i.e., $A_n(\mathbf{k}_n)$ is sharply peaked around a particular $\mathbf{k}_n$ determined by Eqs. (15a)–(15c). Then the second factor on the right side of Eq. (16) is almost constant so that $A_n(\mathbf{k}_n)$ is the same as $A_I(\mathbf{k})$ except for a multiplying factor. Thus the nth diffracted wave will have the same shape as the incident wave but will have a smaller overall intensity. This is just the case of the laser discussed in the introduction. Whether the laser beam shines directly on the grating or is first passed through a single slit, the pattern incident on the grating is reproduced at the classical diffraction angles.

Second, suppose the incident amplitude is sharply peaked for wave vectors near a given direction but with a broad spread of wavelengths. For each value of wavelength the situation is as described in the last paragraph. Thus for each wavelength the nth-order diffracted wave will have the same shape as the incident wave for that wavelength. For different wavelengths the nth-order waves will be diffracted through different angles. The effect of this is to disperse the incident wave into its spectrum of wavelengths while maintaining the intensity distribution for each wavelength.

An interesting example of this last effect can be obtained by projecting a black-and-white slide through a grating. The zeroth-order image reproduces the original picture in black and white. The nature of the higher-order images depends on the nature of the original picture. If the picture consists of narrow light regions on a dark background, each light region acts as the slit of a spectrograph and the higher-order images show the picture spread into its spectral colors. If, on the other hand, the picture consists of narrow dark regions on a light background, the higher-order images reproduce the picture in the boundary colors[4,5] of the background. Further discussion of these effects is beyond the scope of this article.

Finally, if the incident wave amplitude is not sharply peaked around a given direction, the diffracted waves will not reproduce the incident wave except in the zeroth order.

[1] See, for example, Frank L. Pedrotti and Leno S. Pedrotti, *Introduction to Optics* (Prentice-Hall, Englewood Cliffs, NJ, 1987), Chap. 19.

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[3] Reference 1, Sec. 19-6.

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Newton's law of cooling—A critical assessment

Colm T. O'Sullivan

Department of Physics, University College, Cork, Ireland

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The regime of applicability of Newton's law of cooling is considered in some detail. Three distinct models of the cooling of hot bodies under laboratory conditions are compared experimentally. A model found to be applicable over a reasonably wide range of temperatures and cooling conditions is presented.

I. INTRODUCTION

Newton's law of cooling is invoked in a wide range of contexts in applied science. A recent example, and one that has caused considerable interest, is the reported observation[1] of nuclear fusion at room temperature, but the law is also applied in other areas, for example, in materials science,[2,3] high-temperature superconductivity,[4] and atmospheric physics.[5] Newton's law can be invoked in a wide variety of contexts including in the measurement of the heat capacity of calorimetric systems, in determining heat losses to the surroundings during experimental runs, etc. Because of the widespread use of this law of cooling and, in particular, because of the importance of the cold fusion results, if confirmed, it would seem appropriate to carry out a critical study of the regime of applicability of the basic assumptions involved in applying the law in these contexts.

The law governing the cooling of hot bodies by convection first appeared in a paper read by Newton at the Royal Society on 28 May 1701 and published anonymously in Philosophical Transactions for March and April 1701 (p. 824).[6] The law states that the rate of heat loss per unit area from a body is directly proportional to the temperature difference between the body and the surrounding fluid medium[7] in contact with the body. It was realized from as early as 1740 at least[8] that Newton's model was not applicable to all situations and the question seems to have been a matter of much debate throughout the 18th and 19th centuries. Clearly, other heat loss mechanisms,[9] in particular radiation, must be considered. Furthermore, a distinction must be made between cooling by convection currents arising from the heating of the surrounding medium directly by the cooling body ("natural convection"), on the one hand, and by convection currents resulting from external influences ("forced cooling"), on the other. This article considers the relative significance of these factors in laboratory benchtop experiments and similar situations.[10]

II. MODELS OF COOLING OF THERMAL SYSTEMS

At least three distinct models (laws of cooling) that attempt to describe the cooling of warm systems in a laboratory environment are to be found in standard textbooks on general physics and heat. These models may be summarized as follows.

