Supplementary Information (SI) for New Journal of Chemistry.

Supplementary file

Anomalous increase in the thermal conductivity of water on the addition of liquid-exfoliated Magnesium Diboride sheets

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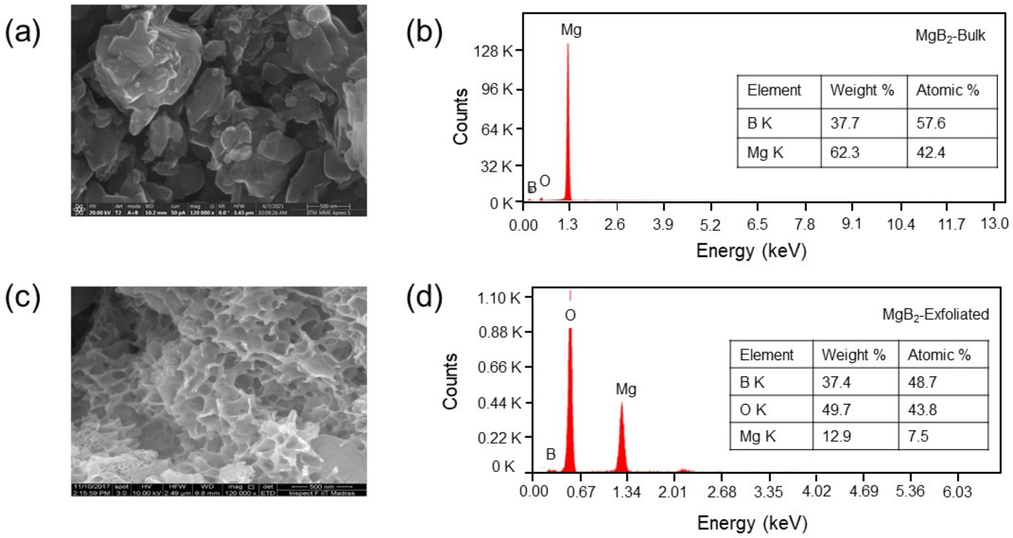
Morphology and composition of MgB_2 before and after exfoliation:



Element	Weight %	Atomic %
B K	37.7	57.6
Mg K	62.3	42.4

Element	Weight %	Atomic %
B K	37.4	48.7
O K	49.7	43.8
Mg K	12.9	7.5

Figure S1 (a) (b) SEM micrographs and (c) (d) EDAX signals of oven dried MgB_2 powder samples before and after exfoliation respectively.

The scanning electron microscope (SEM) image shown in Figure S1 indicates a significant transformation in the morphology and structure of MgB_2 after the liquid exfoliation process. As observed in Figure S1 (a), the initial morphology of MgB_2 prior to the exfoliation process comprises large agglomerates of powder particles with discernible thin sheets present in them. The energy-dispersive X-ray spectroscopy (EDAX) analysis depicted in Figure S1(b) reveals that the elemental composition of these agglomerates predominantly consists of boron and magnesium.

In contrast, the SEM image after exfoliation process, shown in Figure S1 (c) reveals the formation of thin, porous sheets thickness ranging from 5 – 30 nm with a mean dimension of (16.34 ± 6.16) nm, as detailed in the distribution plot in Figure S2. The EDAX spectra shown in Figure S1 (d) highlight a significant amount of oxygen alongside boron and magnesium, confirming below reaction,

