Temperature in non-equilibrium states: a review of open problems and current proposals

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Abstract

The conceptual problems arising in the definition and measurement of temperature in non-equilibrium states are discussed in this paper in situations where the local-equilibrium hypothesis is no longer satisfactory. This is a necessary and urgent discussion because of the increasing interest in thermodynamic theories beyond local equilibrium, in computer simulations, in non-linear statistical mechanics, in new experiments, and in technological applications of nanoscale systems and material sciences. First, we briefly review the concept of temperature from the perspectives of equilibrium thermodynamics and statistical mechanics. Afterwards, we explore which of the equilibrium concepts may be extrapolated beyond local equilibrium and which of them should be modified, then we review several attempts to define temperature in non-equilibrium situations from macroscopic and microscopic bases. A wide review of proposals is offered on effective non-equilibrium temperatures and their application to ideal and real gases, electromagnetic radiation, nuclear collisions, granular systems, glasses, sheared fluids, amorphous semiconductors and turbulent fluids. The consistency between the different relativistic transformation laws for temperature is discussed in the new light gained from this perspective. A wide bibliography is provided in order to foster further research in this field.

Contents

1. Introduction

Temperature is one of the central and most emblematic quantities in both equilibrium thermodynamics and statistical mechanics, up to the point that thermodynamics could be tentatively defined as the study of the macroscopic equilibrium properties of systems for which temperature is one of the fundamental variables. Nevertheless, its apparently intuitive relation with our physiological sense of hot and cold is misleading and its rigorous theoretical foundations and practical measurements are subtle and far from trivial. Indeed, our sense of temperature is related not only to temperature itself, but it relies too on the rate of gain or loss of heat across the skin. Thus, metals feel colder than wood despite them being at the same actual temperature; and we feel a body to be warmer if we have been previously in contact with a colder body rather than with a hotter body. From a theoretical point of view, the definition of temperature requires the support of two fundamental laws: the zeroth and the second laws of thermodynamics. The zeroth law defines an empirical temperature relating to the transitivity of mutual thermal equilibrium. The second law establishes the meaning of hotter and colder by stating the direction of the flow of heat from hotter to colder bodies, and defines an absolute temperature, independent of the material properties of the system used to evaluate it. Finally, from a practical perspective, it is well known that thermometry, the science of temperature measurement, is subtle and delicate, and requires very different methods at different ranges of temperature. Despite this, the fundamental aspects of temperature in equilibrium states can be considered to be well defined and understood. We will therefore turn our attention to the conceptual challenges arising when temperature in non-equilibrium steady or quasi-steady states is considered. The difficulties in fast unsteady non-equilibrium states are wider and deeper, and we will not consider them in this review.

Basic questions in non-equilibrium thermodynamics concern the definition and meaning of entropy and absolute temperature out of equilibrium, which lie at the heart of thermodynamics and statistical mechanics (Bridgman 1961). These basic concepts call for a discussion of non-equilibrium situations, where it is not clear which are the macroscopic variables that should be chosen for the description of non-equilibrium states, nor the extent of the validity of the usual statements of the basic laws of thermodynamics. Classical irreversible thermodynamics (de Groot and Mazur 1962, Haase 1969, Gyarmati 1970, Glansdorff and Prigogine 1971), grounded on the local-equilibrium hypothesis, assumes that the basic thermodynamic concepts do not require a reformulation out of equilibrium, but that usual equilibrium quantities may be locally applied to systems in non-equilibrium states. In fact, even in situations where it is well known that full equilibrium thermodynamics does not strictly apply, such as, for instance, in glasses, it is often assumed, in an implicit way, that the temperature concept remains valid, either related to room temperature in the simplest approaches or to subtler definitions, as will be seen throughout this review.

When the assumption of local equilibrium is no longer tenable (see, for example, Truesdell (1969), Keizer (1987), Jou *et al* (1988, 1999, 2001), Muschik (1990), Eu (1992), Müller and Ruggeri (1993), Sieniutycz (1994), Silhavy (1997), Maugin (1999)) one is faced with the problem of defining temperature and entropy in non-equilibrium conditions. This can occur, for instance, when the relaxation times of some internal degrees of freedom are long or when the values of the fluxes or the gradients present in the system are high. These situations are found both in macroscopic and microscopic theoretical and practical approaches; some authors have been aware of these limitations. For instance, we may quote McLennan (1989) who states: 'Clearly, there is no zeroth law for a non-equilibrium situation. The reading of a "thermometer" may depend on its orientation, shape, surface properties, and so on; other variables of the system being observed, such as the gradient of the "temperature" or its rate

of change, may also influence the reading. Non-equilibrium temperature is introduced for theoretical convenience rather than to take advantage of a basic principle'. Therefore, the idea that temperature is a quantity measured by a sufficiently small and fast thermometer turns out to be conceptually naive and insufficient practically, and it is thus necessary to go beyond this simplistic statement in order to grasp the complexities of this concept. In any case, it is essential to know what is the actual meaning of the quantity being measured by all types of thermometer in steady states, and its relation to other quantities in the system.

From the thermodynamic point of view, different concepts of 'non-equilibrium temperatures' have been considered in several contexts, so that it is easy to find in scientific literature quantities such as dynamical temperatures, contact temperatures, effective temperatures, generalized temperatures, quasi-temperatures, among others. The meaning of temperature in non-equilibrium situations has also been discussed in microscopic approaches, as in information theory, kinetic theory of gases, fluctuation–dissipation relations and computer simulations. In areas directly related to applications or experiments the question of temperature in non-equilibrium states has also arisen and is being examined in a very active way. Typical situations are found in glasses, sheared fluids, granular materials, amorphous semiconductors, turbulent fluids or chaotic systems or, in a spatially smaller scale, nuclear materials and nanoscale systems among others.

Different proposals in dissimilar fields are not surprising, as research has been started from very different perspectives and motivations. These range from very pragmatic ones to highly speculative ones, and have been often based on convenient *ad hoc* extrapolations of some well-known equilibrium thermodynamic relations to non-equilibrium situations. No effort has been made, however, to compare the different proposals and to appraise, if possible, their mutual consistency. The main goal of this paper is in fact to contribute to a stimulation of this connection. Let us emphasize that we do not pretend to give a wholly satisfactory and definitive answer to the complicated question of temperature in non-equilibrium situations, but to foster discussion on this topic and to provide a wide bibliography to researchers interested in this basic question.

Let us add also that temperature is not the sole intensive thermodynamic quantity in need of a proper definition in non-equilibrium states, as this problem also arises, for instance, in pressure or in chemical potential. These definitions may be of particular interest, because of their consequences on, for instance, phase diagram theory, electrolyte solutions and electrochemical systems. In several situations, the corrections with respect to the local-equilibrium values implied by the generalized definition turn out to be measurable and to have practical interest (Keizer 1987, Criado-Sancho *et al* 1991, Nettleton 1996c, Baranyai and Cummings 1999), but here we will focus our discussion on temperature.

The paper is organized as follows. In order to recall the multiple definitions of temperature in equilibrium states, part A is a review of equilibrium situations from the perspectives of thermodynamics (section 2) and of statistical mechanics (section 3). Part B discusses the theoretical foundations for analysing temperature in non-equilibrium situations, by means of macroscopic (section 4) and microscopic (section 5) approaches. Part C is devoted to showing explicit illustrations (section 6) and to outlining the phenomenological use of effective non-equilibrium temperature in several kinds of system (section 7), such as atomic nuclei, granular systems, glasses, sheared fluids, amorphous semiconductors and turbulent hydrodynamic systems. Note that we do not pretend to explore the physical details of such diverse systems, but to stress the main ideas closely related to the concept of temperature.

A general overview of our presentation is given in table A, where we discuss temperature from four different perspectives, comparing directly equilibrium and non-equilibrium situations: (1) general laws of thermodynamics (in particular, the zeroth and

Table A. General overview of equilibrium expressions containing absolute temperature and their use in non-equilibrium situations.

	Section	
	Equilibrium	Non-equilibrium
Definitions from fundamental laws		
Zeroth law: empirical temperature	2.1	4.1, 4.2, 4.4
Carnot theorem: absolute temperature		
$\dfrac{T_2}{T_1} = \dfrac{Q_2}{Q_1}$	2.2	4.1, 4.3
Definitions containing entropy or entropy flux		
Gibbs relation		
$T = \left(\dfrac{\partial U}{\partial S}\right)_{V,N}$	2.3	4.1, 4.3
Entropy flux		
$\boldsymbol{J}^s = T^{-1}\boldsymbol{q} + \cdots$	2.3	4.1, 4.3
Effective definitions from macroscopic quantities		
Equations of state		
Internal energy		
$U = U(T, H, X) = U_{\text{eq}}(T_{\text{eff}}, H)$	5.1	7.3
Magnetization		
$M = M(T, H, X) = M_{\text{eq}}(T_{\text{eff}}, H)$	3.4	7.3
Transport quantities		
Electrical conductivity		
$\sigma = \sigma(T, H, X) = \sigma_{\text{eq}}(T_{\text{eff}}, H)$		7.4
Einstein relation		
$k_{\text{B}}T = \dfrac{D}{\mu}$	5.3	7.5
Semimicroscopic or microscopic definitions		
Fluctuation theory: second moments		
of fluctuations		
$k_{\text{B}}T = \dfrac{\langle(\delta m)^2\rangle}{(\partial m/\partial h)}$	5.3	7.3
Fluctuation–dissipation relations between the		
response function $R(t, t_{\text{w}})$ and the		
correlation function $C(t, t_{\text{w}})$		
$R(t, t_{\text{w}}) \equiv \dfrac{1}{T_{\text{eff}}}\dfrac{\partial C(t, t_{\text{w}})}{\partial t_{\text{w}}}$	5.3	7.3
Kinetic theory: average kinetic energy		
$\frac{3}{2}k_{\text{B}}T = \langle\frac{1}{2}mv^2\rangle$	3.1	5.1, 6.1
Configurational temperature: averages of		
intermolecular potential energy		
$\dfrac{1}{k_{\text{B}}T} = \dfrac{\langle\nabla_{\text{r}}^2 V\rangle}{\langle|\nabla_{\text{r}}V|^2\rangle}$	3.2	5.4, 6.1
Radiation temperature: wavelength		
corresponding to maximum power emission		
$\dfrac{1}{k_{\text{B}}T} = \dfrac{2.823}{hc}\lambda_{\text{max}}$	3.2	6.2
Statistical mechanics: distribution function		
$Pr \propto \exp[-(k_{\text{B}}T)^{-1}H + \cdots]$	3.2, 3.4	7.2
Information theory: Lagrange multiplier		
conjugate to energy $\beta \equiv (k_{\text{B}}T_{\text{eff}})^{-1}$		
$Pr \propto \exp(-\beta H + \cdots)$	3.3	5.2, 6.2, 6.3, 7.6

second laws), (2) fundamental thermodynamic equations based on entropy and entropy flux, (3) thermodynamic equations of state or phenomenological transport equations, and (4) microscopic approaches. In all of these perspectives, generalized definitions of temperature appear, which are of practical use at least in some restricted domains of phenomenology. In equilibrium, all these definitions lead to the same result, but out of equilibrium different definitions, implying different methods of measurement, yield different results. At the end of the paper, in table B, we summarize the main difficulties encountered in each tentative definition of temperature in non-equilibrium situations.

