Modern calorimetry: going beyond tradition

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Abstract

Calorimetry has been a traditional tool for obtaining invaluable thermodynamic information of matter, the free energy. We describe recent efforts to go beyond this traditional calorimetry. After introducing dynamic heat capacity, we present the various experimental methods to measure it. Applications and future prospects are also given. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

At the turn of the 20th century studies of heat capacity of solids at low temperatures played an important role in revealing the quantum character of nature [1]. This example vividly illustrates the power of calorimetry in science. As a matter of fact calorimetric measurements reveal so great a deal of information about matter that calorimetry, whose name originates from the now obsolete caloric theory of heat described, for example, by Lavoisier [2], has become an indispensable tool for modern day research in chemistry, physics, materials science, and biology (see the example [3]). This is due to the fact that it allows one to directly monitor the free energy change of a given system as the external parameter such as temperature varies. This unique ability of calorimetry follows from the fact that it measures heat capacity as

well as heat itself. Heat capacity at constant pressure is defined thermodynamically by

$$C_p = \frac{\mathrm{d}H}{\mathrm{d}T} = T\frac{\mathrm{d}S}{\mathrm{d}T} \tag{1}$$

where T, H, and S are the temperature, the enthalpy, and the entropy of a given system, respectively. Thus, from the measured heat (such as latent heat, heat of reaction, etc.) and heat capacity, one may be able to reconstruct the free energy of the system as a function of temperature or some other thermodynamic variable.

Despite these positive attributes and historic roles of calorimetry, one may naturally ask a question in the beginning of a new millennium, is there any new scientific aspect in calorimetry which will continue to attract attention and require genuine efforts of researchers in the 21st century? This question appears particularly pertinent, if we consider the fact that calorimetry is generally known as an old discipline dealing with thermodynamics of bulk materials, while a large portion of the recent research efforts in various

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fields seem to be directed to a understanding of the dynamic and/or local properties of matter.[1] In this short paper, I wish to address the question from a personal point of view.

Measurement of a thermodynamic quantity is the usual notion that is tied to calorimetry, since heat capacity is normally recognized as a static thermodynamic quantity as defined above. However, it is possible to go beyond this traditional understanding and generalize heat capacity as a dynamic quantity. Indeed, it is precisely my point that calorimetry should be generalized into the dynamic and/or local regime to be able to deal with new scientific issues in the coming years. In particular, the dynamic generalization should empower calorimetry to deal with dynamic phenomena in condensed matter, and at the same time may even enable it in certain cases to become a local probe. Here, I wish to describe the general principle and practice of *dynamic calorimetry* (formally defined below), and only briefly touch upon the generalization into the local regime. The details of local calorimetry will be published [4].

Let us start with the formal definition of generalized *dynamic heat capacity*. Of course, the term implies that heat capacity is a quantity which may depend on either measuring time or frequency. The concept of dynamic heat capacity appears natural if one recalls that static thermodynamic quantities are time-averaged (or ensemble-averaged). In other words, they are static not because they do not change in time, but because they change too rapidly on the experimental time scale. Suppose, for instance, that a system contains a dynamic process relaxing with a characteristic time τ which lies within our experimental time window, then this will result in a time-dependent heat capacity $C_p(t)$ depending on the time scale of measuring. In the frequency domain, this would lead to the complex frequency-dependent heat capacity $C_p(\omega)$, and $C_p(\omega)$ of this system would show a dispersion in its real part and a peak in its imaginary part at $\omega \approx \tau$.

One can utilize the linear response theory to formally define dynamic heat capacity [5], and $C_p(\omega)$ can be written in terms of enthalpy correlation function

$$C_p(\omega) = C_p^0 - \frac{i\omega}{k_B T^2} \int_0^\infty dt\, e^{-i\omega t} \langle \delta H_R(0)\delta H_R(t)\rangle \tag{2}$$

where C_p^0 is the usual static heat capacity, δH_R the slowly relaxing portion of enthalpy fluctuation, and $\langle \cdot \rangle$ denotes thermal averaging. The static heat capacity can be written as a sum of the fast part C_p^∞ (due to phonons in condensed matter which is our concern), and the slow part.

$$C_p^0 = C_p^\infty + \frac{\langle \delta H_R^2\rangle}{k_B T^2} \tag{3}$$

From Eq. (2) it is easy to see that the slow relaxation of enthalpy governed by the system dynamics is the origin of the dynamic, or frequency-dependent, heat capacity and therefore one can probe the slow dynamics of the system by measuring the dynamic heat capacity. Of course, it goes without saying that this would be possible only if the slow part of enthalpy fluctuation lies within the experimental time scale. Throughout this paper, I shall use dynamic calorimetry to collectively represent the calorimetric methods which allow the measurements of dynamic heat capacity.

