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### Peltier tip calorimeter

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A novel calorimeter, termed as the Peltier tip calorimeter, is developed. The calorimeter consists of a single thermocouple junction, called the Peltier tip, which is used as a heater and a sensor simultaneously. We demonstrate that the Peltier tip calorimeter is capable of measuring the heat capacity of a small solid sample with submilligrams of mass and also the thermophysical properties of a liquid such as heat capacity and thermal conductivity. It is also proposed that a Peltier tip be used as a local calorimeter for scanning thermal microscopy. © 2006 American Institute of Physics. [DOI: 10.1063/1.2204584]

#### I. INTRODUCTION

Measurements of thermal properties, heat capacity, and thermal conductivity of condensed matter constitute one of the major characterizations of their physical properties, and thus calorimetry plays a crucial role in physics, chemistry, biology, etc. Heat capacity measurements, for example, allow one to directly monitor the free energy change of a given system as the external parameter such as temperature varies. Measurements of thermal conductivity of a solid at low temperatures offer a way to investigate the elementary excitations, which participate as heat carriers or limit the mean free path of heat carriers in the system. As for thermal conductivity of a liquid, it is essential to understanding the fundamental transport properties of the liquid, and its importance seems to grow further with the recent development of nanofluids.

ac calorimetry, initially developed in the 1960s, has been mainly used to measure heat capacity of a solid sample, in which a small amount of heat is supplied to the sample either by Joule heating or light heating and the ensuing temperature oscillation is measured at a judicially chosen frequency. 4-6 Recently we described a new type of ac calorimeter, the Peltier ac calorimeter (PAC);<sup>7</sup> the PAC utilizes a junction of very thin thermocouple wires as a heat source (Peltier effect) and a separate thermocouple junction as a sensor. By using very thin wires of 25  $\mu$ m (1 mil) or 12.5  $\mu$ m (1/2 mil) diameter we were able to avoid the addenda problem in the calorimeter, which limits accuracy in the case of measuring heat capacity of submilligram samples. Since it is obvious that an ac calorimeter has a potential of being a dynamic probe, the PAC was turned into a dynamic calorimeter and it was shown to possess a wide dynamic range, which is not achievable with traditional ac calorimeters.8

A pair of dissimilar metallic wires with a junction is

called a thermocouple and normally used as a temperature sensor. In using a thermocouple as a temperature sensor, the Seebeck effect is utilized. On the other hand, the reverse effect, i.e., the Peltier effect, is also well known; when an electric current flows in a thermocouple, the junction acts either as a heat source or a sink according to the current direction. Here we wish to demonstrate that a single thermocouple junction can work as a point heat source/sink and a temperature sensor simultaneously. We shall call a thermocouple used in this way the Peltier tip. We further show that the Peltier tip has a great potential as a calorimetric device and introduce a novel calorimetric method, termed as the Peltier tip calorimeter (PTC). This simple act of having only a single thermocouple in the calorimeter opens up new capabilities, perhaps at the expense of slightly less sensitivity; in addition to the functionality of the PAC, the PTC possesses excellent characteristics as a calorimeter for thermal characterization of liquids and the surface of solids. In the next section we will begin by expounding the principle of the Peltier tip calorimeter in detail, and then following is the description of the experimental performance of the calorimeter. These two sections constitute the core of this article. In the final section, various ideas for the use of the Peltier tip, including the Peltier thermal microscope, are proposed.

## II. PRINCIPLE OF THE PELTIER TIP CALORIMETER

Let us start with a situation illustrated in Fig. 1(a): A thermocouple consisting of two dissimilar wires,  $TC_L$  and  $TC_R$ , is connected to copper leads at  $P_1$  and  $P_2$  and has its junction in contact with a sample at  $P_3$ . When an ac electric current oscillating at angular frequency  $\omega$  ( $\equiv 2\pi f$ , where f is the frequency),  $I(t) = I_0 \cos(\omega t)$ , flows in the thermocouple, the voltage appearing between  $P_1$  and  $P_2$  may be expressed as