$$MgB_2 + 2H_2O \rightarrow 2\, B - H + Mg(OH)_2$$

$$2\, B - H + 2H_2O \rightarrow 2\,(B - OH) + 2H_2\uparrow$$

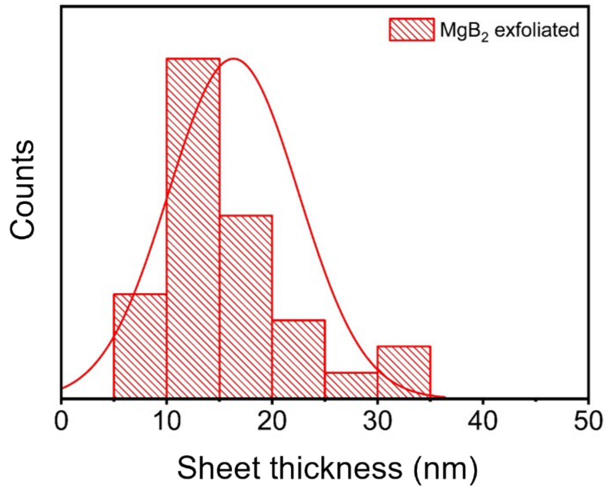


Figure S2 Sheet thickness normal distribution plot, Mean = 16.34 nm, Standard deviation = 6.16 nm.

HOT DISK Experiment:

The hot disk technique for the measurement of thermal properties of different samples uses a hot disk sensor, which is placed in the middle of the liquid sample holder as shown below:

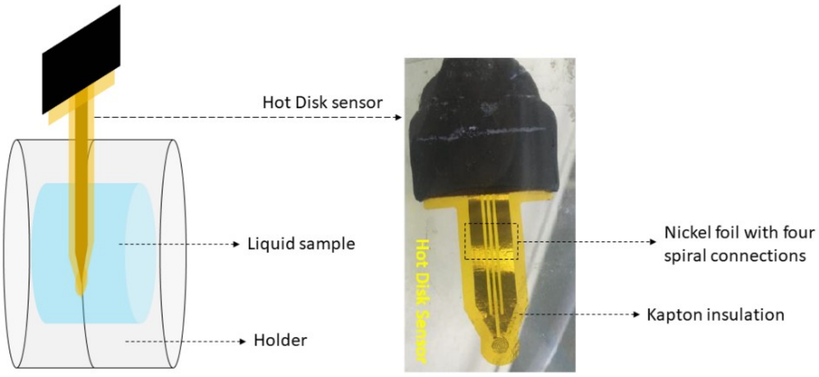


Figure S3 Shows a schematic of the liquid sample holder in the left panel and a pictograph of the hot disk sensor 7577 in the right panel. The sensor 7577 comprises a 2 mm radius with Kapton insulation to protect the Nickel sensor from the corrosive environment. As observed, the nickel sensor foil consists of four connections to the spiral end. The two closest to the spiral end carry the heating current, and the other two sense or control the voltage drop at the spiral end. The design is adjusted to the four-probe method for the measurement of resistance change during the transient heating of the sample, which is a measure to calculate the sample's thermal conductivity according to the equation: $R(t) = R_o\{1 + \alpha \cdot [\Delta T_i + \Delta T_s(\tau)]\}$ where, $R_o$is the resistance at t=0, α is the temperature coefficient of the resistivity, ΔT_i is the constant temperature difference that develops almost momentarily over the insulating layer and is the transient temperature $\Delta T_s(\tau)$. [Hotdisk TPS2500S manual].

The sensor used for the transient measurements was 7577. The control parameters for the measurements were sensor size, time, and heating power. The radius of 7577 sensors is 2 mm, which states that the probe depth ($\Delta_p \leq 2r$) of the measurement should be less than 4 mm. For the maximum measurement time calculation, thermal diffusivity (K) and probing depth (Δ_p) and the sensor size (r = 2 mm) are used according to the below equations:

$$\Delta_p = 2\sqrt{K.t}$$

For water, $K = 0.143$ mm^2 s^{-1}, that allows to use maximum measurement time of 28 s. The time used for all of the measurement here was 10 s.