2. General principle of dynaminc calorimetry

In this section, I briefly expound the general principle of dynamic calorimetry. As usual with any dynamic experiment, dynamic calorimetry can be conducted in either time or frequency domain. The results obtained in the time domain are related to those acquired in the frequency domain by the Fourier transform, and vice versa. It should also be pointed out that there are again two ways, designated as types A and B, of measuring the dynamic heat capacity of a given system in the time domain (and the same is true in the frequency domain). In type A, one may attempt to induce a temperature jump in the system by thermally attaching the system to a heat reservoir whose temperature is not at the same value as that of the system, and measure the response $\delta\langle H\rangle$. The variation of the enthalpy of the system can be monitored by watching the heat flow $\dot{Q}_{fl}$ from

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[1] A consensus regarding the current status of calorimetry was reached by the participants of the 6th Lähnwitz Seminar on Calorimetry in the final discussion session.

the reservoir to the system, since $\delta\langle H\rangle = \int dt\dot{Q}_{fl}$ by the first law of thermodynamics. This is the method used in commercial differential scanning calorimeters (DSC) where temperature is varied according to a programmed schedule and the resulting power is measured. The converse situation occurs in the type B. One supplies a known amount of heat to the system and monitors the ensuing temperature response with a sensor.

To expose the difference of the two methods more clearly, a schematic diagram depicting the situation is shown in Fig. 1. Fig. 1(a) illustrates the type A, where the system is in intimate contact with the reservoir. Now suppose that there is a step-like temperature jump δT in the reservoir. The same δT shift will be established in the system temperature via the heat flow from the reservoir to the system. If one carefully analyzes $\dot{Q}_{fl}$ as a function of time, one will find that it consists of two parts: the instantly responding part, $\dot{Q}_{fl}^{\infty}$, and the more slowly responding part, $\dot{Q}_{fl}^{R}$. In other words, the system takes up $Q_{fl}^{\infty} = \int dt\dot{Q}_{fl}^{\infty}$, which is due to the fast degrees of freedom (phonons in most cases of interest), and brings up its temperature (or more accurately its phonon temperature) by δT instantly. However, it takes time for its slow degrees of freedom to respond and they will absorb $\dot{Q}_{fl}^{R}$ gradually from the reservoir to reach equilibrium.[2] The opposite situation is encountered in the type B, depicted in Fig. 1(b), where a constant amount of heat is supplied to the system and the temperature of the system is followed. Here at the instant when heat is supplied, the energy is shared only among the fast degrees of freedom, and then part of energy slowly diffuses into the slow degrees of freedom. Thus, the temperature of the system first shows a step-like jump which is then followed by a gradual decrease as a part of the supplied heat energy is acquired by the slow degrees of freedom.

At this point it is worthwhile to emphasize that what one measures with a sensor and calls the temperature of a system is actually that of the fast degrees of freedom of the system, with which the sensor is
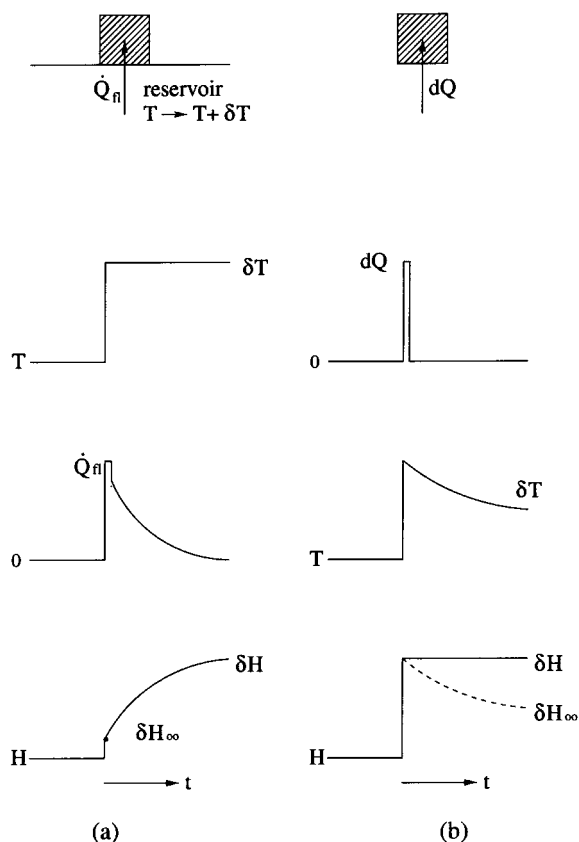