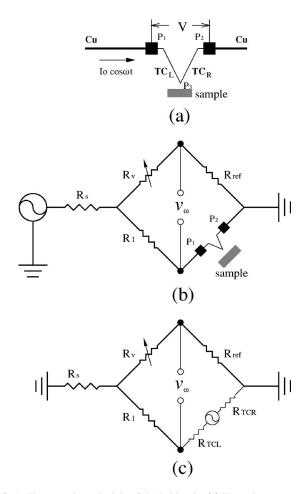


FIG. 1. The operation principle of the Peltier tip. (a) The voltage appearing between the points, P<sub>1</sub> and P<sub>2</sub>, when an electric current flows, includes the signal due to the Peltier effect at P3. This Peltier signal carries thermal information of the sample, which is in contact with the junction. TC<sub>L</sub>, TC<sub>R</sub>, and Cu denote two thermocouple wires and copper leads, respectively. The diameter of the thermocouple wires are either 25 or 12.5  $\mu$ m while that of the copper leads is 2 mm. The junctions P<sub>1</sub> and P<sub>2</sub> are anchored at a massive copper block. (b) The measuring circuit adopting a Wheatstone bridge with a variable resistor  $R_n$  for balancing.  $R_s$  is the source resistance of 1 k $\Omega$ , and  $R_1$  and  $R_{\rm ref}$  are the bridge resistors with fixed values. The signal at  $\omega$ ,  $\mathcal{V}_{\omega}$  is picked up with a lock-in amplifier. (c) The equivalent circuit for the measurement of the Peltier signal induced by the tip. In a symmetrical bridge a replica of the Peltier tip is used as the reference resistor  $R_{\rm ref}$ , and the junction of the Peltier tip generates a signal as indicated in the figure. All other signals except the one due to the Peltier effect disappears.  $R_{TC_1}$  and  $R_{TC_2}$ represent the resistance of thermocouple wires, and their sum is equivalent

$$V = I_0 R_0 \cos \omega t + \Delta S |\delta T_{\omega}| \cos(\omega t + \phi) + V_{\text{IH}}, \tag{1}$$

where  $R_0$  and  $\Delta S$  are the resistance and Seebeck coefficient of the thermocouple, respectively. The first term, of course, is a simple Ohmic voltage drop across the thermocouple caused by the current. The second term represents a Seebeck voltage due to the temperature oscillation at the junction  $(P_3)$  and carries thermal information of the sample. This temperature oscillation at  $\omega$ ,  $\delta T_{\omega}$ , is induced by the power oscillation at the junction due to the Peltier effect and its magnitude and phase shift are determined by the heat capacity and thermal conductivity of the sample. It is noted that while the Peltier effect also occurs at the junctions  $P_1$  and  $P_2$  where thermocouple wires and copper leads meet, the associated temperature oscillations can be kept negligible compared to that at  $P_3$ 

by making the junctions thick and anchoring them to a massive copper block. This is due to the fact that the magnitude of temperature oscillation at a junction caused by the Peltier effect for a given electric current is determined by the corresponding heat current per unit area [see Eq. (3) below]. In experiments thermocouple wires of diameter 25 or 12.5  $\mu$ m were used, and copper wires of thickness of 2 mm were attached to the thermocouple wires as leads. Also anchoring to a massive copper block suppresses temperature oscillations at the junctions.

The third term represents Joule heating effects and in turn consists of three terms:

$$V_{\rm JH} = V_{2\omega} + V_{1\omega} + V_{3\omega},\tag{2}$$

where  $V_{2\omega}$ ,  $V_{1\omega}$ , and  $V_{3\omega}$  are signals generated by Joule heating at frequencies  $2\omega$ ,  $\omega$ , and  $3\omega$ , respectively. These terms arise as follows. The current through the wires generates resistive heating along the wires themselves at  $2\omega$ . Then some of this heat would be transferred to the sample and induce a temperature oscillation at the same frequency. This temperature oscillation of the sample gives rise to a Seebeck voltage at the junction,  $V_{2\omega}$ . Note that while the sample is heated by both the Peltier effect at the junction (at  $\omega$ ) and the Joule heating along the wires (at  $2\omega$ ), there is no interference between these since the governing equation is linear. Thus measuring and analyzing only the Peltier signal would provide thermal characterization of the sample. In addition to  $V_{2\omega}$ , however, there appear two more terms in Eq. (2). The origin of these terms is also Joule heating, that is, the resistance of the wires would possess a small oscillating component at  $2\omega$  as a result of self-heating and the Ohmic voltage drop which is a product of the resistance and current includes  $V_{1\omega}$  and  $V_{3\omega}$ . Note that since the resistive heating is proportional to  $I_0^2$ , both  $V_{1\omega}$  and  $V_{3\omega}$  are proportional to  $I_0^3$ . The well-known  $3\omega$  method is based on measuring the third harmonic signal  $V_{3\omega}$  from a metallic heater in contact with a sample. 10,11