A. Newtonian cooling

Newton's 1701 model is mentioned in most texts. The rate of heat loss per unit area from a body at temperature T is given by

$$\frac{1}{A}\frac{dQ}{dt}=h'(T-T_a), \tag{1}$$

where T_a is the temperature of the fluid (most commonly air) surrounding the body. The constant of proportionality h' is sometimes called the heat transfer coefficient.[11] The regime of validity of the model is usually given by $(T-T_a)\ll T$ and it is often stated that forced cooling must be involved. The latter requirement means that a significant current in the fluid is required to carry away heat energy to the environment, the value of h' depending on the magnitude of the current.

A plausibility argument can be made for the dependence of $(T-T_a)$ given in (1). The cooling body is considered to be surrounded by a layer of still fluid ("boundary layer") adhering to the surface through which heat energy has to be conducted before being carried away by the convective currents outside the layer. If the layer is considered to be uniform, the heat transfer coefficient can be understood to be the ratio of the thermal conductivity of the fluid to the mean thickness of the boundary layer. Even where the boundary layer is neither sharply delineated[12] nor uniform over the whole body, a linear dependence on $(T-T_a)$ is to be expected if the thermal conductivity plays the role described.

B. Dulong–Petit cooling

Several authors suggest that in certain circumstances a more appropriate description of cooling of a hot body is given by

$$\frac{1}{A}\frac{dQ}{dt}=g(T-T_a)^n. \tag{2a}$$

Taylor[13] states that the value of n lies between 1.3 and 1.6 "depending on the freedom of circulation of air." Nelkon and Parker[14] and Burns and McDonald[15] give a value of $n=\frac{5}{4}$.

The origin of this model goes back to 1818 when the French Académie des Sciences offered a prize of 3000 francs for the study of a number of problems, one of which was to determine the laws governing the cooling of bodies in a vacuum. The response stimulated one of the earliest collaborations between Pierre Dulong and Alexis Petit.[16] In their prize-winning memoir, Dulong and Petit undertook a detailed reexamination of Newton's law of cooling, distinguishing between losses from radiation and those from contact with the surrounding medium. Following a number of remarkable experiments they arrived at a series of laws relating to different special cases.[17]

The $\frac{5}{4}$-power law involved in the Dulong–Petit model may be explained as follows. While the heat transfer coefficient h' in Eq. (1) is considered to be independent of the temperature of the cooling body, in circumstances where convection currents in the surrounding fluid are induced solely by the buoyancy of that part of the fluid heated directly by the cooling body itself (natural convection), the value of h' will depend on $(T-T_a)$. Heat losses due to natural convection from vertical surfaces were studied theoretically by Lorentz[18] in the 1880s and experimentally by Langmuir[19] in the 1910s. In this case, and in the case of a number of other geometrical configurations,[20,21] the heat transfer coefficient was found to be proportional to $(T-T_a)^{1/4}$ and thus

$$\frac{1}{A}\frac{dQ}{dt}=g(T-T_a)^{5/4}. \tag{2b}$$

The situation described here is not normally applicable to laboratory benchtop experiments unless considerable care has been taken to exclude externally induced drafts. Nevertheless, the Dulong–Petit model has been applied with some success in situations where natural convection does not dominate.[22] A possible explanation of this is given in Sec. IV.