Fig. 1. Schematic diagram showing two methods of measuring dynamic heat capacity. (a) *Type* A: A system is thermally attached to the reservoir and the temperature of the reservoir jumps from T to $T + \delta T$ at a certain instant (top and second figure). The heat flow $\dot{Q}_{fl}$ from the reservoir to the system, as described in the third figure, is measured. An instantaneous heat absorption, corresponding to δH_{∞}, by the fast degrees of freedom is followed by the gradual heat flow caused by the absorption due to the slow degrees of freedom (bottom figure); (b) *Type* B: A certain amount of heat, dQ, is given to a system (as sketched in the top and second figure), and the change in T is followed in time. T jumps instantaneously, and this jump is accompanied by a gradual decrease as the supplied heat energy is shared by the slow degrees of freedom (third figure). The decrease in δH_{∞} appears as an increase in the internal enthalpy $\delta\langle H_R\rangle$ by the same amount (bottom figure).

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[2] Here we are arbitrarily dividing degrees of freedom in condensed matter into fast and slow ones. Generally, the phonon time scale (of order of picosecond) would be instantaneous for the present purpose, but the slow time scale may range from hundreds of seconds (mHz) to micro-second (MHz).

in direct thermal contact. In what follows, I shall enumerate various experimental methods which are currently in use to measure dynamic heat capacity. Technical details of these methods, however, are completely left out, and the interested reader should refer to the literature [6].

3. Modulation calorimetry

3.1. Traditional ac calorimetry

Traditional ac calorimetry [7,8], which belongs to type B, is a calorimetric technique in which a small amount of oscillating heat is supplied to a sample either by Joule heating or heating by light and in either case the ensuing temperature oscillation is measured. Since this temperature oscillation is inversely proportional to the heat capacity of the sample in the proper regime, one can determine the heat capacity of the sample by carrying out measurements at a judicially chosen frequency. While this method was mainly used to determine static heat capacity of materials, it is natural to extend the technique as a dynamic probe.

Consider a situation where an oscillating power of frequency ω is applied to a sample of typical thickness d and thermal diffusivity D. Then the thermal wavelength $\lambda = \sqrt{D/\omega}$ characterize the length over which the temperature oscillation decays, and the condition, $d \ll \lambda$, must be satisfied in order that the sample may be regarded as oscillating in temperature as a whole, i.e. without a temperature gradient. Since the lack of a temperature gradient in the sample is prerequisite for an ac calorimeter to work as a dynamic calorimeter, one may add metallic wires for a liquid sample to enhance thermal conduction in the sample and may make it as thin as possible for a solid sample. However, there exists an unavoidable limit in this approach due to the fact that the thermal wavelength decreases as frequency increases, and eventually beomes shorter than d. Since the geometry of a sample here is not particularly well defined, it is very hard to deal with the situation where a temperature gradient exists in the sample. So, the method is usually limited to less than 1 Hz for liquids or dielectric crystals and perhaps tens of Hertz for metallic solids.

3.2. 3ω calorimetry

In order to extend the dynamic range of calorimetry, one has to deal with the temperature gradient effect, rather than try to avoid it. One method, which has been successful, is to take advantage of a well-defined geometry with thickness of a sample much larger than the thermal wavelength. Here one faces a heat-diffusion problem in a semi-infinite medium with a heater on the surface that generates the oscillating power. The well-defined geometry of the sample in this case enables one to solve the heat diffusion equation exactly, and it turns out that the surface temperature oscillation is determined by the thermal properties of the medium. Thus, one can extract the dynamic heat capacity by measuring the surface temperature oscillation as a function of the frequency of the oscillating power.