The Peltier tip calorimetry we propose here is based on the fact that if one can isolate the signal due to the second term in Eq. (1) out of the total signal between  $P_1$  and  $P_2$ , one would be able to pick up thermal properties of the sample which is in point contact with a thermocouple. An obvious difficulty, however, in isolating  $\delta T_{\omega}$  in Eq. (1) is the presence of other contributions at the same frequency  $\omega$ , that is, the first term in Eq. (1) and  $V_{1\omega}$  in Eq. (2). It is rather straightforward to eliminate the first term in Eq. (1); this is achieved by adopting a Wheatstone bridge circuit as illustrated in Fig. 1(b). Since both  $|\delta T_{\omega}|$  due to the Peltier effect and  $|V_{1\omega}|$  from Joule heating decrease as the frequency increases, balancing and elimination of a large signal at  $\omega$  due to resistance  $R_0$  are easily performed at a high frequency (~10 kHz) using the variable resistor  $R_v$ . Even after balancing, however,  $V_{1\omega}$  still has to be eliminated from the measured signal  $V_{\omega}$  at  $\omega$  to isolate  $\delta T_{\omega}$ . Two methods are available for this purpose. The first one takes advantage of the fact that the magnitude and phase of  $V_{3\omega}$  are the same with those of  $V_{1\omega}$  as already proved in the  $3\omega$  method. Thus by measuring the voltage at third harmonic  $(V_{3\omega})$ , simultaneously with measuring the signal at  $\omega$  ( $V_{\omega}$ ), and then subtracting it from the measured signal at  $\omega$ , one can extract  $\delta T_{\omega}$  from the data. This method, however, is not a direct one but relies on the assumption, albeit proven, and therefore leaves something to be desired.

The second method, which we adopted in the experiment, utilizes a symmetrical Wheatstone bridge. Suppose one chooses a replica of the Peltier tip in Fig. 1(b), that is, another thermocouple of the same materials and of the same length and diameter as the reference resistor. Then  $R_{ref}$  would be equal to  $R_0$ . With the junction of the reference thermocouple thermally grounded to a massive copper block, the bridge is balanced by tuning the variable resistor  $R_n$ . When the bridge balancing is achieved, all the signals except  $\delta T_{\omega}$ would disappear. Figure 1(c) is the equivalent circuit for measuring  $\delta T_{\omega}$  using the second method. The junction of the Peltier tip can be thought of as a signal source, and the voltage signal appearing at frequency  $\omega$  in the balanced bridge is measured with a lock-in amplifier. The typical resistances for the Wheatstone bridge with a K-type Peltier tip (alumelchromel) were  $R_1$ ,  $R_v = 100 \Omega$  and  $R_0$ ,  $R_{ref} = 30 \Omega$ .

# III. PERFORMANCE OF THE PELTIER TIP CALORIMETER

In verifying the performance of the Peltier tip calorimeter, let us start with the simplest case, that is, a Peltier tip sitting alone in a vacuum ( $\sim 10^{-5}$  Torr) without a sample. As can be seen in Fig. 1(a), the heat generated at the junction point P<sub>3</sub> by the Peltier effect would diffuse away to the thermal bath (a copper block) via conduction through the thermocouple wires. (Compared to wire conduction, gaseous conduction is negligible.) The junction points P<sub>1</sub> and P<sub>2</sub> are anchored on a heavy copper block which constitutes heat bath. Since the length and diameter of the two thermocouple wires, TC<sub>L</sub> and TC<sub>R</sub>, are equivalent, the situation may be simplified to the case of a single wire with the same length and diameter, thermal conductivity  $\kappa^{\text{wire}}(=\kappa^{\text{TC}_L}+\kappa^{\text{TC}_R})$ , and heat capacity (per unit volume)  $C_p^{\text{wire}} (= C_p^{\text{TC}_L} + C_p^{\text{TC}_R})$  connected to the heat bath. As a sinusoidal power  $P_0 \exp(i\omega t)$  is generated at the junction point P<sub>3</sub>, the temperature oscillation at the same point is given by solving the one-dimensional heat diffusion equation:

$$\delta T_{\omega} = \frac{j_0}{\kappa^{\text{wire}} k^{\text{wire}}} \tanh(k^{\text{wire}} d), \tag{3}$$

where d is the length of the wire,  $k^{\text{wire}}$  is the thermal wave number defined as  $k^{\text{wire}} = \sqrt{i\omega C_p^{\text{wire}}}/\kappa^{\text{wire}}$ , and  $j_0$  is the power density, i.e.,  $P_0$  divided by the cross section area of the wire.

Figure 2 is the plot of  $\delta T_{\omega}$  of Peltier tips as a function of frequency. The data displayed were obtained by adopting a symmetrical bridge with two K-type (alumel-chromel) thermocouples, one of which was used as the reference resistor. The diameter of the thermocouples were either 25 or 12.5  $\mu$ m; the length was fixed at d=2.4 mm. The amplitude of the current applied was 0.225 mA (rms). As can be seen from Eq. (3), the thermal conductivity of the wire is easily obtained from the dc limit,  $\delta T_{\omega} = (j_0 d / \kappa^{\rm wire})$ , while the thermal wave number (and therefore heat capacity) of the wire is determined from curve fitting. We have fitted simultaneously the set of real and imaginary parts to Eq. (3), and the results

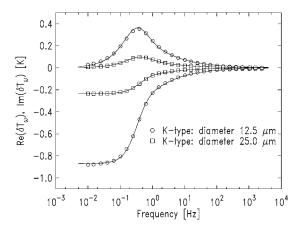


FIG. 2. The real and imaginary parts of  $\delta T_{\omega}$ , obtained for thermocouples without a sample, are plotted as a function of frequency. K-type thermocouples with diameters of 25 and 12.5  $\mu$ m were used as a Peltier tip. The symbols denote the data points, and the solid lines represent the fitting results. The measured data were fitted to Eq. (3).

are excellent as shown by the solid lines in Fig. 2. The curve fitting yields the values at room temperature of  $\kappa^{\text{wire}}$  and  $C_p^{\text{wire}}$  to be 49.3 W/m K and 8.40 J/cm<sup>3</sup> K, respectively. These values are in perfect agreement with those of the literature. Thus we may conclude as a whole that the scheme for the Peltier tip calorimeter is on the right track. Now let us move on to the cases with samples.

Now suppose that a tiny solid sample is attached to the Peltier tip, then there arise two time constants:  $\tau_{\rm ext}$  and  $\tau_{\rm int}$ .  $\tau_{\rm ext}$  is the time it takes for heat energy in the sample to leak into the heat bath and is called the external relaxation time. The external relaxation time is determined by the total heat capacity of the system and the thermal conductance of the wires.  $\tau_{int}$  designates the time for heat diffusion in the sample and depends on its size. Since  $au_{\text{int}}$  can be made small by reducing the sample size and  $\tau_{\rm ext}$  reasonably large by using thin wires (of diameter of 25 or 12.5  $\mu$ m as was done in the present experiment), one may judicially choose a measuring frequency  $\omega$  which satisfies  $\tau_{\text{int}} \ll \omega^{-1} \ll \tau_{\text{ext}}$ . The former condition,  $\tau_{\text{int}} \ll \omega^{-1}$ , means that the sample is heated/ cooled uniformly without a temperature gradient, while the latter condition,  $\omega^{-1} \ll \tau_{\rm ext}$ , puts the ac calorimeter in the quasiadiabatic regime. Then in this regime the magnitude and phase of  $\delta T_{\omega}$  is determined simply from the definition of heat capacity:

$$C_p = \frac{dQ/dt}{d\delta T/dt} = \frac{\prod I_0 \cos \omega t}{d\delta T/dt}.$$
 (4)

Here  $\delta T$  represents temperature oscillation and its amplitude is  $\delta T_{\omega}$ . (dQ/dt) denotes the power and is equal to  $\Pi$ , the Peltier coefficient, times the current. Thus

$$\delta T = \frac{\Pi I_0}{\omega C_p} \cos(\omega t - \pi/2). \tag{5}$$

Note that the phase of  $\delta T_{\omega}$  is  $-\pi/2$  in Eq. (5), so the imaginary part directly gives the heat capacity of the sample.