A. Equilibrium situations

In this first part, we review the status of temperature in classical thermodynamics and equilibrium statistical mechanics. Such a review, though seemingly elementary, is necessary in order to have at hand the tools and concepts required for further exploration of temperature in non-equilibrium situations. It reminds us of the subtleties involved in the definition of temperature and it will be helpful in the discussion of the proposals to generalize this concept to non-equilibrium states, since most of them are based on extrapolations of equilibrium relations.

2. Equilibrium thermodynamics

The concept of empirical temperature is introduced in classical thermodynamics through the zeroth law. Empirical temperature is not universal, as it is dependent on thermometers. The concept of a universal, absolute temperature is obtained by means of the second law, by using Carnot's theorem. When absolute temperature has been introduced, it is possible to define a new thermodynamic quantity, entropy, and absolute temperature may then be expressed as its partial derivative with respect to internal energy (Callen 1960, Kestin 1979). The basic ideas concerning temperature in equilibrium thermodynamics are briefly recalled here, because throughout the paper it will be discussed to what extent they may be extrapolated to non-equilibrium situations. A collection of definitions of temperature and heat proposed by classical authors (Clausius, Kelvin, Maxwell, Gibbs, Kirchhoff), as well as by recent authors, may be found in the paper by Monleón-Pradas and Gómez-Ribelles (1997) or in the book by Smorodinsky and Ziescher (2000). Pedagogical discussions on equilibrium temperature may be found, for instance, in Miller (1952), Ehrlich (1981) and Baierlein (1990).

2.1. The zeroth law and empirical temperature

The zeroth law of thermodynamics, stated by Fowler and Guggenheim (1939), is chronologically the last of the four laws of thermodynamics. However, from a conceptual perspective, it is a starting point because it is necessary—but not sufficient—to establish the concept of temperature. The zeroth law states that if two systems are in thermal equilibrium with a third one, they will be in mutual thermal equilibrium with each other when put in direct thermal contact. This transitivity of thermal equilibrium—together with the obvious properties of reflexivity and commutativity—induces a partition of the space of thermodynamic states of the systems into classes of equivalence constituted by all those states that are in thermal equilibrium with each other. These classes are called isotherms, to which a label called empirical temperature may be attached.

To define thermal equilibrium one should avoid, at this stage of presentation, any reference to heat flow, because heat is a quantity defined by the first law, which is logically posterior to the zeroth law. Thus, one may define thermal equilibrium between two systems forming an

isolated system when they are considered as a whole, as the situation in which they reach a state where no temporal change in the values of their respective variables is observed.

The zeroth law is not sufficient for a full characterization of the temperature concept. Indeed, this temperature is related to thermal equilibrium, but not to heat transfer and, consequently, it does not bear any relation to the intuitive concepts of hot or cold, nor to the concept of heat. In addition, the label characterizing isotherms need not have a monotonic and continuous set of values, but, in principle, its values might be randomly attributed to each different isotherm, only on condition of avoiding assigning the same value to two different classes of equivalence. To relate temperature and heat transfer, the second law of thermodynamics is needed.

Since the transitivity property is not restricted to thermal equilibrium between states of the same system, the empirical temperature must have the same value for the corresponding isotherms of any systems. A given system may then be selected as a thermometer, and any property of the system, sufficiently sensitive and univocally related to temperature, may be chosen as a thermometric property. Examples of usual thermometric properties are the length of a fluid column, the electric resistance of a metallic resistor or of a semiconductor, the thermoelectric power of a thermocouple, and the emittance of a black body. We are defining a thermometric scale when a value of temperature is attached to each value of such a thermometric property.

Any thermometric scale requires the specification of the position of the origin (zero degrees) and the magnitude of the degree. In the oldest thermometric scales, the degree was defined by dividing the interval between the values of the temperature of two fixed points into a given number of subdivisions—usually 100. For instance, in the Celsius scale, 0°C corresponds to equilibrium between ice and liquid water and 100°C to equilibrium between vapour and liquid pure water both at the pressure of 1 atm. In the original definition of the Fahrenheit scale, 0°F was assigned to the temperature of equilibrium between ice and liquid water saturated with common salt and 100°F to the temperature of a healthy human body. The 0 and 100°C corresponded approximately to 32 and 212°F, respectively, which were later taken as exact values for these fixed points. Modern definitions of thermometric scales use only one unique fixed point, such as the triple point of water, to which an arbitrary value is assigned—this value is taken as 273.16 K in the Kelvin absolute scale. The value assigned to the temperature of the fixed point determines the magnitude of the degree.

One basic problem with empirical temperature is that despite the fact that two different thermometers may be calibrated to have the same values of temperature at two given fixed points, in general they will not exactly coincide at any other point if they are made of different materials. To avoid this dependence of temperature on the thermometric materials is one of the basic challenges of classical thermodynamics. One way to remove this dependence was the observation that all gases at sufficiently low pressures follow the same equation of state

$$pV = NR(t + 273.15) = NRT, \tag{2.1}$$

with N being the mole number, R a universal constant (the ideal-gas constant), t the temperature in degrees Celsius and T the so-called ideal-gas temperature scale. Thus, pressure (at constant volume) and volume (at constant pressure) of ideal gases are thermometric properties, which indicate a temperature, independent of the properties of the particular gas being used in the thermometer. It depends on the general properties of ideal gases, i.e. on the common behaviour of all real gases as their pressure is reduced. However, to establish a truly absolute scale—i.e. completely independent of the material and not restricted to low-pressure gases—the second law is needed. William Thomson attained this important conclusion in 1848 on the basis of Carnot's theorem on the efficiency of heat engines (Erlichson 2001).

2.2. Carnot theorem and the definition of absolute temperature

In 1824, S Carnot published the essay titled 'Sur la puissance motrice du feu et les machines propres à développer cette puissance'. One of its main results was the theorem stating that 'no heat engine working between two given heat reservoirs can be more efficient than a reversible engine working between those reservoirs'. As a corollary, it follows that all reversible engines working between two given heat reservoirs have the same efficiency. If Q_1 is the heat absorbed by the engine from the hotter reservoir in one cycle, Q_2 is the heat delivered to the colder reservoir and W is the work done by the engine per cycle, then the efficiency η is defined as

$$\eta = \frac{W}{Q_1}. \tag{2.2}$$

Carnot used the caloric theory of Lavoisier, which considered heat as a substance, and assumed conservation of caloric. We will skip historical details and assume from now on energy conservation—which was formulated between 1840 and 1850 by researchers such as Mayer, Joule, Colding or Helmholtz. According to this principle, one has $W = Q_1 - Q_2$ and therefore (2.2) may be written as

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}. \tag{2.3}$$

Thus, according to Carnot's theorem, the ratio Q_2/Q_1 only depends on the empirical temperatures ϑ_1 and ϑ_2 characterizing the heat reservoirs, i.e.

$$\frac{Q_2}{Q_1} = \Phi(\vartheta_1, \vartheta_2). \tag{2.4}$$

Thomson's idea of defining an absolute temperature scale was to use the fact that the function $\Phi(\vartheta_1, \vartheta_2)$ in (2.4) is universal (i.e. independent of any details of the engine and the reservoirs) and factorizable as

$$\frac{Q_2}{Q_1} = \Phi(\vartheta_1, \vartheta_2) = \frac{\varphi(\vartheta_2)}{\varphi(\vartheta_1)}, \tag{2.5}$$

where $\varphi(\vartheta)$ is another universal function, which was interpreted as an absolute temperature. Indeed, by assigning to $\varphi(\vartheta)$ a value in a reference state 1, its value at any other state 2 could be assigned in a universal way by measuring Q_2 and Q_1 in a reversible cycle of a heat engine working between both states. Since the ratio Q_2/Q_1 is universal, the ratio $\varphi(\vartheta_2)/\varphi(\vartheta_1)$ is also universal and the value of $\varphi(\vartheta)$ in state 2 is then independent of the working substance of the engine.

Of course, this definition of absolute temperature is not operative in practice. However, when the efficiency of an ideal-gas engine is considered, it is found that

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}, \tag{2.6}$$

T being the ideal-gas temperature. Since the ratio Q_2/Q_1 is universal, $\varphi(\vartheta)$ may be identified—at the exception of a multiplicative constant which determines the magnitude of the degree—as the ideal-gas temperature scale, which then becomes an absolute scale, and which is more practical than the measurement of Q_2/Q_1 in a reversible cycle.

However, from a practical point of view, the gas thermometer is very cumbersome. Therefore, a series of practical rules were set up by the International Temperature Scale (ITS) of 1927 and adopted by the seventh General Conference of Weights and Measures to overcome the practical difficulties of gas thermometry. Further modifications were introduced in meetings of the Committee of Weights and Measures held between 1948 and 1990. A practical scale

consists of specifying temperature values (according to the absolute scale) of a set of fixed points and thermometric interpolation rules between these fixed points. Using these rules, any laboratory may calibrate with a high precision its own thermometers (Kestin 1979).