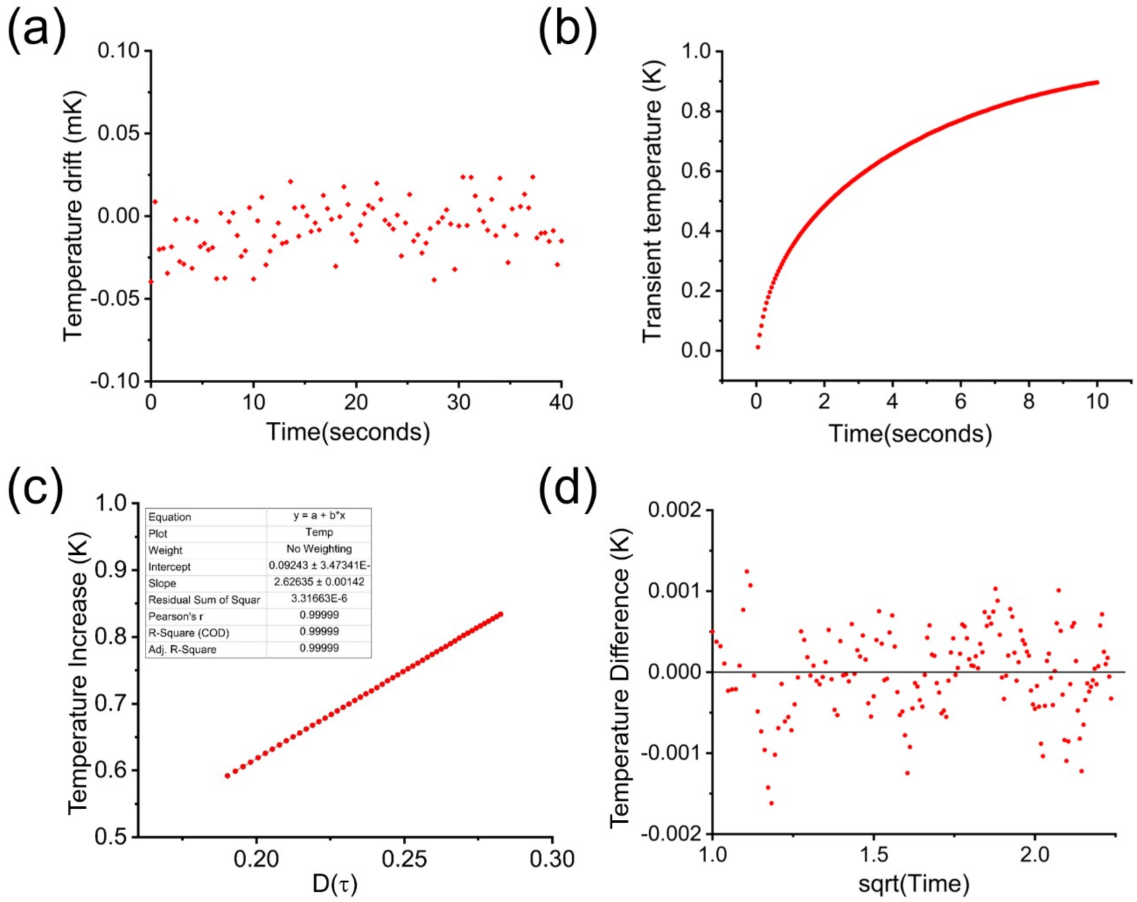
For the heating power, the starting point was estimated using the below transient temperature equation:

$$\Delta T_s(\tau) = P_o\left(\pi^{3/2} r \,.\, \lambda\right)^{-1} D(\tau)$$

Where, r = 2 mm, $\Delta T_s(\tau)$ is the transient temperature which relates to the boundary function $D(\tau)$ as $D(\tau) = 0.5\ \Delta T_s$, considering the situation when the sample has a limited extension in the direction perpendicular to the sensor for a good approximation. P_o is the heating power and λ is the approximate thermal conductivity of the sample which is in the case of water, 0.6 W/mK at 25 °C. Considering a typical value of temperature increase, like 1 K, it allows to use the power of approximately 30 mW. The heating power used for the measurements was 20 mW. The measurements are repeated minimum 5 times to attain less than 5% of standard deviation in the measured values from the plots. The calculations are done for the 4 seconds time range to avoid the effect of sensors and the boundary. (Note: After each measurement 15 mins of the rest time was given system to reach equilibrium state again before starting the new measurement).