In order to check the validity of the PTC as a calorimeter for small solid samples, the heat capacity of an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> sample of mass 265  $\mu$ g was measured. The junction of an E-type thermocouple (chromel-constantan) with diameter of

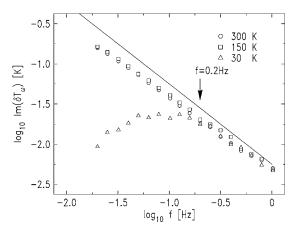


FIG. 3. A synthetic  $Al_2O_3$  sample of mass of 265  $\mu g$  is attached to a Peltier tip. The frequency dependence of the imaginary part of  $\delta T_{\omega}$  is shown for temperatures of 30, 150, and 300 K. The solid line is a guide to eyes with the slope of -1. At 30 K, the data points below 0.1 Hz deviate from the straight line with slope of -1. The measuring frequency was chosen to be 0.2 Hz as indicated with an arrow.

25  $\mu$ m was attached to the sample using a tiny amount of GE 7031 varnish for electrical insulation and good thermal contacts. Then to determine the proper regime where the heat capacity of the sample is inversely proportional to  $\delta T_{\omega}$ , the frequency dependence of  $\delta T_{\omega}$  was measured at 30, 150, and 300 K. The current used was 0.45 mA (rms). It can be seen from Fig. 3 that while  $\delta T_{\omega}$  is proportional to  $f^{-1}$  in the measured frequency range at 150 and 300 K, the data obtained at 30 K expose a large deviation from the  $f^{-1}$  behavior at low frequencies. This is mainly caused by the fact that the external relaxation time  $\tau_{\rm ext}$  becomes short at low temperatures due to the small value of the heat capacity of the sample. (An increase of thermal conductivity of the thermocouple wires may also contribute.) The measuring frequency was selected to be 0.2 Hz, which puts the PTC in the proper ac calorimetry regime even at 30 K.

Having selected the measuring frequency, we have carried out the measurements of the heat capacity of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the temperature range from 20 to 40 K. Figure 4 is the plot of the heat capacity converted from the raw data. While the data points match well the reference values above 150 K,

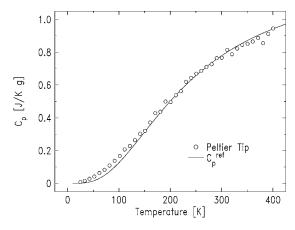


FIG. 4. Specific heat capacity of  $Al_2O_3$  measured by the Peltier tip calorimeter. The measuring frequency was 0.2 Hz. The solid line displays the reference values

they show a small but systematic deviation below 100 K. The cause of this deviation is not completely clear, but it may be caused by various reasons, for example, excessive Joule heating effect or improper choice of glue attaching the sample to the Peltier tip. In particular, the Joule heating along the thermocouple wires contributes a  $2\omega$  component in the ac signal and an associated dc offset of  $\sim 1$  K below 100 K. At any rate these measurements demonstrate that the Peltier tip operated at a judicially chosen frequency is indeed a microcalorimeter by itself in proper temperature ranges.