C. Newton–Stefan cooling

Most authors refer to the fact that whenever a body is at a higher temperature than its surroundings it will lose energy by radiation as well as by the conduction–convection process. In this case, in addition to the terms on the right-hand side of Eqs. (1) and (2), the effect of the radiation emitted from and absorbed by the surface of the system must be included. The principle governing heat energy emitted and absorbed in this way was not known to Newton or to Dulong and Petit. In fact, it was over 60 years after the experiments of Dulong and Petit that Josef Stefan proposed that the rate at which energy is emitted radiatively from the surface of a body is proportional to the fourth power of its temperature. In his original 1879 paper, Stefan[23] took the results of Dulong and Petit, together with experiments by Tyndall[24] on incandescent platinum wires, as his starting point. He also pointed out that the Dulong–Petit model was in agreement with his T^4 law. Boltzmann's elegant derivation[25] of Stefan's law from thermodynamic considerations followed in 1884.

In principle, all three mechanisms discussed above are involved in the cooling of a laboratory benchtop system and in some situations all three may play a significant role. In most circumstances, however, normal drafts in the room result in forced cooling being dominant over natural convection. In this case the total heat loss per unit area due to Newtonian cooling and radiative heat transfer is given by

$$\frac{1}{A}\frac{dQ}{dt}=h(T-T_a)+\epsilon\sigma(T^4-T_r^4), \tag{3}$$

where T_r is the mean temperature of the sources of thermal radiation in the environment of the system, ϵ is the emissivity of the surface, and σ is Stefan's constant. If it is assumed that $T_r=T_a$ (see, however, Sec. VI), then the right-hand side of (3) is a function of $(T-T_a)$ and (3) can be written[26] as

$$\frac{1}{A}\frac{dQ}{dt}=a\theta+b\theta^2+c\theta^3+d\theta^4, \tag{4}$$

where $\theta=T-T_a$ and the constants have the following values:

$$a=h+4\epsilon\sigma T_a^3 \quad (\sim h+6\ \mathrm{W\,m^{-2}\,K^{-1}}),$$
$$b=6\epsilon\sigma T_a^2 \quad (\sim 0.03\ \mathrm{W\,m^{-2}\,K^{-2}}),$$
$$c=4\epsilon\sigma T_a \quad (\sim 6\times10^{-5}\ \mathrm{W\,m^{-2}\,K^{-3}}),$$
$$d=\epsilon\sigma(\sim\times10^{-8}\ \mathrm{W\,m^{-2}\,K^{-4}}).$$

The numbers in parentheses are the numerical values of the constants for $T_r = 300$ K and $\epsilon = 1$.

III. USE OF TEMPERATURE VERSUS TIME DATA IN CALORIMETRIC EXPERIMENTS

In many experimental situations, the temperature of the calorimetric system is measured at regular time intervals. To explain such data by means of any of the models requires the integration of an equation of the form

$$\frac{C}{A}\frac{dT}{dt} = f(T), \tag{5}$$

where C is the heat capacity of the system of $f(T)$ represents the function on the right-hand side of Eq. (1), (2), or (3). Thus $\theta = (T - T_a)$ at any instant can be determined from

$$\int \frac{d\theta}{f(\theta)} = -\frac{A}{C}t, \tag{6}$$

where it is assumed that the heat capacity is independent of temperature over the range of temperature involved in the experiment. The function $1/f(\theta)$ is integrable in closed form in all three cases but, while the integration is simple (and familiar) in the first two cases, the solution in the Newton–Stefan case [Eq. (3)] yields a very complicated expression containing at least seven terms.[27]

If $(T - T_a)$ is not too large, however, the series on the right-hand side of (4) converges reasonably rapidly and, in this case, a satisfactory approximation to the Newton–Stefan model is given by

$$-\frac{C}{A}\frac{d\theta}{dt} = a\theta + b\theta^2, \tag{7}$$

which can be integrated easily to give

$$\theta = \theta_0 e^{-\beta t}/[1 + \Gamma\theta_0(1 - e^{-\beta t})], \tag{8}$$

where $\beta = (h + 4\epsilon\sigma T_a^3)A/C$, $\Gamma = 6\epsilon\sigma T_a^2/(h + 4\epsilon\sigma T_a^3)$, and θ_0 is the value of $(T - T_a)$ at $t = 0$. Accordingly, the variation of temperature with time in the three models outlined in Sec. II can be written as follows:

(i) Newtonian cooling:

$$T - T_a = (T_0 - T_a)e^{-\beta t}, \tag{9a}$$

(ii) Dulong–Petit cooling:

$$T - T_a = [(T_0 - T_a)^{-1/4} - (\tfrac{1}{4})\beta t]^{-1/4}, \tag{9b}$$

(iii) Newton–Stefan cooling:

$$T - T_a = (T_0 - T_a)e^{-\beta t}/ [1 + \Gamma(T_0 - T_a)(1 - e^{-\beta t})]. \tag{9c}$$

It should be noted that when the quadratic term in (7) can be neglected ($\Gamma = 0$) the Newton–Stefan model reduces to Newtonian cooling. Nevertheless, in this case, the value of the heat transfer coefficient h' determined on the basis of Newton's law of cooling will exceed the "true" value of h by $4\epsilon\sigma T_a^3$.

IV. APPLICATION OF THE DULONG–PETIT MODEL

The Dulong–Petit model has been found to be reasonably valid in the case of cooling by convection of bodies in low drafts, but where the special considerations of Sec. II B are not strictly applicable. This is consistent with Stefan's explanation of the Dulong–Petit results and a simple understanding of why this is so can be found from the following exercise. A set of data can be generated using the equation

$$y = h(T - T_a) + \epsilon(T^4 - T_a^4) \quad 300 < T < 400,$$

taking $\epsilon = 5.7 \times 10^{-8}$ and $T_a = 300$. A nonlinear curve-fitting routine can then be used on this data set to find the best fit to the function $y = g(T - T_a)^n$ with g and n as fitting parameters. When this exercise is carried out over a range of realistic values of $h(h < 25)$, the values of n obtained fall in the range 1.1 to 1.4, the value $n = 1.25$ occurring at around $h = 18$. Thus it would appear that the Dulong–Petit model can be understood in this context as nothing more than an attempt to describe combined conductive–convective and radiative cooling by a power-law relationship.

Obviously, for a particular value of h, a value of n can be found that gives a better description of the cooling of a hot body than that provided by Newton's law of cooling, consistent with the statement of Taylor quoted above. Because of the dependence of n on the value of the heat transfer coefficient, however, the Dulong–Petit model is of limited usefulness in practice except, of course, where natural convection alone is involved. Even in these latter circumstances the contribution from radiative heat loss will be significant.

V. EXPERIMENTAL TEST OF THE MODELS

The following experimental arrangement was used to assess the relative validity of the three models in typical experimental situations. Two accurately calibrated (± 0.2 K) rod thermistors (RS part 151-120) were connected to the A/D port of a microcomputer (Acorn BBC Model B). One thermistor was inserted in a cylindrical block of aluminum, the block and this thermistor together comprising the system under study. The heat capacity of this system was determined from the mass and specific heat capacity of its components and was also measured using standard calorimetric techniques. Both approaches yielded values for C/A close to 5500 J K^{-1} m^{-2}.

The aluminum block with the thermistor inserted was heated to around 100 °C and suspended inside a large cardboard box (the reason for enclosing the system in a box is important and will be discussed in Sec. VI). The second thermistor was placed inside the box at about 500 mm from the block and used to monitor the temperature of the surrounding air. This latter thermistor was cylindrical in shape (radius ~2 mm), had a highly polished stainless steel surface, and was oriented to present minimum cross section to the hot cylinder. No increase in the reading from this thermistor due to radiation absorbed from the hot body was observed; in fact, the temperature measured by this thermistor varied very little throughout any experimental run.