HOT DISK Results:

Before data acquisition, the surrounding of the sample need to be stable which means temperature drift should be avoided. To achieve stable surrounding, a silicon oil bath was used with an automatic temperature controller setup. The controller of the silicon oil bath was allowed to run for 3 hours before starting the measurement at required temperature. Figure S4 is the DI water initial measurement collected after 3 hours of controller run time. Figure S4 (a) is the temperature drift plot showing the temperature variation over 40 seconds. The data point close to 0 K states the stability of the measurement system. Figure S4 (b) is the transient temperature plot representing the increase from 0-1 K range for the 20 mW heating power and 10 seconds measurement time. Figure. S4 (c) is the calculated transient plot depicting the optimal fit of the data points to the transient temperature equation: $\Delta T_s(\tau) = P_o\left(\pi^{3/2} r \, . \, \lambda\right)^{-1} D(\tau)$. Here the optimal linear fitting was found in the time interval of 1 to 2.5 sec. Figure. S4 (d) shows the residual plot between the calculated and measured data. A random scatter plot indicates the measurement in stable state.



Equation	y = a + b*x
Plot	Temp
Weight	No Weighting
Intercept	0.09243 ± 3.47341E-
Slope	2.62635 ± 0.00142
Residual Sum of Squar	3.31663E-6
Pearson's r	0.99999
R-Square (COD)	0.99999
Adj. R-Square	0.99999

Figure S4 graph showing the data obtained from hotdisk TPS2500S instrument (a) temperature drift (b) transient temperature increase (c) calculated transient temperature with linear fit plot using the equation: $\Delta T_s(\tau) = P_o\left(\pi^{3/2} r . \lambda\right)^{-1} D(\tau)$ where $P_o\left(\pi^{3/2} r . \lambda\right)^{-1}$ is the slope of the plot stating the inverse relation with the thermal conductivity (λ) and (d) residual plot of the calculation. The graphs are collected for DI water to check for stable surrounding and system stability.

The plots shown in Figure S5 are the calculated transient temperature of DI water and exfoliated MgB_2 added DI water at different volume fraction, ϕ (0.010, 0.012, 0.014, 0.016, 0.018, and 0.020). Table S1 shows the linear fit parameters and thermal conductivity of the respective volume fractions. The decrease in the slope with respect to the concentration states the increase in the thermal conductivity on addition of the MgB_2.

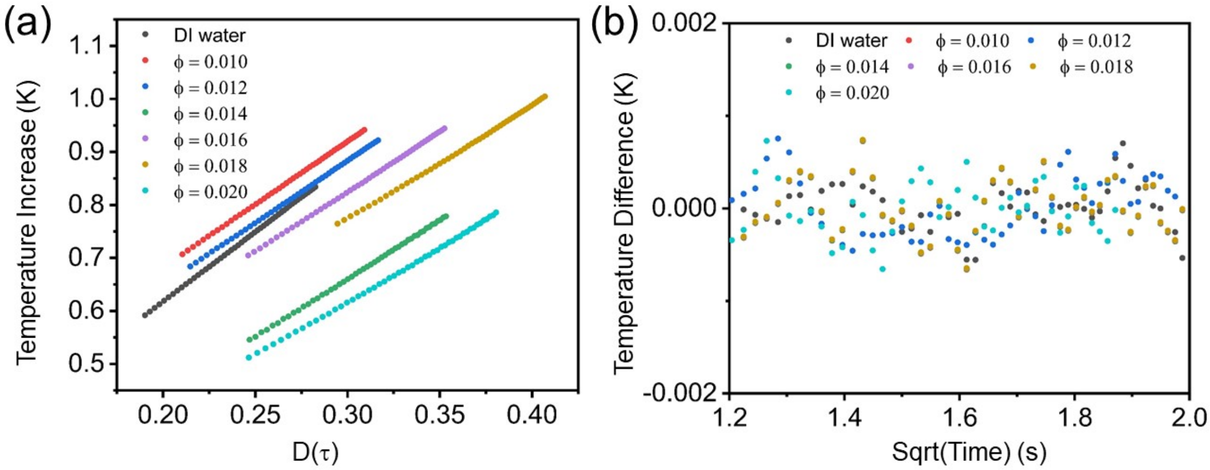


Figure S5 (a) transient temperature increase graph with function $D(\tau)$ showing decrease in the slope of the linear plots with increase in the concentration of the exfoliated MgB_2 sheets (b) residual plot showing the scattered points indicating the quality of the measurements.