2.3. Entropy, entropy flux and absolute temperature

The realization that heat is not a substance (caloric) but a form of energy transfer led to the formulation of the first principle, which states the existence of a state function U, internal energy, the changes of which are given by

$$\Delta U = W + Q, \tag{2.7}$$

W and Q being, respectively, the work done on the system and the heat supplied to the system. However, the first law is not enough to obtain Carnot's theorem. Thus, in 1850 and 1851 the second law of thermodynamics was independently established by Clausius and Kelvin by means of two celebrated statements. The first asserts that 'it is impossible for a heat engine, working in a cycle, to produce no other effect than that of extracting heat from a colder reservoir and supplying it to a hotter reservoir' (Clausius' statement). The second states that 'it is impossible for a heat engine working in a cycle to produce no other effect than that of extracting heat from a reservoir and performing an equivalent amount of work' (Kelvin's statement). Both statements are equivalent to each other and to Carnot's theorem. Clausius' statement links temperature with the flow of heat from hotter to colder bodies, in agreement with experience.

It is seen, thus, that the thermodynamic definition of temperature involves many subtleties. It requires both the zeroth law (transitivity of thermal equilibrium) and the second law (definition of absolute temperature and the relation of temperature to heat transfer).

To provide a mathematical formulation of the second law, Clausius introduced in 1865 the concept of entropy, S, as a function of state where the differential is

$$dS = \frac{\hat{d}Q_{\text{rev}}}{T}. \tag{2.8}$$

Here, $\hat{d}Q_{\text{rev}}$ means the heat exchanged in a reversible process, and T is the absolute temperature of the reservoirs that are supplying or absorbing heat from the system. Recall that $\hat{d}Q_{\text{rev}}$ is not an exact differential, as it depends on the process, but in contrast $(1/T)\,\hat{d}Q_{\text{rev}}$ is integrable. Note that definition (2.8) only allows one to define entropy in equilibrium states, which are connected to an equilibrium reference state by means of a reversible process. According to the Clausius formulation of the second law, entropy cannot decrease in isolated systems; this fixes a direction to possible processes in isolated systems.

It follows from (2.8) that $\hat{d}Q_{\text{rev}} = T\,dS$; furthermore, for compressible ideal (non-viscous) fluids, $\hat{d}W_{\text{rev}} = -p\,dV$. Then, the first and second laws, (2.7) and (2.8), may be combined in the expression

$$dU = T\,dS - p\,dV. \tag{2.9}$$

When changes in the composition of the system, characterized by the number of moles N_i of each species i, are taken into account, this expression generalizes into the Gibbs equation

$$dU = T\,dS - p\,dV + \sum_i \mu_i\,dN_i, \tag{2.10}$$

with μ_i being the respective chemical potential of species i.

From (2.10), the standard thermodynamic definition for equilibrium absolute temperature follows

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V, \{N\}}, \tag{2.11}$$

where $\{N\}$ denotes all numbers of moles. This expression will play an important role in our further considerations concerning thermodynamic temperature.

A different definition of temperature, also called flux temperature, may be given in terms of the ratio of the energy and the entropy fluxes, instead of the ratio of the energy and entropy densities as (Landsberg and Tonge 1980)

$$T_J \equiv \frac{J^u}{J^s}. \tag{2.12}$$

In fact, this definition is of interest in non-equilibrium situations, because in strict equilibrium the fluxes vanish. Anyway, we briefly mention it here for the sake of completeness, and we will discuss in greater detail the relation between temperature and non-equilibrium flux in section 4.3.2. Note that absolute temperature is related to the entropy and the internal energy contents of the system, whereas flux temperature is defined in terms of entropy and energy fluxes passing through a surface. For isotropic blackbody radiation, the energy flux is $J^u = (c/4)(U/V)$ and the entropy flux $J^s = (c/4)(S/V)$, where c is the speed of light in vacuum, or, in terms of temperature, $J^u = \sigma T^4$ and $J^s = (4/3)\sigma T^3$, where σ is the Stefan–Boltzmann constant, and thus

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \left(\frac{\partial J^s}{\partial J^u}\right)_V, \qquad T_J = \frac{\sigma T^4}{4/3\sigma T^3} = \frac{3}{4}T. \tag{2.13}$$

This definition of temperature is particularly useful in the analysis of solar energy conversion, because it takes place in a steady-state situation, in such a way that its efficiency must be evaluated from balance equations implying the fluxes of energy and of entropy associated with radiation. Landsberg and Tonge (1980) provide a wide discussion of this topic.

Finally, it should be recalled that the third law of thermodynamics also has some connections with the concept of temperature, as it describes situations where absolute temperature tends to zero. This law, formulated by Nernst in 1906, states that when absolute temperature tends to zero, entropy tends to a constant (usually taken as zero, following a suggestion by Planck), i.e. to a value that is independent of pressure, volume, composition, magnetic fields or any other variable whatsoever. It was subsequently realized that the third law implies that absolute zero cannot be attained in a finite number of processes, in such a way that this law may be also formulated in terms of the unattainability of the absolute zero of temperature.

2.4. Temperature and gravitation: thermodynamics of black holes

An attractive example, where some hypotheses concerning entropy yield information on temperature beyond the range of current experimental information, is the black hole. Indeed, following a result by Hawking, according to which the total area of the event horizon of a black hole cannot decrease, Bekenstein (1973) put forward the hypothesis that an entropy proportional to the horizon area A could be associated with black holes. Thus, he made the assumption that

$$S = \alpha k_B \frac{A}{L_p^2} = 4\pi\alpha k_B \frac{R^2 c^3}{\hbar G}, \tag{2.14}$$

where L_P is the Planck length, defined as $L_P \equiv (\hbar G/c^3)^{1/2}$, G the gravitational constant, α a dimensionless constant, the value of which cannot be predicted on purely dimensional grounds, and R is the Schwarzschild radius of the black hole, namely $R = 2GM/c^2$. The existence of such entropy implies that black holes have a non-vanishing temperature. Indeed, the energy U of a black hole is related to its mass M as $U = Mc^2$, in such a way that one has

$$\frac{1}{T} = \frac{\partial S}{\partial U} = 32\pi\alpha k_B \frac{GM}{\hbar c^3}. \tag{2.15}$$

The fact that T is not zero would imply that black holes should radiate, which was considered initially as a contradiction, because in the classical theory black holes are defined by their inability to radiate. However, Hawking (1975) was able to show from microscopic arguments that, when quantum effects are taken into account in the vacuum surrounding the black hole, it seems to radiate according to a well-defined Planckian spectrum characterized by temperature T with the dimensionless constant α being 1/4. This surprising result, the first in which gravitational effects and quantum effects were combined, gave a strong impetus to the thermodynamics of black holes and demonstrated once more the strength of the thermodynamic formalism, which was able to anticipate microscopic theories.

3. Statistical physics

This section is devoted to reviewing microscopic statements on absolute temperature in equilibrium statistical mechanics, the kinetic theory of gases and informational microscopic descriptions in order to have a panoramic overview of relations where the extrapolation to non-equilibrium is taken as a basis for defining non-equilibrium temperature.

3.1. Kinetic theory of gases

In the simplest microscopic model, ideal gases are considered to consist of rigid particles that collide elastically with the walls of the container. By examining the force exerted by the collisions of the particles on the walls and comparing this expression with the ideal-gas law (2.1), namely $p = (N/V)RT = nk_BT$, one arrives at the conclusion that

$$\tfrac{3}{2}k_B T = \left\langle \tfrac{1}{2}m\boldsymbol{c}^2 \right\rangle, \tag{3.1}$$

with n being the number density, i.e. the number of particles per unit volume, $\boldsymbol{c}$ the velocity of the particles and the angular brackets denoting the average over the velocity of the particles. This identification of absolute temperature in terms of the average translational kinetic energy has been very influential in kinetic theory and computer simulations, where it is assumed that it remains valid even in the absence of thermal equilibrium. This relation is indeed very easy to grasp, as it allows us to identify the internal energy as the disordered or chaotic kinetic energy, but it has several limitations that will be commented on below.

As the three components of the velocity must follow the same properties in an isotropic space, it follows that

$$\left\langle \tfrac{1}{2}mv_x^2 \right\rangle = \left\langle \tfrac{1}{2}mv_y^2 \right\rangle = \left\langle \tfrac{1}{2}mv_z^2 \right\rangle = \tfrac{1}{2}k_B T. \tag{3.2}$$

This is at the basis of the so-called equipartition theorem. The generalization of this result to other situations (such as, for instance, two-dimensional gases and elastic solids) caused several problems to classical physics, because a strict application of it led to incorrect values for specific heats. It was only after the introduction of quantum physics that it was possible to understand that not all degrees of freedom are excited at some given temperature.

A more general analysis of gases shows that the distribution of the particle velocities in a gas at equilibrium must satisfy a statistical distribution function of the form

$$f(\boldsymbol{c}) \propto \exp\left(-\frac{1}{2}\frac{mc^2}{k_B T}\right). \tag{3.3}$$

Thus, T has a more detailed statistical meaning connected not only to the average value of the energy but also to the details of the distribution function. Note that the meaning of T in (3.3) is more restrictive than in (3.1); indeed, one can, in principle, extend (3.1) to any possible distribution function, whereas in (3.3) T characterizes a well-defined Gaussian distribution. Thus, (3.3) indicates more clearly than (3.1) the limitations of extrapolating equilibrium concepts to non-equilibrium situations.

3.2. Statistical mechanics

In equilibrium statistical mechanics, temperature appears in several different settings: as a parameter in equilibrium ensembles, as a measure of fluctuations; or as a dynamical quantity. Here, we will examine these three possibilities.

3.2.1. Equilibrium ensembles. In the 1870s, L Boltzmann formulated a statistical theory not restricted to ideal gases. He showed that the energy distribution function in any system at thermal equilibrium at temperature T has the canonical form

$$f(E) \propto \exp\left(-\frac{E}{k_B T}\right). \tag{3.4}$$

In principle, E is the energy of the whole system, but if the system consists of non-interacting, independent parts, this function may be reformulated independently for each part. In the particular case of ideal gases, E is the sum of the kinetic energy of all the particles and (3.4) may be factorized to give (3.3) for the one-particle distribution function. Starting from (3.4), it is possible to derive in a general way the equipartition theorem, according to which the average value of the energy related to quadratic degrees of freedom has the value $\frac{1}{2}k_B T$.