The 3ω method adopts a clever idea of using a metallic heater on the surface simultaneously as a temperature sensor that measures the surface temperature oscillation [9–11]. Since the sensor is at the same position as the heater (it is the heater itself), one does not encounter a problem associated with the fact that the temperature oscillation decays within the thermal wavelength which becomes short at high frequencies. Thus, one can raise the upper limit of the dynamic range of modulation calorimetry. The reason why it is called the 3ω method is the following: since one uses Joule-heating by passing an electric current at a certain frequency ω through a metallic heater on the surface of a material, the surface temperature oscillation occurs at 2ω. This temperature oscillation induces resistance oscillations in the heater at the same frequency, and then the voltage drop across the heater itself would include a term at 3ω. This 3ω signal is detected to yield the dynamic heat capacity of the material at 2ω. The currently available frequency in 3ω calorimetry ranges approximately from 0.01 to 50 kHz [12].

3.3. Differential scanning temperature modulated calorimetry

A differential scanning temperature modulated calorimeter (DSTMC) is a commercially available calorimeter, which allows one to do dynamic calorimetry.[3] DSC are distinct from the modulation calorimeters described above in that they belong to type A. A DSC measures the heat flow to a sample, which is

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[3] Previously DSTMC was called by a variety of abbreviation such as MTDSC, TMDSC, DDSC, MDSC, ODSC, etc., and ICTAC recommended provisionally the use of MTDSC in its publication. However, the working group on temperature modulated calorimetry, set up in 1997 by ICTAC and chaired by B. Wunderlich, examined the situation thoroughly and settled on DSTMC.

necessary to keep up with the prescribed temperature variation, normally linear heating or cooling, of the reservoir (or the block). In DSTMC, this conventional temperature program has a superimposed periodic temperature variation, so that

$$T(t) = T_0 + \beta t + A \sin \omega t \qquad (4)$$

where T_0 is the initial temperature, β the underlying heating rate, and A and ω the amplitude and frequency of modulation, respectively. By measuring the response of the sample to this temperature variation one can, at least in principle, obtain dynamic information as a function of frequency. Although DSTMC has contributed to the widespread use of modulation calorimetry, there remains some problems to be clarified before it can be used reliably as a dynamic calorimetric tool. A particualrly serious problem is that the signal one gets from DSTMC seems to be not only due to the sample properties, but also due to the calorimeter itself. Currently much effort is being spent on this problem [13].

3.4. Peltier calorimetry

Peltier calorimetry is an ac calorimetric method developed specifically for the heat capacity measurements, dynamic as well as static, of minute samples [14]. Most conventional calorimetric methods require indispensable addenda (heater and sensor) to be put on a sample and the mass of these addenda may even be greater than that of the sample in case of minute sample masses. The results of this situation are the loss of sensitivity and accuracy in determining the absolute value of heat capacity. In other words, the unavoidable calibration procedure (removing the background due to the addenda) introduces uncertainty in both accuracy and precision. Peltier calorimetry overcomes this difficulty by utilizing the well-known Peltier effect of a thermocouple as an ac power source; the junction of a very thin thermocouple (of diameter 1 mm or less) attached to a sample is so tiny that its mass is totally negligible and therefore it can play the role of an ideal heater. It should be pointed out that a thermocouple cannot only heat, but also cool the system, whereas other power sources such as Joule heating or heating by light can only heat the system. The temperature oscillation is sensed with another thermocouple which again does not disturb the system. Peltier calorimetry

is superior to other modulation methods in that the experimental setup is simple, the average temperature of a sample is at, not above as in traditional ac calorimetry, the bath temperature, and it directly yields absolute values of the heat capacity of submilligram samples without the necessity of a calibration procedure.