Table S1 Linear fit parameters and thermal conductivity of the respective volume fractions in DI water.

Samples	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
DI water	2.626 ± 0.001	0.99999	0.596
MgB_2-DI water ϕ = 0.010	2.374 ± 0.001	0.99999	0.690
MgB_2-DI water ϕ = 0.012	2.340 ± 0.001	0.99999	0.710
MgB_2-DI water ϕ = 0.014	2.203 ± 0.004	0.99991	0.715
MgB_2-DI water ϕ = 0.016	2.255 ± 0.003	0.99995	0.722
MgB_2-DI water ϕ = 0.018	2.145 ± 0.006	0.99974	0.731
MgB_2-DI water ϕ = 0.020	2.040 ± 0.007	0.99969	0.742

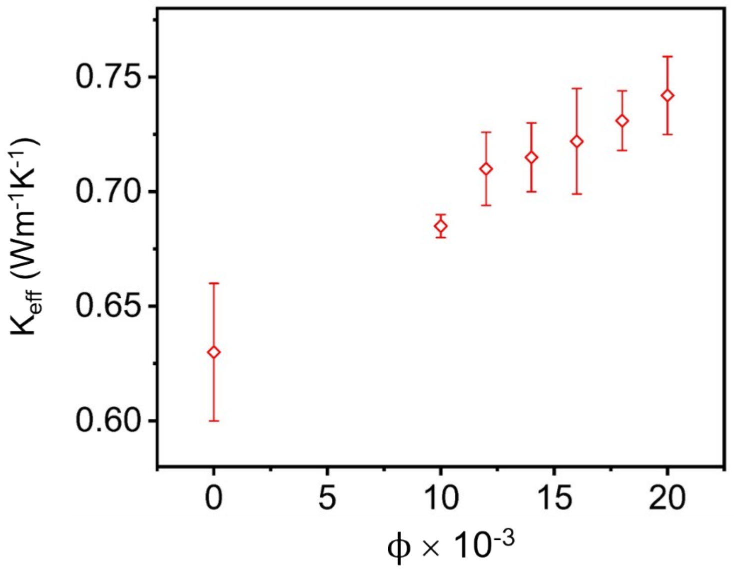


Figure S6 shows the increase in the effective thermal conductivity (K_{eff}) plot with volume fraction. The data points and error lines shown in the plot is an average and standard deviation of K_{eff} of 5 measurements with a rest time of 15 min after each measurement.

