studies in network thermodynamics, Elsevier, Amsterdam, The Netherlands, 1986.

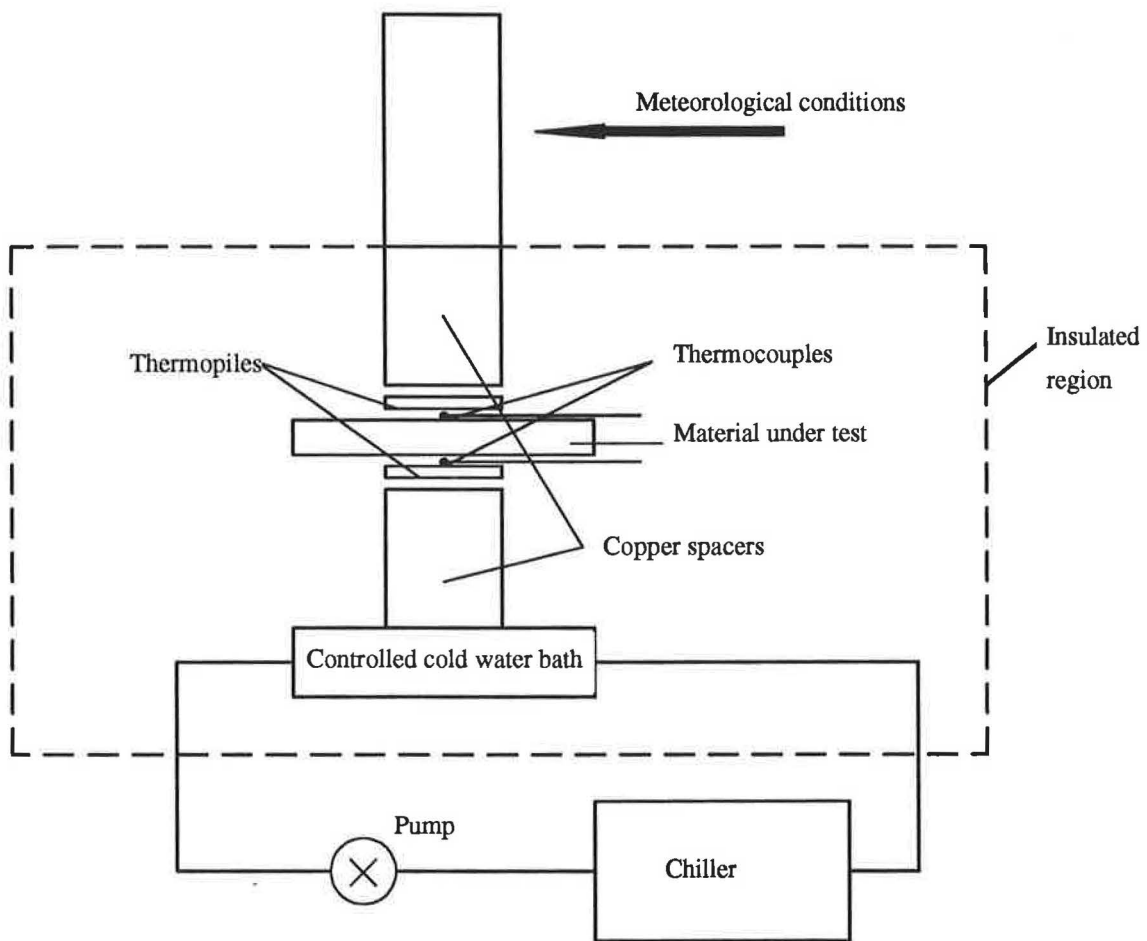


Figure 1. A schematic diagram of the experimental arrangement.