When the system does not have a constant number of particles but is in contact with a particle reservoir that imposes on it a constant value of the chemical potential μ, the canonical distribution function (3.4) must be generalized to the macrocanonical distribution

$$f_N(E, N) \propto \exp\left(-\frac{E}{k_B T} + \frac{\mu N}{k_B T}\right). \tag{3.5}$$

The expression for entropy is

$$S = -k_B \int f_N \ln f_N \, \mathrm{d}\Gamma_N \tag{3.6}$$

with $\mathrm{d}\Gamma_N$ being related to the element of volume in the phase space as $\mathrm{d}\Gamma_N = \mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{p}_1 \cdots \mathrm{d}\boldsymbol{r}_N\mathrm{d}\boldsymbol{p}_N \times (h^{3N}N!)^{-1}$, where N is the number of particles of the system. This definition is valid at equilibrium; out of equilibrium, it has the drawback that according to Liouville's theorem it does not change with time, in contrast to the macroscopic entropy.

In (3.4) and (3.5), T is a primitive parameter characterizing the heat reservoir with which the system is in contact. If the system is isolated, temperature does not have such a direct meaning, but must be derived from entropy and internal energy. In the microcanonical ensemble describing isolated systems, entropy is defined from the volume of the available region of the phase space corresponding to energy E or, in a less strict but more convenient way, in terms

of the volume $\omega(E)$ between E and $E + \delta E$ (Mayer and Mayer 1940, Pathria 1972). Thus, one has

$$S(E) = k_{\mathrm{B}} \ln \omega(E) + \mathrm{constant}, \tag{3.7}$$

where $\omega(E) = (\mathrm{d}\Omega/\mathrm{d}E)\delta E$, with $\Omega(E)$ being the volume of the region of the phase space with energy less than or equal to E, namely

$$\Omega(E) = \int_{H(p,q) \leqslant E} \mathrm{d}^N p \, \mathrm{d}^N q, \tag{3.8}$$

in which H is the Hamiltonian. For mathematical convenience, we obtain $\Omega(E)$ and derive $\omega(E)$ from it. From definition (3.7) and relation (2.11), it follows for the temperature

$$T_\omega = \frac{\mathrm{d}E}{\mathrm{d}S} = k_{\mathrm{B}}^{-1} \frac{\omega}{\mathrm{d}\omega/\mathrm{d}E} = k_{\mathrm{B}}^{-1} \frac{\mathrm{d}\Omega/\mathrm{d}E}{\mathrm{d}^2\Omega/\mathrm{d}E^2}. \tag{3.9}$$

An alternative definition for entropy, also proposed by Gibbs, is

$$S(E) = k_{\mathrm{B}} \ln \Omega(E) + \mathrm{constant}, \tag{3.10}$$

where the volume $\Omega(E)$ of the phase space corresponding to energies between 0 and E is considered. From this definition and (2.11) it follows for the temperature

$$T_\Omega = \frac{\mathrm{d}E}{\mathrm{d}S} = k_{\mathrm{B}}^{-1} \frac{\Omega}{\mathrm{d}\Omega/\mathrm{d}E}. \tag{3.11}$$

Both definitions of entropy (3.7) and (3.10), and of temperature (3.9) and (3.11), coincide in the thermodynamic limit, namely, when $N \to \infty$ and $V \to \infty$, with N/V being finite. For finite N and V, the second definition seems preferable (Berdichevsky *et al* 1991). A wide interest in situations where N and V are finite has surged recently because of the increasing technological potential of nanoscale systems.

3.2.2. Temperature and fluctuations. Let us return to the canonical ensemble in order to allow for the possibility of fluctuations, which provide another way to relate temperature to physical observable quantities, often used in non-equilibrium situations. In the canonical ensemble, the internal energy of the system fluctuates and the second moments of the energy fluctuations are related to temperature as

$$\langle (E - \langle E \rangle)^2 \rangle = k_{\mathrm{B}} C_v T^2, \tag{3.12}$$

with C_v being the thermal capacity of the system. In the macrocanonical ensemble, not only the energy, but also the particle number may fluctuate.

In some situations, one is interested not only on the second moments of fluctuations, but also in their dynamics. The evolution of fluctuations is often studied by the means of stochastic equations, which contain a random noise related to the absolute temperature of the system. Indeed, assume a stationary ensemble of random variables $\boldsymbol{a}(t)$, the average of which will be assumed to vanish (otherwise, the same results may be obtained for $\boldsymbol{a}(t) - \langle \boldsymbol{a}(t) \rangle$). Assume that the variables satisfy a Langevin equation of the form

$$\frac{\mathrm{d}\boldsymbol{a}}{\mathrm{d}t} = -\mathbf{H} \cdot \boldsymbol{a} + \boldsymbol{\xi}(t), \tag{3.13}$$

where $\mathbf{H}$ is a matrix of constant friction coefficients and $\boldsymbol{\xi}$ is a stochastic Gaussian and white noise, satisfying

$$\langle \xi(t) \rangle = 0 \qquad \langle \xi(t)\xi(t') \rangle = \mathbf{\Gamma}\delta(t - t'), \tag{3.14}$$

here $\boldsymbol{\Gamma}$ is a matrix unknown until now, which may be determined from the condition that, in equilibrium, the variables must satisfy a canonical probability distribution of the general form

$$f(\boldsymbol{a}) = \left[(2\pi)^k \det \boldsymbol{\sigma}\right]^{-1/2} \exp\left(-\tfrac{1}{2}\boldsymbol{a}^T \cdot \boldsymbol{\sigma}^{-1} \cdot \boldsymbol{a}\right), \tag{3.15}$$

with $\boldsymbol{\sigma}$ being a matrix of constant coefficients and k being the dimension of the vector $\boldsymbol{a}$. Then, it follows that $\boldsymbol{\Gamma}$ is related to $\mathbf{H}$ and $\boldsymbol{\sigma}$ as (Keizer 1987)

$$\mathbf{H} \cdot \boldsymbol{\sigma} + \boldsymbol{\sigma} \cdot \mathbf{H}^T = \boldsymbol{\Gamma}. \tag{3.16}$$

This is an expression of the fluctuation–dissipation theorem, which relates the intensity of the noise to the frictional coefficients. In particular, assume the simple situation in which the fluctuating variable is the velocity of a particle of mass m immersed in a bath; then

$$m\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = -\gamma \boldsymbol{v} + \boldsymbol{\xi}(t), \tag{3.17}$$

where γ is the friction coefficient between the particle and the bath. Taking into account that in equilibrium the velocity distribution function must have the form (3.3), it follows from (3.15) and (3.16) that the second moments of the noise appearing in (3.17) are given by

$$\langle \xi(t)\xi(t') \rangle = 2\frac{\gamma}{m} k_{\mathrm{B}} T \delta(t - t'). \tag{3.18}$$

Thus, in stochastic simulations it is assumed that the noise is a measure of the temperature of the system; accordingly, one speaks about noise temperature.

A particular situation related to fluctuation–dissipation, which is often used to define or 'measure' temperature in some situations (Behringer 2002, Makse and Kurchan 2002, Bonn and Kegle 2003), is Einstein's relation between mobility μ' and the diffusion coefficient D, namely

$$D = k_{\mathrm{B}} T \mu', \tag{3.19a}$$

in the linear (near equilibrium) regime. Since D is connected to the second moments of the displacement in Brownian motion and μ' is related to steady velocity under an external field, both coefficients may be associated with displacements of particles and their ratio may be used as a measure of an effective temperature. However, (3.19a) is a particular case of a more general relation, namely (Hope *et al* 1981)

$$D = \mu' n \left(\frac{\partial \mu}{\partial n}\right)_{T,p}, \tag{3.19b}$$

where μ is the chemical potential. For ideal systems, $\mu = \mu^*(T, p) + k_{\mathrm{B}} T \ln n$ and (3.19b) reduces to (3.19a). Thus, the relation between D and μ' is more directly related to chemical potential than to temperature itself; this must be kept in mind when using (3.19) to define temperature out of equilibrium.

3.2.3. Dynamical temperature. In the previous definitions of temperature examined in section 3.2.1, dynamics does not play a direct role, because the average is carried out over equilibrium ensembles. However, in molecular dynamics simulations, it is more direct and useful to perform time averages over the trajectory of the system in the phase space. To be able to go from a dynamical to a thermodynamical description in a classical Hamiltonian system, it must exhibit ergodicity, i.e. dynamical time averages may be replaced with ensemble averages. This equivalence has been proved only in a few situations, but it is believed that in the thermodynamic limit, i.e. when the systems are large, both averages coincide. However, molecular simulations deal with a relatively small number of particles and this equivalence

is questionable. Thus, the recent thrust in molecular dynamics simulations has stimulated a renewed interest in algorithms to evaluate temperature from the dynamics of a system.