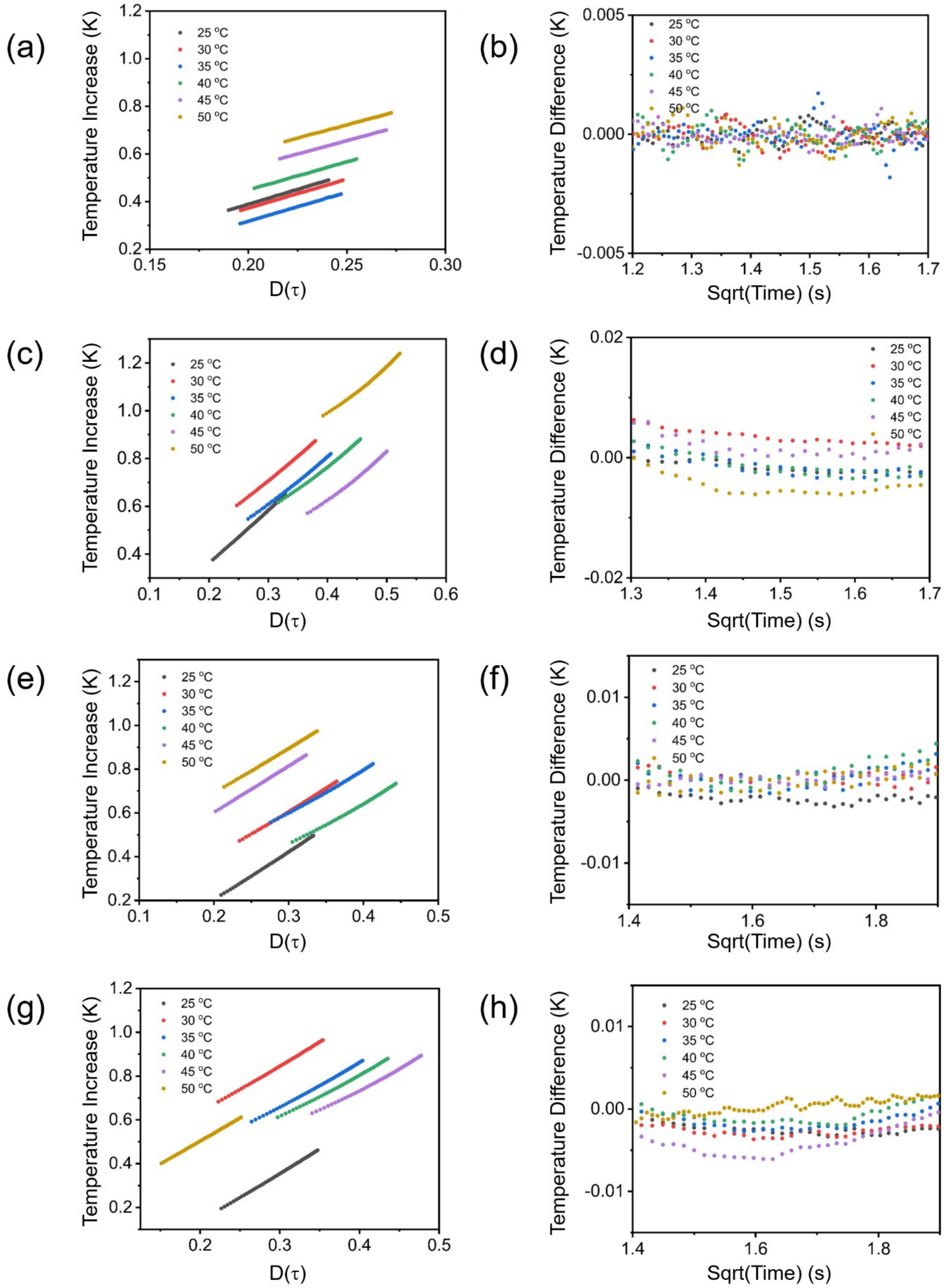


Figure S7 (a) transient temperature increase graph with function $D(\tau)$ with respect to increase temperature for (a) DI water (c) MgB_2-DI water ($\phi = 0.014$) (e) MgB_2-DI water ($\phi = 0.016$) (g) MgB_2-DI water ($\phi = 0.018$) and residual plot showing the scattered points indicating the quality of the measurements for (b) DI water (d) MgB$_2$-DI water ($\phi = 0.014$) (f) MgB$_2$-DI water ($\phi = 0.016$) and (h) MgB$_2$-DI water ($\phi = 0.018$) .

Table S2 Linear fit parameters and thermal conductivity of DI water at different temperatures.

Sample: DI water			
Temperature (°C)	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
25	2.498 ± 0.003	0.99991	0.598
30	2.432 ± 0.003	0.99989	0.661
35	2.430 ± 0.004	0.99985	0.665
40	2.356 ± 0.004	0.99980	0.684
45	2.238 ± 0.002	0.99992	0.721
50	2.224 ± 0.004	0.99980	0.723

Table S3 Linear fit parameters and thermal conductivity of MgB$_2$-DI water ($\phi = 0.014$) at different temperatures.