A novel extension of Peltier calorimetry is the Peltier thermal microscope, which would enable one to measure local thermophysical properties of matter at small length scales. For this purpose, we have shown that a single junction can be used simultaneously as both power source and sensor [4]. It must be stressed that this represents a conceptual deviation from the normal notion that a power source and a sensor are required separately in calorimetry and constitutes a major step toward a local calorimeter. Then, substitution of a thermocouple for a tip in an atomic force microscope would constitute a thermal microscope [15]. A potentially very useful characteristic of the Peltier microscope is that one can change the probing length scale (thermal diffusion length) by changing the frequency of a current in the thermocouple. The successful development of the Peltier thermal microscope would be an exciting and important event for this so-called nano-age where the submicrometer local thermophysical properties are in great demand.

4. Adiabatic calorimetry

4.1. Time domain dynamic calorimetry

One of the most difficult tasks in calorimetry is to contain the leakage of heat, since there does not exist a perfect thermal insulator. Even if there were one, radiation would still have to be contained. In adiabatic calorimetry, heat leak from a sample to the surroundings is controlled to zero as tightly as possible. Since Nernst first constructed an adiabatic calorimeter [16], adiabatic calorimetry has been the most accurate method of determining static heat capacity. In addition to this capability an adiabatic calorimeter can be used as a means of dynamic calorimetry in time domain [17]. In time domain dynamic calorimetry, a certain amount of heat is applied instantaneously to a sample and its temperature response is examined in real time.

Recall the situation depicted in Fig. 1(b). Since the adiabaticity is maintained all the time, the variation of temperature in time is nothing but time dependent heat capacity. By varying the values of applied energy, one can induce temperature jumps of varying size. While it is not easy to apply a large amount of power to a sample in modulation calorimetry, there is no difficulty in varying the temperature jump sizes in time domain dynamic calorimetry. Thus, this feature of the time domain method allows one to study nonlinear temperature relaxation [18].

4.2. Scanning adiabatic calorimetry

One classical method to extract dynamic calorimetric information from a system is to perform scanning experiments. In this method the experimental time scale is set by the scanning rate dT/dt. Traditionally commercial differential scanning calorimeters have been utilized for this purpose [19], but adiabatic calorimeters can also be operated in the scanning mode. Since the adiabatic condition between the sample and the shield must be maintained during operation, it is usual that the scanning mode is adopted in a heating experiment [20]. However, it is necessary to measure heat capacity during cooling as well as heating at various scanning rates to extract dynamic information if a substance shows frequency dependence in heat capacity. This situation motivated us to develop a method to use an adiabatic calorimeter in a rate-scanning mode at variable rates during both heating and cooling [21]. In the cooling mode, a constant temperature difference is maintained, and then there is a heat flow from the sample to the shield. It turns out that one can control the cooling rate by varying the size of the temperature difference. The heat flow in this case is not a leak, but is used as a negative input power in a controlled fashion. The calorimeter used in this way can be operated in both heating and cooling modes in the scanning range of 0.01–2 K/min. It is noted that adiabatic dynamic calorimetry belongs to type B.

5. Applications and future outlook

In this paper, I have outlined dynamic calorimetric techniques currently in use. Modulation calorimetry of type B, where one supplies a small oscillating heat input to a sample, allows one to measure the dynamic heat capacity in addition to the usual static heat capacity under equilibrium conditions. One can measure dynamic heat capacity directly with a traditional ac calorimeter. However, the dynamic range provided by this method is quite limited, below 1 Hz in many cases with solids as well as liquids. To extend the dynamic range, one can use the 3ω method. While this method raises the upper frequency limit to tens of kilo hertz, one has to pay the price of being involved with thermal conductivity. To get dynamic heat capacity data, one has to perform separate measurements of the thermal conductivity. A commercial DSTMC, which belongs to type A, is a convenient tool for qualitative purposes, but it seems that there remains some problems to be solved before it can become a quantitative dynamic calorimeter. A Peltier calorimeter is an attractive method for obtaining the dynamic heat capacity of minute samples. Currently, a Peltier thermal microscope, a variation of the Peltier calorimeter, is under development. An adiabatic calorimeter is the most accurate tool for heat capacity and latent heat measurements. In particular, the latent heat information is very difficult to obtain with other methods. With the advance in computer control and electronics technology, the operation of adiabatic calorimeters has become less tedious and less time-consuming. This advance has allowed the time domain dynamic calorimetry where one follows the temperature change of the system under adiabatic conditions, after a certain amount of heat is given to a system. Enthalpy relaxation, including nonlinear relaxation, can be studied in real time with adiabatic calorimeters.