In particular, Rugh (1997, 1998) has provided a dynamical approach to the statistical description of classical Hamiltonian systems, which is based on the global geometric structure of the energy surface. Indeed, according to the Birkhoff theorem, the time average depends on the energy surface only, and not on a particular trajectory, in such a way that it is meaningful to study the surface instead of a selected physical trajectory. Rugh derives a dynamical expression for temperature for Hamiltonian dynamical systems, the average of which yields the temperature in microcanonical ensembles. This dynamical approach makes use of the thermodynamic relation (2.11) by expressing the entropy in terms of the logarithm of the volume of the phase space as in (3.7) or (3.10). In particular, it is able to show that

$$\frac{1}{k_{\mathrm{B}} T(E)} = \lim_{t \to \infty} \frac{1}{t} \int_0^t \Phi(x(t')) \, \mathrm{d}t', \tag{3.20}$$

with Φ being the function

$$\Phi \equiv \nabla \cdot \left(\frac{\nabla H}{|\nabla H|^2} \right), \tag{3.21}$$

where H is the classical Hamiltonian of the system and the gradient refers to the full phase space, i.e. the derivative with respect to $\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N, \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N$. Thus, in this approach temperature is related to the curvature of the energy surface rather than to the properties of the square of the momenta related to the kinetic definition of temperature. Then, it provides an elegant geometric view, because it does not rely on singling out the momenta as privileged variables. Note that, for the sake of further comments, the function Φ may also be written as

$$\Phi = \frac{\nabla \cdot \nabla H}{\nabla |H|^2} - 2d^2 H \frac{(\nabla H) \cdot (\nabla H)}{|\nabla H|^4}, \tag{3.22}$$

d being the dimensionality of the phase space (usually $6N$). Combining (3.20) and (3.22), the former may be approximated as

$$\frac{1}{k_{\mathrm{B}} T} = \left\langle \frac{\nabla \cdot \nabla H}{|\nabla H|^2} \right\rangle + O\left(\frac{1}{N} \right), \tag{3.23}$$

where the brackets denote a microcanonical average. The second term vanishes in the thermodynamic limit. Relation (3.23) may also be written as

$$\frac{1}{k_{\mathrm{B}} T} = \frac{\langle Nd/m + \nabla_r^2 V \rangle}{\left\langle \sum_{i=1}^N p_i^2/m^2 + a|\nabla_r V|^2 \right\rangle}, \tag{3.24}$$

where V is the potential energy and a is a constant having suitable dimensions. (Note that, in fact, one should write the average of the ratio, which is not equal to the ratio of averages in general.) Originally, Rugh's proposal was made for systems when energy is the only first integral, but it has been generalized to situations where other first integrals are relevant.

Since Rugh's formalism does not singularize the momenta as privileged variables for studying temperature, it invites the study of temperature as related to configurational variables. Of course, this idea is not completely new, because the classical equipartition theorem states that for interparticle potential energy quadratic in positions, the average energy in positional degrees of freedom is given by $\frac{1}{2} k_{\mathrm{B}} T$, in such a way that in harmonic oscillators one may well define a configurational temperature in the canonical ensemble as

$$\tfrac{1}{2} k_{\mathrm{B}} T_{\mathrm{conf}} \equiv \left\langle \tfrac{1}{2} \kappa (\Delta x)^2 \right\rangle \tag{3.25}$$

with κ being the elastic constant and Δx the deviation with respect to the average position. In Rugh's formalism, the idea of a configurational temperature may be extended to more general situations, without assuming a quadratic form for the potential energy, and it has thus aroused much interest in researchers working on liquid systems or on nonlinear lattices (Giardina and Livi 1998).

The ratio of the first terms of the numerator and denominator in (3.24) gives the usual kinetic temperature, and the ratio of the second terms gives the so-called configurational temperature (Butler *et al* 1998, Toth and Baranyai 1999, Baranyai 2000a). At equilibrium, both temperatures (kinetic and configurational) are equal, i.e.

$$\frac{3m}{\langle p^2 \rangle} = \frac{1}{k_{\mathrm{B}} T} = \frac{\langle \nabla_r^2 V \rangle}{\langle |\nabla_r V|^2 \rangle}. \tag{3.26}$$

Distinction between kinetic and configurational temperature is important, for instance, when kinetic temperature cannot be controlled directly or when the system is not in equilibrium. Furthermore, it has been found that in some occasions configurational temperature correctly accounts for the heat fluxes where kinetic temperature fails to do so, as will be discussed in section 5.4. However, how both temperatures contribute to heat conduction is still an open problem (Hatano and Jou 2003).

The derivation of thermodynamic temperature has been generalized to canonical and to molecular dynamics ensembles by Jepps *et al* (2000). Indeed, since linear momentum is conserved in non-equilibrium molecular dynamics (NEMD) simulations, and since periodic boundary conditions are assumed, the ensembles explored in molecular dynamics are not the full usual microcanonical or canonical ensembles, but some subsets of them, in such a way that convenient generalizations of Rugh's proposal are needed. Rickzayen and Powles (2001) and Jepps *et al* (2000) have generalized Rugh's definition of temperature by noting that

$$\frac{1}{k_{\mathrm{B}} T} = \left\langle \nabla \cdot \left(\frac{\boldsymbol{B}}{(\boldsymbol{B} \cdot \nabla H)} \right) \right\rangle, \tag{3.27}$$

where $\boldsymbol{B}$ is an arbitrary continuous and differentiable vector in phase space. In some sense, (3.27) may be seen as a generalization of the equipartition theorem, as it is valid for any vector field $\boldsymbol{B}$. However, out of equilibrium different vector fields $\boldsymbol{B}$ could yield different values for T.

Rugh's expression corresponds to the particular case when $\boldsymbol{B} = \nabla H$. Another choice of $\boldsymbol{B}$ in (3.27) is $\boldsymbol{B} = \nabla V$, which yields the configurational temperature as

$$\frac{1}{k_{\mathrm{B}} T_{\mathrm{config}}} = \left\langle \nabla \cdot \frac{\nabla V}{(\nabla V)^2} \right\rangle = \left\langle \frac{\nabla^2 V}{(\nabla V)^2} \right\rangle \left[1 + O\left(\frac{1}{N}\right) \right]. \tag{3.28}$$

Following the derivation of Rugh, Butler *et al* (1998) have used the requirement that the configuration temperature (3.28) must reproduce the temperature used in the Monte Carlo acceptance criterion as a thermodynamic check of consistency of statistical algorithms. If this is not satisfied the algorithm does not properly describe the potential energy of the system. The dynamical definition of temperature has been recently extended to some non-equilibrium situations on the basis of molecular dynamics, as will be seen in section 5.4.

In this section, temperature has been related to geometrical properties of the space phase. In a macroscopic perspective, Hamiltonian theories have been proposed as a unifying basis for the description of the evolution equations of thermodynamic systems (Dzyaloshinkii and Volovick 1980, Grmela 1984, 1993, 2001, Grmela and Öttinger 1997, Öttinger and Grmela 1997). Indeed, it is known that the microscopic equations of motion of the particle are Hamiltonian and that the evolution equations of ideal fluids are also Hamiltonian. Thus,

it seems logical to ask that in coherent formulations of mesoscopic evolution equations, the reversible part should be Hamiltonian, whereas the dissipative part is written in terms of a dissipation potential. In this formulation, the geometrical setting is outlined and temperature, as well as other thermodynamic variables, is related to geometrical properties of suitable surfaces in the thermodynamic space.

3.2.4. Quantum effects. The result (3.1), which implies $C_v = \mathrm{d}U/\mathrm{d}T = \frac{3}{2}R$, is not compatible with the third law of thermodynamics, one of the consequences of which is that the specific heat vanishes at $T = 0$. These, and other, drawbacks led to the application of quantum ideas to statistical physics, leading to two kinds of statistics that are different from the classical Boltzmann one. Thus, quantum systems with an antisymmetric wavefunction (half-integer spin particles) obey the Fermi–Dirac statistics, the distribution function of which is the well-known expression for particles with energy ε

$$f(\varepsilon) \propto \{\exp\left[(\varepsilon - \mu)/k_{\mathrm{B}}T\right] + 1\}^{-1}, \tag{3.29}$$

where μ is the chemical potential. For quantum systems with a symmetric wavefunction (integer-spin particles), the Bose–Einstein distribution leads to the distribution function

$$f(\varepsilon) \propto \{\exp\left[(\varepsilon - \mu)/k_{\mathrm{B}}T\right] - 1\}^{-1}. \tag{3.30}$$

In these statistics, the average value of the kinetic energy for ideal gases is not given by (3.1) but it satisfies a more complicated relation with T. Thus, relation (3.1) is not universally valid, even in equilibrium situations, but some generalizations of equipartition have been explored (Menon and Agrawal 1992). Instead, the macroscopic relation (2.11) is also satisfied in the quantum regime. A particularly important application of (3.30) is the Planck energy density distribution $u(\omega)$ of blackbody radiation as a function of the angular frequency ω (for which $\mu = 0$ and $\varepsilon = \hbar\omega$). The result is

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^2} \frac{1}{\exp(\hbar\omega/k_{\mathrm{B}}T) - 1}. \tag{3.31}$$

This leads, for the wavelength of maximum emission of radiation, to the well-known Wien law

$$\lambda_{\max} = 0.354 \frac{hc}{k_{\mathrm{B}}T} \tag{3.32}$$

and yields for the total energy density U integrated over all frequencies

$$U = \frac{\pi^2}{15} \frac{k_{\mathrm{B}}^4}{(\hbar c)^3} T^4 \equiv 4\frac{\sigma}{c} T^4. \tag{3.33}$$

These three expressions are used to obtain the temperature T of radiation, by fitting the full spectrum or a part of it, by starting from the wavelength of maximum emission or from the total energy emitted.

3.2.5. Fractal effects. We briefly mention some attempt to extend the Boltzmann–Gibbs statistical mechanics to fractal situations (Tsallis 1988, 1999, Tsallis *et al* 1998). An entropy S_q is defined in terms of the distribution function $f(x)$ as

$$S_q = -\frac{k_{\mathrm{B}}}{1 - q} \int f(x)[1 - f^{q-1}(x)]\,\mathrm{d}x, \tag{3.34}$$

where x denotes the set of variables describing the system and q a (usually) non-integer parameter. In the limit when q tends to 1, one obtains from (3.31) the usual Boltzmann definition for the entropy (3.6). In fact, it has been argued (Luzzi *et al* 2002b) that the

q exponent depends strongly on the features of the system, and that definition (3.34), or similar ones, could be useful as a generating functional of practically helpful heterotypical distribution functions rather than being a truly fundamental extension of the entropy. The main feature of (3.34) is its non-extensive character: the entropy of a system composed of two subsystems A and B, the joint probability distribution function of which may be factorized, i.e. $f_{AB}(x_A, x_B) = f_A(x_A) f_B(x_B)$, turns out to be

$$S_q(A + B) = S_q(A) + S_q(B) + (1 - q)\frac{1}{k_B} S_q(A) S_q(B). \tag{3.35}$$

Note that this expression assumes that q has the same value for A and B; this is not general, however, because q may depend strongly on the system. Anyway, we want to investigate the zeroth principle formally in this restricted situation. To do this, we examine thermal equilibrium in an isolated system composed of two subsystems A and B in mutual thermal contact (Abe 1999, Rama 2000, Martínez *et al* 2001a,b, Toral 2003). Suppose that the interaction energy between both subsystems is negligible, in such a way that $U(A+B) = U(A)+U(B)$. Assuming that the total entropy is given by (3.35), the condition of the maximum entropy characterizing thermal equilibrium reads as

$$\frac{\partial S_q(A)}{\partial U(A)}[1 + (1 - q)S_q(B)]\delta U(A) + \frac{\partial S_q(B)}{\partial U(B)}[1 + (1 - q)S_q(A)]\delta U(B) = 0. \tag{3.36}$$

From energy conservation, one has $\delta U(A) = -\delta U(B)$, and condition (3.36) may be rewritten as

$$\frac{1}{1 + (1 - q)S_q(A)}\frac{\partial S_q(A)}{\partial U(A)} = \frac{1}{1 + (1 - q)S_q(B)}\frac{\partial S_q(B)}{\partial U(B)}. \tag{3.37}$$

Thus, the condition of thermal equilibrium is not directly related here to the equality of the derivative of the entropy with respect to internal energy. We have mentioned this result for the sake of completeness but we will not study these kinds of situations here.