Sample: MgB$_2$-DI water ($\phi = 0.014$)			
Temperature (°C)	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
25	2.229 ± 0.003	0.99988	0.707
30	2.045 ± 0.006	0.99947	0.760
35	1.960 ± 0.009	0.99884	0.782
40	1.926 ± 0.013	0.99773	0.785
45	1.966 ± 0.018	0.99600	0.763
50	2.043 ± 0.020	0.99457	0.732

Table S4 Linear fit parameters and thermal conductivity of MgB$_2$-DI water ($\phi = 0.016$) at different temperatures.

Sample: MgB$_2$-DI water ($\phi = 0.016$)			
Temperature (°C)	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
25	2.210 ± 0.003	0.99987	0.714
30	2.096 ± 0.005	0.99962	0.743
35	1.959 ± 0.010	0.99875	0.782
40	1.939 ± 0.012	0.99804	0.782
45	2.125 ± 0.001	0.99996	0.763
50	2.055 ± 0.003	0.99982	0.787

Table S5 Linear fit parameters and thermal conductivity of MgB_2-DI water (ϕ = 0.018) at different temperatures.

Sample: MgB_2-DI water (ϕ = 0.018)			
Temperature (°C)	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
25	2.203 ± 0.004	0.99982	0713
30	2.154 ± 0.005	0.99973	0.732
35	2.007 ± 0.008	0.99920	0.765
40	1.950 ± 0.010	0.99849	0.763
45	1.944 ± 0.014	0.99717	0.775
50	2.099 ± 0.002	0.99995	0.762