Ventilation flaps were provided in the top of the box and in the sides near the bottom. In addition, a small fan was inserted in one side of the box. By running the fan at different speeds and/or by opening or closing the ventilation holes as required a range of different draft conditions were generated inside the box. Temperature *versus* time data were obtained for four different draft conditions as follows.

Draft 1: Vents closed, fan off;

Draft 2: Vents open, fan off;

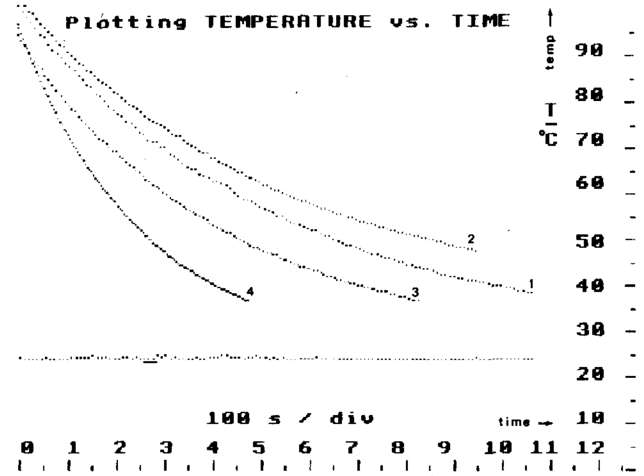

Fig. 1. Dump of computer screen showing typical cooling curves corresponding to the four draft conditions investigated.

Draft 3: Vents open, fan at half speed;

Draft 4: Vents open, fan at full speed.

In each case, 120 pairs of data points, as well as the corresponding air temperature, were plotted on the computer screen and recorded on disk; four such cooling curves are shown in Fig. 1.

Each of the three models described, i.e., Eqs. (9a)–(9c), was compared with the observed data using a derivative-free nonlinear regression routine (PAR) from the BMDP statistical package[28] running on a VAX/11 780. The most straightforward indication of the goodness of fit of the data to the models is the "sum of the residues" (Σ_{res}) computed by the program. The results are summarized in Table I; the lower the value of Σ_{res}, the better the fit.

The Newton–Stefan model clearly provides the best fit to the data under all cooling conditions, the value of Σ_{res} always lying between 0.9 and 2.2. While there is one fitting parameter more here than in the other two cases, this third parameter is statistically significant having a P value < 0.0001 in all except the highest draft conditions. At lower drafts the Dulong–Petit model ($\Sigma_{res} = 11$) provides a better description than Newton's law of cooling ($\Sigma_{res} = 49$) but is much less satisfactory than the Newton–Stefan model. Under the largest draft (Draft 4) the Newtonian model is much better than the Dulong–Petit model and provides as good a fit ($\Sigma_{res} = 1.0$) as in the Newton–Stefan case but is significantly less satisfactory than the Newton–Stefan model in all other circumstances.

The fitting parameters generated by the program can be used to determine the various constants in the models, viz. h' in the Newtonian case, g in the Dulong–Petit model, and h and $\epsilon\sigma$ in Newton–Stefan cooling. The values thus calculated are also listed in Table I. Under the highest draft conditions Newton's law of cooling yields the same value of $h(\sim 20\ \mathrm{W\,m^{-2}\,K^{-1}})$ as the Newton–Stefan model, when correction has been made for the contribution from the linear part of the radiation term in (3). Finally, the values of $\epsilon\sigma$ obtained from the Newton–Stefan model turn out to be of the same order of magnitude as Stefan's constant, thereby giving additional confirmation of the theoretical basis of this model.

At larger drafts, i.e., $h > 20\ \mathrm{W\,m^{-2}\,K^{-1}}$, Newton's law of cooling provides an equally good description as the Newton–Stefan model at the sensitivity of the experiment described. This represents the start of the regime where the conduction–convection process begins to dominate and Newton's law of cooling may be applied. As discussed above, however, radiation still plays a role in that the value of the heat transfer coefficient determined assuming Newtonian cooling exceeds the "true" value of h by $4\epsilon\sigma T_a^3$ (or approximately $6\ \mathrm{W\,m^{-2}\,K^{-1}}$ at $T_a = 300\ \mathrm{K}$). Unless the draft is very large (i.e., $h \gg 4\epsilon\sigma T_a^3$), this factor must be taken into consideration in any attempt to estimate the mean thickness of the boundary layer using Newton's law of cooling.