3.3. Information theory: equilibrium ensembles

Information theory is another field where the question concerning absolute temperature arises in a natural way. Informational statistical thermodynamics (IST) introduces a state function referred to as the informational-statistical entropy, which depends on the basic whole set of macro-variables chosen for the description of the macroscopic state of the system (Grandy 1980, 1987, Luzzi and Vasconcellos 1990, Ramos *et al* 2000, Luzzi *et al* 2001, 2002a). This is the generalization of the entropy function of equilibrium thermodynamics and classical irreversible thermodynamics, the expressions of which are recovered in the appropriate limit. As a general rule, the energy of the different subsystems that form the system under experimentation is taken as part of the basic set of macro-variables.

Information statistical thermodynamics is a statistical thermodynamics initiated by Hobson (1996) on the basis of the variational approach to statistical mechanics proposed by Jaynes in the 1950s (Jaynes 1957a,b). This method consists of the maximization of Gibbs statistical entropy, subjected to certain constraints on the average values of a given set of variables for, in that way, deriving the probability distribution function. This asserts that the probability should be taken to maximize the average missing information of the system, subjected to the constraints imposed by the available information. Here, we will focus our attention on equilibrium states but we will give a general presentation that will be applied to non-equilibrium steady states in section 5.2.

Assume that we know the mean values $\langle A_i \rangle$ of a set of extensive observables $A_i(\mu')$ with μ' denoting the positions and momenta of the N particles composing the system, i.e. $\mu' = \{r_1, p_1, \ldots, r_N, p_N\}$. We look for the probability density that maximizes the global entropy S defined by

$$S = -k_B \int f_N(\mu') \ln f_N(\mu') \, d\Gamma_N, \tag{3.38}$$

with $d\Gamma_N$ defined below (3.6), subject to the constraints expressing the known average values of the controlled variables, namely

$$\int f_N(\mu') A_i(\mu') \, d\Gamma_N = \langle A_i \rangle. \tag{3.39}$$

The constraints (3.39) are introduced through a set of Lagrange multipliers λ_i corresponding to the quantities A_i and one maximizes the quantity

$$-k_B \int \left[f_N \ln f_N + f_N(\lambda_0 - 1) + f_N \sum_i \lambda_i \cdot A_i(\mu') \right] d\Gamma_N. \tag{3.40}$$

This yields a generalized canonical distribution of the form

$$f_N = Z^{-1} \exp \left[-\sum_i \lambda_i \cdot A_i(\mu') \right], \tag{3.41}$$

where $Z(\lambda_i)$ is a generalized partition function that follows from the normalization condition for f_N, namely

$$Z = \exp[-\lambda_0 + 1] = \int \exp \left[-\sum_i \lambda_i \cdot A_i(\mu') \right] d\Gamma_N. \tag{3.42}$$

In this expression, the dot denotes the convenient scalar product between each microscopic operator A_i (scalar, vector, tensor, ...) and its respective conjugate Lagrange multiplier.

It is important to note that (3.41) is not the true statistical distribution function but a 'coarse-grained' or 'instantaneously frozen' distribution (Luzzi *et al* 2001, 2002a) which only describes the probability of the projection of the true distribution over the subspace of the basic variables (the 'informational subspace'). The relation between the true and the coarse-grained distributions depends on the details of the projection operator. Thus, (3.41) must be understood as an auxiliary coarse-grained operator that lacks, for instance, information concerning the macroscopic evolution of the variables. The relation between this auxiliary distribution and the true distribution has been worked in detail in Luzzi *et al* (2001, 2002a).

The explicit expressions of the Lagrange multipliers in terms of the average values of the basic variables are derived from constraints (3.39). The latter may be written in the compact form

$$-\frac{\partial \ln Z}{\partial \lambda_i} = \langle A_i \rangle, \tag{3.43}$$

as it follows from definition (3.42) of Z and relations (3.39). The introduction of the distribution density (3.41) in definition (3.38) for the entropy yields

$$S = k_B \left[\ln Z + \sum_i \lambda_i \cdot \langle A_i \rangle \right]. \tag{3.44}$$

The differential of S obtained from (3.44) is

$$dS = k_B d \ln Z + \sum_i \langle A_i \rangle \cdot d\lambda_i + \sum_i \lambda_i \cdot d\langle A_i \rangle = \sum_i \lambda_i \cdot d\langle A_i \rangle, \tag{3.45}$$

once we take into account (3.43). Comparison of (3.45) with the macroscopic Gibbs equation yields a general physical interpretation for the Lagrange multipliers. For instance, in an equilibrium system with a given value of the average internal energy and of the particle number, (3.41) becomes

$$f = Z^{-1} \exp\left(-\lambda_1 H - \lambda_2 N'\right), \qquad (3.46)$$

with N' being the particle-number operator. Equating the differential of the entropy in terms of the Lagrange multipliers with the macroscopic Gibbs equation (2.10) one obtains

$$dS = k_B \lambda_1 \, dU + k_B \lambda_2 \, dN = T^{-1} \, dU - \mu T^{-1} dN, \qquad (3.47)$$

which allows one to identify $\lambda_1 = 1/k_B T \equiv \beta$ and $\lambda_2 = -\mu/k_B T \equiv \alpha = -\beta\mu$. With these identifications, (3.46) is the macrocanonical probability distribution function.

Ingarden and Nakagomi (1992) and Jaworski (1981, 1983) have introduced the concept for second- and higher-order temperatures, by assuming a distribution function of the form

$$f = Z^{-1} \exp\left(-\lambda_1 H - \lambda_1' H^2\right), \qquad (3.48)$$

which includes information not only on the average of the energy but also on higher-order moments (in particular, second moments related to fluctuations). The corresponding averages are

$$\langle H \rangle = U, \qquad \langle (H - U)^2 \rangle = \langle H^2 \rangle - U^2 = \sigma_U^2 > 0. \qquad (3.49)$$

When $\sigma_U = 0$, there are no fluctuations and the system becomes perfectly isolated; thus, σ_U has a simple physical interpretation as a measure of physical isolation. The generalized reciprocal temperatures are then defined as

$$\theta_1^{-1} = \left(\frac{\partial S}{\partial U}\right)_{\sigma_U^2} = \lambda_1 + 2\lambda_1' U, \qquad \theta_2^{-1} = \left(\frac{\partial S}{\partial \sigma_U^2}\right)_U = \lambda_1', \qquad (3.50)$$

or, alternatively, in terms of $\Delta = \langle (H - U)^2 \rangle U^{-2}$

$$(\theta_1')^{-1} = \left(\frac{\partial S}{\partial U}\right)_\Delta = \lambda_1 + 2\lambda_1' \frac{\langle H^2 \rangle}{U}, \qquad (\theta_2')^{-1} = \left(\frac{\partial S}{\partial \Delta}\right)_U = \lambda_1' U^2. \qquad (3.51)$$

This proposal could be of interest in situations where fluctuations are not negligible, such as near phase transitions or critical points, in metastable states or in systems with a small number of degrees of freedom (e.g. nanosystems). In our opinion, the idea of introducing the square of the Hamiltonian or the fluctuations of the energy as independent variables may be very interesting in some situations, but to attribute the meaning of temperature to the conjugate variable of the square of the Hamiltonian is unnecessary and confusing. Instead, we think it would be more useful to look for its true physical meaning, which is clearly different from that of a temperature because it is not an intensive quantity.

3.4. Negative absolute temperature

An illustration of the generality of relation (2.11) between entropy and temperature, in contrast to the kinetic identification (3.1), is the possibility of negative absolute temperature, which is allowed in the former and forbidden in the latter. It is clear that (3.1) does not admit this possibility, which is found, however, in systems where the entropy is not a monotonically increasing function of the internal energy, such as, for instance, magnetic systems (Ramsey 1956). Indeed, since $T = (\partial U/\partial S)_{V,N,...}$, T will be negative when S decreases for increasing U. For instance, the internal energy of magnetic systems has an upper bound (corresponding to the state in which all the magnetic moments are aligned in the direction opposite to the

magnetic field H). If one assumes a system with N magnetic moments with spin $\frac{1}{2}$, the energy takes the form $U = -\mu H N_+ + \mu H (N - N_+)$, whereas the entropy is

$$S = k_B \ln \frac{N_+!(N - N_+)!}{N!}. \tag{3.52}$$

It follows that $1/T = (\partial S/\partial U)_N$ is positive for $-N\mu H < U < 0$ (S increases with U) and negative for $0 < U < N\mu H$ (S decreases with increasing U). However, the existence of negative temperatures does not imply that the system reaches zero temperature: temperature changes sign at infinity rather than at zero. States with negative temperature are hotter than states with positive temperature, as they tend to give energy to the latter when put in mutual thermal contact. Thus, the scale from cold to hot runs in fact as $+0\,\text{K}, \ldots, +273\,\text{K}, \ldots, +\infty\,\text{K}$, $-\infty\,\text{K}, \ldots, -273\,\text{K}, -0\,\text{K}$; thus, a natural choice of a temperature scale would be provided by $-1/T$, which runs according to this ordering. In fact, the conditions for the existence of states at negative temperatures are very restrictive, in such a way that in practice they are rarely met except in some mutually interacting nuclear spin systems, in which it was first produced by Purcell and Pound (1951).

