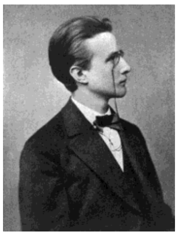
Max Planck and a thermodynamic enigma

In April 1911, only a few months before the first Solvay Conference on physics, Max Planck is invited by the French Physical Society to give a talk on his research. His chosen topic is one of central importance in thermodynamics: the relation between temperature and energy. The account of Planck's talk in the *Journal de Physique*, a predecessor of the *European Physical Journal* now co-published by EDP Sciences, offers a glimpse into the excitement and turmoil of physics at the beginning of the twentieth century. At this time, early developments in quantum theory and its implications were becoming increasingly difficult to ignore.

In his speech, Planck highlights the non-trivial relation between two central thermodynamic quantities, temperature and energy. As he points out, the discipline of thermodynamics has greatly benefited from understanding the distinction between temperature and heat, and from the instruments – thermometers and calorimeters – that can measure these quantities precisely.

Heat corresponds to a transfer of energy – between a system and its surroundings, for example – as a result of a temperature difference. It can be seen, as Planck writes, as a "special form of energy" quantified by means of its mechanical equivalent. Temperature, by contrast, is more difficult to relate to energy. A temperature difference between two bodies indicates the direction in which heat flows between them in the same way that a potential difference fixes the direction of an electric current. Planck notes how this analogy breaks down as soon as one considers two systems in thermal equilibrium with a third. The fact that it is possible to conclude that these two systems are also in thermal equilibrium with one another is "a very remarkable and very important circumstance" for Planck, who stresses that no equivalent of what we now know as the zeroth law of thermodynamics holds for electrical systems.

What tools can help shed further light on the relations between thermodynamic quantities or on their magnitudes? At the time of Planck's writing, the kinetic theory of gases had been successfully used to derive some accurate quantitative predictions. In this model, the temperature of an ideal gas is proportional to the average kinetic energy of the atoms or molecules that it is made of. Thermal equilibrium is identified as the condition where the atoms or molecules of two bodies in contact with one another have the same average kinetic energy. As Planck explains, the kinetic theory has led Boltzmann and Gibbs to formulate a result known as the equipartition theorem. He summarises this as follows: for a



system in statistical equilibrium, the same quantity of energy must be assigned to each independent variable that determines the energy of the system.

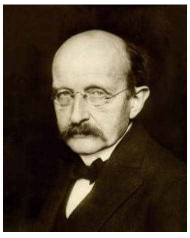
When Planck addresses his audience in Paris, the equipartition theorem is thought to be of fundamental relevance to thermodynamics. For some of his peers, even, this theory already answers the question about the relation between temperature and energy. Planck therefore explains the joint application of the kinetic theory and the equipartition theorem, and what can be deduced from it, before presenting his own ideas.

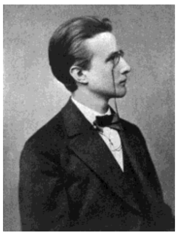
According to the kinetic theory, to characterise a gas, liquid or solid body it is necessary to take into account the vectorial velocities of its molecules (or atoms). If a system comprises a number of such bodies in a state of statistical equilibrium, it follows from the equipartition theorem that each velocity component of each molecule in the whole system has the same average energy. Consequently, thermal and statistical equilibrium will coincide provided that the temperature of a body is taken to be a measure of the average energy associated with any velocity component of any molecule in or, more generally, with any independent variable describing the body.

By 1911 it is becoming increasingly apparent that applying the equipartition theorem over-enthusiastically to some properties of matter and radiation leads to serious deviations from what is observed experimentally. As Planck explains, the failure of this theorem to deal accurately with radiation is best shown in the issue of black-body radiation: a puzzle that he knows extremely well. The problem with matter is exemplified by the issue of the specific heats of solids, which has captured the attention of the young Einstein.

So, what does Planck propose to make of the role of the equipartition theorem in thermodynamics? He does not think it should be entirely rejected, but that it should be interpreted as a special case of a more general principle.

He devotes the rest of his talk to sketching this more general concept. He starts by identifying a state of statistical equilibrium between two bodies that are isolated from everything but each other, and can thus exchange heat through conduction or radiation, as one characterised by a maximum probability. Equating this state with thermal equilibrium enables him to express the temperature T of a body as a function of log P, where P is the probability that the body has energy E. As an after-thought, he adds that this result allows him to define the entropy of a system as S = k log P, where k is Boltzmann's constant. Boltzmann originally proposed that the entropy of a system may be calculated through this simple relation (although he referred to W – the number of ways in which the constituents of the system can be arranged to achieve the same total energy – rather than P). The





celebrated formula, which is inscribed on Boltzmann's grave, is however due to Planck.

This way of relating temperature and energy through the probability P satisfies Planck. However, he does not know how to express P as a function of energy in a general manner: exceptions are special cases such as that of an ideal gas, which he includes in the paper. To calculate P for, say, a polyatomic gas, one needs to know how many degrees of freedom characterise the movements of the atoms it comprises. Is it fair to assume that each constituent in the gas moves freely as a point system obeying Hamilton's equations? This is where Planck identifies the issue with the equipartition theorem: in his view, it systematically over-estimates the number of independent variables that determine P. In searching for a condition that will let him reduce this number, he turns to the hypothesis he introduced a decade earlier to shed light onto the problem of black-body radiation. This "hypothesis of the elements of energy" – in other words, the existence of energy quanta – has since then shaken the entire research field.

In the thermodynamic context considered here, energy quantisation restricts the number of intra-molecular degrees of freedom because the molecular vibrations responsible for observable heat emission and absorption phenomena can only take on energy values that are integer multiples of a finite quantity ε. This quantity is determined by (and, in fact, proportional to) the vibration frequencies. As a consequence, two molecules vibrating at different frequencies have different average energies even if they have the same temperature. This is in stark contrast with the view based on the equipartition theorem: there is no more equal distribution of energy. Notably, Planck remarks that if ε is small or the temperature is high, his approach and the one based on the equipartition theorem agree.

Planck does not hide his optimism about the importance of this "hypothesis of the elements of energy", which in 1911 was already supported by a number of experimental observations (thanks also to the independent work of Einstein). He remains, however, duly cautious about the exact formulation and reach of this hypothesis. Indeed, he concludes that "as for a definitive judgement on the value of this new hypothesis, only experiment – as is the case with all problems in physics – can provide it."

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