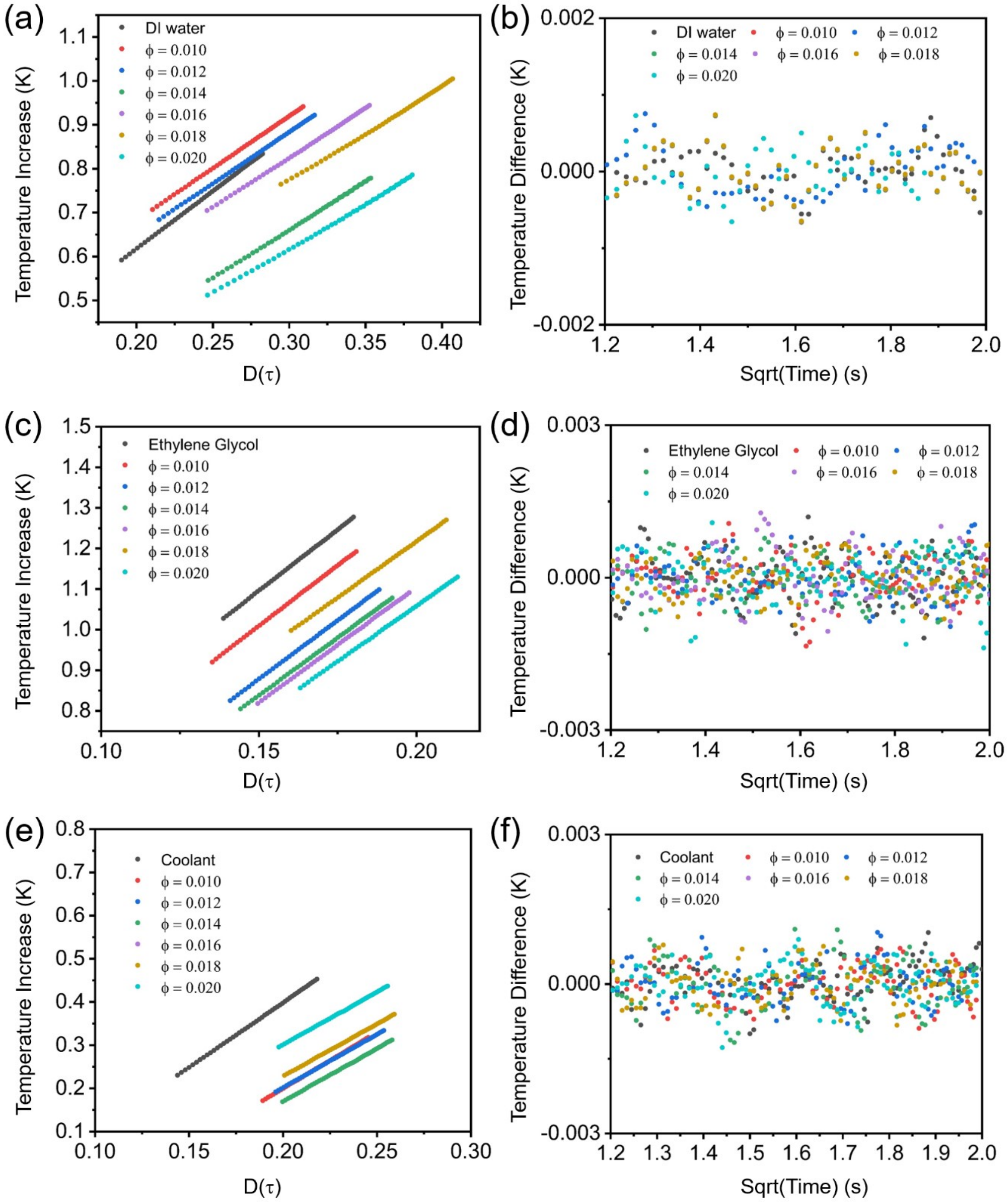


Figure S8 (a) transient temperature increase graph with function $D(\tau)$ with respect to increase temperature for (a) MgB$_2$-DI water (c) MgB$_2$-Ethylene Glycol (e) MgB$_2$-coolant and residual plot showing the scattered points indicating the quality of the measurements for (b) MgB$_2$-DI water (d) MgB$_2$-Ethylene Glycol and (f) MgB$_2$-coolant.

Table S6 Linear fit parameters and thermal conductivity of the respective volume fractions in DI water.

Samples	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
DI water	2.626 ± 0.001	0.99999	0.596
MgB_2-DI water ϕ = 0.010	2.374 ± 0.001	0.99999	0.690
MgB_2-DI water ϕ = 0.012	2.340 ± 0.001	0.99999	0.710
MgB_2-DI water ϕ = 0.014	2.203 ± 0.004	0.99991	0.715
MgB_2-DI water ϕ = 0.016	2.255 ± 0.003	0.99995	0.722
MgB_2-DI water ϕ = 0.018	2.145 ± 0.006	0.99974	0.731
MgB_2-DI water ϕ = 0.020	2.040 ± 0.007	0.99969	0.742

Table S7 Linear fit parameters and thermal conductivity of the respective volume fractions in Ethylene Glycol.

Samples	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
Ethylene Glycol (EG)	6.035 ± 0.005	0.99996	0.267
MgB_2-EG ϕ = 0.010	5.962 ± 0.005	0.99996	0.270
MgB_2-EG ϕ = 0.012	5.786 ± 0.003	0.99998	0.279
MgB_2-EG ϕ = 0.014	5.688 ± 0.004	0.99997	0.283
MgB_2-EG ϕ = 0.016	5.687 ± 0.005	0.99996	0.284
MgB_2-EG ϕ = 0.018	5.536 ± 0.003	0.99998	0.291
MgB_2-EG ϕ = 0.020	5.467 ± 0.004	0.99997	0.295

Table S8 Linear fit parameters and thermal conductivity of the respective volume fractions in DI water + Ethylene Glycol mixture (coolant) in the ratio of 70:30.

Samples	Slope	R^2 (COD)	Thermal conductivity, λ (W m^{-1} K^{-1})
coolant	3.000 ± 0.002	0.99997	0.538

MgB_2-coolant $\phi = 0.010$	2.597 ± 0.002	0.99997	0.621
MgB_2-coolant $\phi = 0.012$	2.466 ± 0.002	0.99993	0.655
MgB_2-coolant $\phi = 0.014$	2.452 ± 0.004	0.99986	0.658
MgB_2-coolant $\phi = 0.016$	2.423 ± 0.004	0.99987	0.667
MgB_2-coolant $\phi = 0.018$	2.418 ± 0.003	0.99991	0.668
MgB_2-coolant $\phi = 0.020$	2.437 ± 0.003	0.99991	0.664