The possibility of negative temperatures requires some modification of the conventional statements of the second law. For example, to the Kelvin–Planck statement must be added the impossibility of performing an amount of work on a cyclic thermal engine by rejection of the equivalent amount of heat to a negative-temperature reservoir (Ramsey 1956).

On more general grounds, the possibility of negative temperature could be found in any system with two energy levels, E_1 and E_2. Indeed, in equilibrium one would have, according to Boltzmann statistics,

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{E_2 - E_1}{k_B T}\right) \tag{3.53}$$

with g_i being the degeneracy of the respective levels. This relation may be inverted and yields

$$k_B T = (E_1 - E_2) \ln\left(\frac{g_1}{g_2}\frac{N_2}{N_1}\right). \tag{3.54}$$

Thus, one finds that T becomes negative when the level with higher energy has the highest occupation number (if one assumes, for simplicity, that the degeneracy of both levels is the same).

Systems of vortices in two-dimensional fluids are a less known example of systems that may have negative temperatures. Onsager (1949) was the first to apply the methods of statistical mechanics to the description of vortex motions in two-dimensional flows. This was possible because of the Hamiltonian form of the equations of vortex motion, namely

$$k_i \frac{dy_i}{dt} = -\frac{\partial H(x,y)}{\partial x_i}, \qquad k_i \frac{dx_i}{dt} = \frac{\partial H(x,y)}{\partial y_i}, \tag{3.55}$$

where $i = 1, \ldots, N$ correspond to the vortices, x_i and y_i are the Cartesian coordinates of the ith vortex, k_i is its circulation (the integral of the velocity along a closed line of motion around the centre of the vortex). The Hamiltonian H includes the energy of vortex–vortex and vortex–container interactions. The difference with statistical mechanics of gases is that the volume of the container bounds the phase space of each vortex, independently of the energy. The argument by Onsager (1949) was the following one. When energy tends to infinity, the volume of the accessible region of the phase space defined in (3.8) tends to a constant, namely $\Omega(E) \to A^N = $ constant, where A is the area of the system, because in this limit any position

in the container becomes accessible for each vortex. Thus, in this limit $d\Omega/dE$ tends to zero and, from the relation

$$0 \leqslant \frac{d\Omega}{dE} = -\int_E^\infty \frac{d^2\Omega}{dE^2}\,dE, \tag{3.56}$$

it follows that $d^2\Omega/dE^2$ must be negative for some values of the energy E, and accordingly the temperature (3.9), $T = k_B^{-1}(d\Omega/dE)/(d^2\Omega/dE^2)$, must be negative for such values of E.

Onsager's remark on the possibility of negative temperature for vortices has attracted the attention of many researchers (Montgomery 1972, Taylor 1972, Seyler 1974, Kraichnan and Montgomery 1980, Berdichevsky *et al* 1991). Let us mention that Berdichevsky *et al* (1991) pointed out that T always remains positive if the alternative definitions (3.10) and (3.11) for S and T are used instead of (3.7) and (3.8). In this case, $T = k_B^{-1}\Omega/(d\Omega/dE)$ will not become negative but will tend to infinity for large enough energy. This difference in the behaviour of the two different definitions of temperature is an interesting illustration of the fact that they are not equivalent, except in the thermodynamic limit, where $N \to \infty$.

3.5. Finite-size effects

We end this review of basic concepts concerning temperature in equilibrium situations by mentioning that among the several conceptual limits of temperature in equilibrium are those related to finite-size effects (Hill 2002), such as, for instance, in systems at nanometric scale like atomic and molecular clusters (Jellinek and Goldberg 2000, Andersen *et al* 2001) or atomic nuclei (section 7.2). In the thermodynamic limit of infinite systems, the results for temperature in the several ensembles coincide, but this is not so when finite-size effects must be taken into account because fluctuations have an important role. Amongst the very active pieces of research in this area let us mention cluster research, which deals with the definition of phases and phase transitions in small clusters. For instance, Jellinek and Goldberg (2000) have computed the entropy, temperature and specific heat in the two different microcanonical definitions (3.8) and (3.10) for the aluminium clusters Al_7, Al_{13}, Al_{55} and Al_{147}. Since these systems are not very large, they are suitable for dynamic computer analysis, and they have fostered the analysis of the correspondence between dynamical and statistical approaches, and the re-examination of some fundamental notions of thermodynamics and statistical mechanics, amongst which, of course, is the concept of temperature. We do not deal in greater detail with this interesting and active topic because our aim is the understanding of temperature in non-equilibrium macroscopic systems, without much emphasis on finite-size effects.

B. Non-equilibrium situations: theoretical bases

Out of equilibrium, introducing the concept of temperature is a much more complicated issue to tackle than at equilibrium. On the one side, its very concept no longer has clear foundations because the classical statements of the zeroth and second laws refer to equilibrium situations; furthermore, entropy is not defined, and therefore the formulation of the second law is problematic. These aspects call for detailed attention to the zeroth and second laws out of equilibrium. From an operational perspective, since in general energy is not equally distributed amongst the several degrees of freedom, different degrees of freedom with different relaxation times may have different temperatures. These temperatures may depend on the time scale of the measurement and the sensitivity of the thermometer to different degrees of freedom. From the microscopic point of view, the distribution function is changed with respect to its equilibrium form, and therefore it cannot be characterized only by temperature, and the

relations that directly connect temperature to some of the properties of the distribution function may be modified. Thus, in this part of the review, we analyse the different macroscopic and microscopic arguments underlying the concept of temperature. We will restrict our attention to non-equilibrium steady or quasi-steady states, because the introduction of fast varying states adds many additional problems, related, for instance, to the thermalization time of the measuring thermometer. A detailed analysis of this basic concept has been sought, in fact, since the early attempts to formulate thermodynamics formalisms for non-equilibrium steady states (Tolman and Fine 1948, Tykodi 1967).

4. Non-equilibrium thermodynamics

In the classical theory of irreversible processes, one assumes the local-equilibrium hypothesis, in which it is supposed that in spite of the fact that the system is globally out of equilibrium, it remains locally in equilibrium. In other words, it is assumed that it may be decomposed in subsystems small enough to be almost homogeneous at the macroscopic scale, and large enough, on the microscopic scale, to have many particles in such a way that macroscopic quantities keep a well-defined meaning. Within this framework, the problem of a generalization of temperature does not even arise: it is assumed that the entropy and all the derived equations of state keep locally the same meaning as in equilibrium, and that temperature coincides with that indicated by a sufficiently small and fast thermometer. The problem of the meaning of entropy and temperature arises when one goes beyond the local equilibrium, because genuinely non-equilibrium contributions must be taken into account in the entropy and, consequently, in temperature. Therefore, we go directly beyond the local-equilibrium regime. Since there are several different continuum thermodynamic theories, the ways of considering entropy and temperature will also be different. Here, we will focus on the topic of temperature; for a more general, but still brief and self-contained comparison of the several non-equilibrium thermodynamic theories, the reader is referred to Muschik *et al* (2001).

4.1. General problems: zeroth and second laws out of equilibrium

First of all, we indicate the general difficulties arising in the extrapolation of the zeroth and second laws of thermodynamics to non-equilibrium steady states, an extension that is far from trivial (Benofy and Quay 1983).

4.1.1. The zeroth law. In equilibrium, all ideal thermometers indicate the same temperature in a system. However, out of equilibrium this situation is no longer satisfied. Imagine, for instance, a system composed of matter and electromagnetic radiation. A thermometer with perfectly reflecting walls will be unaware of radiation and it will indicate the temperature of the gas. In contrast, a thermometer with perfectly black walls will be sensitive to radiation and will indicate a temperature related both to radiation and matter. In equilibrium, gas and radiation have the same temperature, and both thermometers will indicate the same reading. Out of equilibrium, matter and radiation may have different temperatures and different thermometers will yield different readings. Another example of this situation is found in plasmas, where electrons may have a different temperature than ions, or in metals, where electrons may have a different temperature than the lattice. This is due to the very different mass of electrons and ions, which makes that the energy exchange between them is slow and inefficient.

In general, it could be said that it is difficult to think of only one temperature in systems in non-equilibrium steady states. Indeed, as noted previously, different thermometers, sensitive to different degrees of freedom, will give different readings of temperature. For instance, if

there is no energy equipartition, the several degrees of freedom will have different effective temperatures. Therefore, the classical version of the zeroth law will be not satisfied. Indeed, assume that a thermometer is sensitive to a group of degrees of freedom and that it indicates the same temperature in two different systems. This does not imply that when these two systems are put in mutual thermal contact they will be generally in thermal equilibrium with each other. They will be in thermal equilibrium only if they interact through the same degrees of freedom to which the thermometer is sensitive. Thus, the zeroth law may retain a restricted validity if and only if the set of degrees of freedom to which the thermometer is sensitive is conveniently specified.

It could even be that a thermometer is sensitive to some degrees of freedom in one system and to other degrees of freedom in another system. In this case, the fact that the thermometer indicates the same temperature in both systems does not imply at all that these two systems will be in thermal equilibrium when put in contact with each other.

4.1.2. The second law. Using the second law to define temperature is also open to many problems in non-equilibrium, as entropy is not univocally defined. Definition (2.8) of entropy is not directly operative out of equilibrium, because there is not any reversible path reaching a non-equilibrium steady state. Therefore, relation (2.11) will not be useful, unless a definition and an evaluation of entropy out of equilibrium is proposed. There have been several attempts to propose such non-equilibrium entropy: some of them are based on generalizations of thermodynamics beyond local equilibrium and some others are based on microscopic models. In these situations, the knowledge of S could allow one to use (2.11) to obtain the equation of state for temperature.