As for the future research, one may try to extend the dynamic range of the 3ω method above the current frequency limit, tens of kilo hertz. If successful, then the thermal wavelength can enter the submicrometer regime in dielectric materials. This would allow the characterization of thermal properties of thin films with submicrometer thicknesses. This kind of information is not only scientifically interesting (heat capacity and thermal conductivity of a sample with restricted geometry) but also technologically important (efficient heat transport in thin films). The development of noncontact heating at higher frequencies than is available with the present light chopping would be very helpful in enhancing the applicability

of modulation calorimeters. Various techniques for measuring thermophysical properties of thin films utilizing advanced laser technology seem very promising [22]. Although we have generalized heat capacity temporally by defining a dynamic heat capacity, one may also attempt to generalize heat capacity spatially by defining a heat capacity which is wavenumber as well as frequency dependent. This full generalization of heat capacity would constitute a challenge theoretically as well as experimentally. Development of local calorimeters with nanoscale or at least sub-micrometer resolution would be an exciting event. This is particularly urgent to keep up with the current technology trend heading toward the nanometer regime.

Even with the current dynamic range, it is recognized that dynamic calorimetry has wide applications in diverse fields. For example, biological systems, where slow dynamics is often an important occurrence, may be suitable to be studied by dynamic calorimetry. Also of keen interest and a good candidate for dynamic calorimetry is the melting phenomenon, where one can expect contributions from time-dependent processes. Here the latent heat effect and specific heat effects are usually entangled in calorimetric measurements to make the interpretation of data obscure; however, by combining various methods presented here one can hope to disentangle them. One can also expect to find use of dynamic calorimeters in situations involving solids: global thermal hysteresis phenomenon in incommensurate ferroelectrics, heat conduction in porous media and so on.

References

[1] A. Einstein, Ann. Physik 22 (1907) 180.
[2] A. Lavoisier, Elements of Chemistry, Paris, 1789.
[3] B. Wunderlich, Thermal Analysis, Academic Press, San Diego, 1990.
[4] D.H. Jung, I.K. Moon, Y.H. Jeong, unpublished.
[5] Y.H. Jeong, I. K. Moon, Phys. Rev. B 52 (1995) 6381.
[6] Y.H. Jeong, Thermochimi. Acta 304/305 (1997) 67.
[7] P.F. Sullivan, G. Seidel, Phys. Rev. 173 (1968) 679.
[8] I. Hatta, Pure Appl. Chem. 64 (1992) 79.
[9] N. Birge, S. Nagel, Phys. Rev. Lett. 54 (1985) 2674.
[10] D.H. Jung, T.W. Kwon, D.J. Bae, I.K. Moon, Y.H. Jeong, Meas. Sci. Technol. 3 (1992) 475.
[11] I.K. Moon, Y.H. Jeong, S.I. Kwun, Rev. Sci. Instrum. 67 (1996) 29.
[12] D.H. Jung, Y.H. Jeong, unpublished.
[13] C. Schick, G. Höhne (Eds.), Thermochimi. Acta 330 (1999).
[14] I.K. Moon, D.H. Jung, K.B. Lee, Y.H. Jeong, Appl. Phys. Lett. 76 (2000) 2451.
[15] A. Majumdar, J.P. Carrejo, J. Lai, Appl. Phys. Lett. 62 (1993) 2501.
[16] W. Nernst, Ann. Physik. 36 (1911) 395.
[17] B. Wunderlich, M. Dole, J. Polym. Sci. 24 (1957) 201.
[18] I.K. Moon, Y.H. Jeong, Pure Appl. Chem. 69 (1997) 2321.
[19] C. Moynihan et al., New York Acad. Sci. 279 (1976) 15.
[20] J. Thoen, Phase Transitions in Liquid Crystals, Plenum Press, New York, 1992 (Chapter 10).
[21] I.K. Moon, Y.H. Jeong, Rev. Sci. Instrum. 67 (1996) 3553.
[22] Y. Nagasaka, T. Baba, Progress in Heat Transfer, Vol. 3, Japan Society of Mechanical Engineers, 2000.