One very promising application of the Peltier tip may be found in the thermal characterization of liquids. To demonstrate this, we start by solving the heat diffusion equation for a situation where a spherical heater with radius a is embedded in a liquid. The solution to the diffusion equation with spherical symmetry (for  $r \ge a$ ) is the well-known spherical modified Bessel function of the zeroth order,  $e^{-kr}/kr$  where k is a constant. Since the heat generated from the heater both diffuses into the liquid and increases the temperature of the heater itself, the continuity equation at r=a becomes

$$\kappa_l \frac{\partial T}{\partial r} \bigg|_{r=a} = j_1 - (a/3) C_p^{\text{wire}} \frac{dT}{dt},$$
 (6)

where  $\kappa_l$  is thermal conductivity of the liquid and  $j_1$  is the power divided by the surface area of the spherical heater. When  $j_1$  is sinusoidal, the temperature oscillation at r=a at frequency  $\omega$  is given by

$$\delta T_{\omega}(r=a) = \frac{j_1}{\kappa_l k_l + \kappa_l / a + i(1/3) a C_p^{\text{wire}} \omega},$$
(7)

where  $k_l$  is the thermal wave number of the liquid. (The thermal wave number was defined previously.)

The problem just treated is the case of an isolated spherical heat source, but the junction (or heat source) is, in fact, connected to wires and thus there exists additional heat loss by the wire conduction. A similar problem, that is, the heat transfer from a small heated substrate to the surrounding medium including heat leakage through wires, was treated previously in the context of ac microcalorimeter. While the exact solution to the problem would require elaborate efforts, one may attempt, as a simple approximation, to superpose Eq. (7) and Eq. (3) to yield

$$\delta T_{\omega}(r=a) = \frac{j_1}{\kappa_l k_l + \kappa_l / a + i(1/3) a C_p^{\text{wire}} \omega} + \beta \frac{j_0}{\kappa_l^{\text{wire}} k_l^{\text{wire}}} \tanh(k^{\text{wire}} d). \tag{8}$$

Note that in Eq. (8) a new parameter  $\beta$  is introduced; the reasoning behind having  $\beta$  is as follows. While the symmetry associated with the first term is spherical, the presence of the wires in the liquid breaks this symmetry. Then the exact solution to the problem may not take the form of a simple superposition of two independent solutions with different symmetry. Assuming that the presence of the wires constitutes only a small perturbation, a parameter  $\beta$  is introduced to remedy the situation empirically. Thus  $\beta$  signifies the degree of symmetry breaking and represents the strength of the wire conduction. The self-consistent condition of  $\beta$  being

FIG. 5. The frequency dependence of the real and imaginary parts of  $\delta T_{\omega}$  obtained for various liquids. The data were obtained with a Peltier tip of K type immersed in the liquids. The solid lines represent the fitting results of the measured data to Eq. (8).

small should be satisfied to ensure the validity of the simple superposition expressed in Eq. (8).

It is seen that the second term in Eq. (8) can be fully characterized for a given thermocouple by carrying out measurements without a liquid as demonstrated above. Then from the measurements for a thermocouple immersed in a liquid, one may be able to extract thermophysical parameters of the liquid using Eq. (8). Indeed we measured the frequency dependence of the temperature oscillation from a Peltier tip embedded in various liquids. The Peltier tip used was a 12.5  $\mu$ m K-type thermocouple, and the current applied was 2.5 mA (rms). Note that a larger current than that applied to the solid case was required to keep the temperature oscillation reasonably large. Figure 5 illustrates the real and imaginary parts of  $\delta T_{\omega}$  as a function of frequency for three liquids, glycerol, 1,2-propanediol, and toluene. In order to extract thermophysical parameters of the liquids from the data, both real and imaginary parts were fitted simultaneously to Eq. (8) by including the strength parameter  $\beta$  in free variables. Except for  $\beta$  the parameters related to the thermocouple wires in the second term were fixed to previously measured values. The radius of the junction was set at  $a=22 \mu m$  from visual inspection. The solid lines in Fig. 5 indicate the fitting results, and the excellent agreement between the data and fitting suggests that Eq. (8), albeit the result of a simple minded approximation, represents the phenomenon well. The fitting procedures then yielded the thermal conductivity and heat capacity for the three liquids as summarized in Table I. The fact that the value of  $\beta$  remains small (0.04–0.1) for all three cases justifies a posteriori the use of Eq. (8). Also included in Table I are the reference values from the literature; 15 the measured and reference values for the liquids, in particular, glycerol and 1,2propanediol, show remarkable agreement. For toluene with relatively poor thermal conductivity compared to the other liquids, it is understandable that the wire conduction would cause more impact on the isotropic diffusion in the liquid. At any rate, it may be concluded that the PTC is capable of yielding the values of both thermal conductivity and heat capacity with accuracy of 10% or better when applied to liquids. While this absolute accuracy may seem moderate for

TABLE I. The thermal conductivity  $\kappa$  (mW/cm K) and heat capacity  $C_p$  (J/cm³ K) of the liquids directly measured with a Peltier tip calorimeter of K type and diameter of 12.5  $\mu$ m.  $\beta$  is a fitting parameter representing the strength of heat conduction through the wire. For comparison the reference values of thermal conductivity and heat capacity from Ref. 14 are also given.