VI. EFFECT OF LOCAL THERMAL SOURCES

Initially the experiments described above were carried out in the open on a laboratory bench. In these circumstances the "best fit" to the data obtained turned out to be surprisingly poor in all cases with unexpectedly large systematic errors for all models. This effect was traced to the fact that the assumption that $T_r = T_a$ was not valid in this case. This seems to result from the fact that in a modern laboratory the temperature of the radiation sources may be significantly different from the air temperature. Sunlight through large windows, artificial lighting, modern electrical apparatus together with air conditioning all contribute to differences between T_r and T_a. In such circumstances, Eq. (4) contains an additional term, that is

$$\frac{1}{A}\frac{dQ}{dt} = h(T_r - T_a) + a\theta + \text{terms in } \theta^2, \ldots, \text{etc.},$$

where $\theta = T - T_r$ in this case. Thus, even in situations where Newton's law of cooling may otherwise be validly applied, the fractional error involved in neglecting this ef-

Table I. Comparison of the models discussed in the text ($T_a = T_r = 288\ \mathrm{K}$).

	Newtonian cooling $F(t) = h'(T - T_a)$		Dulong–Petit cooling $F(t) = g(T - T_a)^{5/4}$		Newton–Stefan cooling $F(t) = a(T - T_a) + b(T - T_a)^2$		
	Σ_{res}	$\frac{h' - 4\epsilon\sigma T_a^3}{\mathrm{W/m^2/K}}$	Σ_{res}	$\frac{g}{\mathrm{W/m^2/K}}$	Σ_{res}	$\frac{h}{\mathrm{W/m^2/K}}$	$\frac{\epsilon\sigma \times 10^8}{\mathrm{W/m^2/K^4}}$
Draft 1	49	8.9	11	3.5	1.6	0.23	7.4
Draft 2	23	9.1	12	3.7	2.2	1.2	6.9
Draft 3	7.9	12	46	5.1	1.0	5.7	6.0
Draft 3	1.0	22	94	8.9	0.9	21	1.0

fect is approximately

$$[1/(1+h/4\epsilon\sigma T_a^3)][|T_r-T_a|/(T-T_a)],$$

which may be significant where the overall temperature rise is small.

While it is possible to incorporate this effect in any of the models, it is difficult to determine the value of T_r experimentally without the use of an appropriately designed bolometer. If possible, therefore, it is preferable to shield calorimetric experiments from radiation sources; hence the reason for enclosing the system in a box as described above.

In certain circumstances nonradiative as well as radiative heat transfer from the environment may present difficulties in sensitive calorimetric experiments. It has been suggested,[29,30] for example, that heat exchange between the constant temperature water bath and the ambient environment may have been a significant source of error in the cold fusion experiments of Fleischmann and Pons.[1]

VII. CONCLUSIONS

Discussion in standard textbooks of theories describing cooling of warm bodies has been unnecessarily empirical and reticent about the regime of applicability of such theories. The experiments described in this article indicate that a model based on combined conductive–convective (Newtonian) and radiative (Stefan) cooling can be applied with confidence over the range of conditions usually found in laboratory calorimetric experiments provided care is taken to ensure that the temperature of all nearby radiation sources is the same as that of the fluid surrounding the systems. This condition can be achieved most easily by shielding the system from any sources likely to present problems in this regard.

The techniques described here also provide a reasonably simple and pedagogically satisfactory method estimating the value of Stefan's constant without the need for high temperatures or creating a vacuum around the system.

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