	Measured			Reference	
Liquid	К	$C_p$	β	κ	$C_p$
Glycerol	2.83	2.924	0.042	2.85	2.998
1,2-propanediol	1.98	2.384	0.096	2.00	2.598
Toluene	1.53	1.843	0.104	1.31	1.480

some liquids, the PTC would be an excellent and convenient tool in comparing thermophysical properties of different fluids, for example, those of nanofluids with different contents of nanoparticles.

### **IV. OUTLOOK**

The Peltier tip calorimeter is the extension of the Peltier ac calorimeter introduced previously. While the latter utilizes a junction of very thin thermocouple wires as a heat source and a separate thermocouple junction as a temperature sensor, the Peltier tip calorimeter adopts a single thermocouple as a heater and sensor simultaneously. This rather simple act of adopting only a single thermocouple in the calorimeter opens up new capabilities that we have tried to demonstrate. The new capabilities include promising applications such as scanning thermal microscopy and the measurements of thermophysical properties of liquids.

A particularly interesting idea for the use of the Peltier tip is that a tip for an atomic force microscope is replaced by a Peltier tip. Thermocouples, of course, were used previously in the scanning microscopy as temperature sensors; 16 however, the most important feature of the present proposal is that the thermocouple tip here is not just a temperature sensor, but it plays a dual role of a heater and sensor. The Peltier tip is then used as a local calorimeter in the scanning thermal microscope. Currently, in a thermal microscope in the market, a thin Pt wire is being used as a heater/sensor utilizing Joule heating.<sup>17</sup> In this case, an entire probe is heated and heat exchange occurs only where the probe touches the surface. With the Peltier tip, we may expect enhanced performance in thermal property measurements of a solid surface, because the Peltier tip is a point heater/sensor and does not cause a dc temperature offset except the one due to Joule heating.

In order to confirm the possibility of our proposal, we prepared a zigzag patterned Al film on a glass substrate (lateral width of the pattern=25  $\mu$ m, film thickness=30 nm) to check the sensitivity of the Peltier tip as a thermal probe for solid surface. A Peltier tip was then placed on the film, and the Peltier signal was measured while the glass substrate on a XY stage was moved in the lateral direction of the zigzag pattern. Performing the experiment in the air, the real part of the thermal signal turned out to be easily contaminated due to temperature drifts and fluctuations. On the other hand, the imaginary part of the signal faithfully produced oscillations

corresponding to the lateral width of the Al zigzag pattern. For quantitative analysis, it is needed to solve the diffusion equation for a given geometry and control the contact pressure of the Peltier tip to the sample surface. These are in progress. Although the measurements performed here are far from the nanoregime, it surely implies that a single junction can indeed be used as both a heat source and sensor simultaneously in a scanning probe microscope. The successful development of the Peltier thermal microscope would be an exciting and important event for this so-called nanoage when the information for submicron local thermophysical properties is in great demand.

The Peltier tip calorimeter can also be used in the measurements of thermophysical properties of gases, and this in turn would be taken advantage of in developing sensitive pressure (or vacuum) sensors. In fact, vacuum sensors based on the Peltier tip calorimetry were developed and commercialized by POSVAC, Inc. In Also of keen interest is the utilization of the Peltier tip as a acceleration sensor. By applying a current to a Peltier tip located in a cell with air, one may generate air convection from Joule heating in the wires. The Peltier tip then measures temperature at a particular point in the convection pattern, and acceleration would cause a temperature change at the tip. The principle of this Peltier tip accelerometer was demonstrated and its miniaturization for the use in mobile devices is under active development. In the convection pattern and its miniaturization for the use in mobile devices is under active development.

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