To state these comments in a more explicit though less general way, we will tentatively assume that entropy in non-equilibrium states is not exactly equal to the local-equilibrium entropy. That entropy may depend on some non-equilibrium variables (like the fluxes, or gradients, or internal variables, the value of which vanishes at equilibrium). In fact, non-equilibrium entropy is not unique, but in some circumstances suitable definitions may be given which allow us to extend the entropy to some specific non-equilibrium situations.

Thus, we assume that the entropy s per unit mass is a function $s(u, x, q)$, where u is the internal energy, x represents the set of the further variables of equilibrium (e.g. volume, composition, magnetization, etc) and, at last, q denotes the set of non-equilibrium variables on which entropy may depend. To be more explicit, we will assume that

$$s(u, x, q) = s_{\text{leq}}(u, x) - \alpha(u, x)q^2, \tag{4.1}$$

where the first term on the right-hand side corresponds to the local-equilibrium entropy and the second term is the non-equilibrium contribution, which is assumed here to be second-order in the non-equilibrium variables. This implies that we are considering, for didactical reasons, a slight deviation from the local equilibrium value, due to the influence of the extra subset of basic variables q, deemed necessary for a proper characterization of the non-equilibrium state. In some places we will use explicit forms for (4.1), whereas in other situations we will keep x and q unspecified, and we will deal only with formal general aspects. Expressions such as (4.1) may be obtained from several points of view. An example is extended irreversible thermodynamics, which uses the fluxes as non-equilibrium quantities (Jou *et al* 1988, 1999, 2001, Eu 1992, Müller and Ruggeri 1993), although the main ideas can be generalized by taking as an extra variable the non-equilibrium contribution of the full distribution function of the system, leading in this way to a more detailed mesoscopic description (Vilar and Rubí 2001). Other well-known approaches are the theories with internal variables (Maugin 1999) or the recent Hamiltonian theories (Grmela's 1993, 2001, Beris and Edwards 1994). The

reason for proposing a non-equilibrium entropy is that it will allow us to obtain, by suitable derivations, many expressions for quantities in non-equilibrium situations, which may then be compared with the corresponding expressions in equilibrium and also to be checked against experiments looking for a validation of the approach. This opens up the possibility to compare in a single setting rather different definitions for non-equilibrium temperature, as will be seen below. This will be helpful to ask several questions which cannot even be asked within the framework of local equilibrium, but the detailed results will not necessarily be quantitatively exact. For instance, if x and q are extensive quantities, a non-equilibrium temperature θ may be defined as

$$\frac{1}{\theta} \equiv \frac{\partial s}{\partial u} = \frac{1}{T} - \frac{\partial \alpha}{\partial u} q^2, \tag{4.2}$$

where T is the local-equilibrium temperature, which is a space-dependent function.

4.2. A Gedanken experiment: thermometers and Carnot cycles

One of the intuitive difficulties in considering non-equilibrium temperature is that temperature is associated with equilibrium between the thermometer and the system. Therefore, talking about a non-equilibrium temperature seems at first sight a contradiction. In the Gedanken (thought) experiment proposed in figure 1, this apparent contradiction is overcome (Jou and Casas-Vázquez 1992, Casas-Vázquez and Jou 1994). Indeed, on the one side we assume the heat flux q_{rs} between the thermometer and the system; on the other side, the heat flux q_s inside the system itself. Talking about non-equilibrium temperature means that the heat flux q_{rs} between the system and the thermometer vanishes, but that the heat flux in the system is different from zero.

4.2.1. Thermometers. To be explicit, we consider that both systems in figure 1 are compressible fluids. For this example, a good choice of variables x and q are the volume per unit mass v and the heat flux $\boldsymbol{q}$, respectively. If we expand the entropy (4.1) around its local equilibrium value $s_{\text{leq}}(u, v)$ up to the second-order approximation in $\boldsymbol{q}$ we obtain an expression where the derivative with respect to u, at v and $\boldsymbol{q}$ constant, is

$$\theta^{-1}(u, v, \boldsymbol{q}) = T^{-1}(u, v) - \frac{\partial \alpha(u, v)}{\partial u} \boldsymbol{q} \cdot \boldsymbol{q}, \tag{4.3}$$
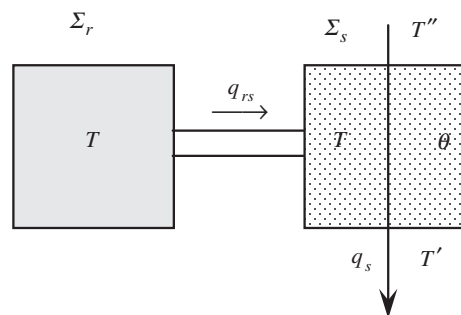
Figure 1. A Gedanken experiment to illustrate the concept of non-equilibrium temperature. Thermal equilibrium between both systems means that the heat flow along the rod connecting them is zero. This means that the temperature is the same at the ends of the connecting rod. However, each system may be far from equilibrium, if it is crossed by a heat flux in the direction orthogonal to the connecting rod. Therefore, temperature at the ends of the rod is not equal in general to local-equilibrium temperature.

which has the form of (4.2). This expression is sufficient to focus our attention on concrete questions concerning conceptual and numerical differences between non-equilibrium absolute temperature and local-equilibrium absolute temperature.

However, at the present stage of the presentation, (4.3) is still only a formal definition. To relate it to measurement, we next examine the operational meaning of temperature by means of the Gedanken experiment of figure 1. We connect both systems by means of a good thermal conductor. One of them Σ_r is at equilibrium whereas the other Σ_s is in a non-equilibrium steady state characterized by a heat flux q_s perpendicular to the connection between both systems (figure 1), and which describes the heat exchange between Σ_s and other reservoirs not indicated in figure 1. Here, we consider q_s as a discrete exchange determined by such external reservoirs, which keep it at a constant value, and we do not need to dwell explicitly on its detailed field character. When the flux q_{rs} between both systems is zero, we will say, according to the zeroth law, that both systems have the same temperature, at the points corresponding to the ends of the connecting bar. Note, however, that this statement does not clarify by itself whether the thermometer (the equilibrium system Σ_r) indicates the local-equilibrium temperature or another temperature. To clarify this point, the second law is needed.

Indeed, the second law is able to relate the heat flux q_{rs} to the temperature gradient (or, since we are dealing in fact with a discrete system, it relates it to the difference in the temperature of both systems). In our analysis, there are at least two possibilities: one of them is that q_{rs} is proportional to ∇T and the other one is that it is proportional to $\nabla \theta$, with θ defined in (4.3). It will be seen in section 4.3.1 that the second law favours the second possibility over the first one, under conditions that will be examined there in detail. If q_{rs} is proportional to ∇T, the thermometer will indicate the local-equilibrium temperature, because both systems must share the same value of T in order that the heat flux q_{rs} vanishes. If, in contrast, q_{rs} is proportional to $\nabla \theta$, the thermometer will indicate the non-equilibrium temperature defined by (4.3).

To be more concrete, consider the situation (which will be discussed on microscopic grounds in section 5.1) in which both systems have the same local-equilibrium temperature T at both ends of the conducting bar (i.e. both systems have the same average kinetic energy per particle). However, one of them (system Σ_s) is out of equilibrium. If the heat flux q_{rs} is proportional to the difference of the local-equilibrium temperature of both systems, it will be zero in this case. If, in contrast, it is proportional to the difference of the values of non-equilibrium temperature θ, then one should have

$$q_{rs} = \lambda_m \frac{\theta_s - \theta_r}{d} = \lambda_m \frac{\theta_s - T}{d}. \tag{4.4}$$

In this expression, λ_m is the thermal conductivity of the rod joining both systems and d is the separation between them, and we have taken into account that in the equilibrium system $\theta_r = T_r = T$, whereas in the non-equilibrium system $\theta_s \neq T_s = T$. If we expand $\theta - T$ up to the second order in $\boldsymbol{q}$, (4.4) may be expressed as $q_{rs} = (\lambda_m/d)\gamma T^2 q_s^2$, with $\gamma = (\partial \alpha/\partial u)$. In this case, a non-vanishing heat flux q_{rs} would be observed despite the fact that the local-equilibrium temperature is the same in both systems.

The measurement of such a heat flux q_{rs} between two systems at the same local-equilibrium temperature T would be a strong support in favour of the generalized absolute temperature θ. However, a macroscopic control of T would require measuring T, but since the question under discussion is precisely whether thermometers measure T or θ, their use should be avoided at this stage of discussion. To avoid this difficulty, one may devise a microscopic interpretation of the experiment based on kinetic theory of gases (Casas-Vázquez and Jou 1994) or to perform a molecular simulation imposing the same value for the average kinetic energy of the particles at both ends of the conductor (see section 5.4).
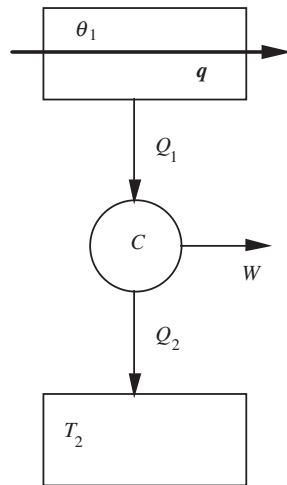
Figure 2. A Carnot engine working between an equilibrium thermal reservoir and a steady-state non-equilibrium heat reservoir. In classical theory and in most of the usual analyses, both thermal reservoirs are assumed to be at equilibrium. A possibility of exploring the non-equilibrium temperature of steady states, it is to assume that one of the heat reservoirs connected to a Carnot engine is in a steady non-equilibrium state.

4.2.2. Carnot cycles between non-equilibrium reservoirs. As mentioned in section 3.2, Carnot theorem on reversible engines provided the clue to Kelvin's definition of an absolute temperature scale, defined in terms of the efficiency of reversible Carnot engines according to expression (2.6). The Gedanken experiment proposed in figure 1 suggests considering a Carnot engine working between two heat reservoirs, one of them at equilibrium and the other one at a non-equilibrium steady state (Lambermont and Lebon 1977, Jou and Casas-Vázquez 1987) (figure 2).

It is well known that for showing the existence of an absolute temperature scale independent of any thermometric substance, W. Thomson (Lord Kelvin) used the result obtained by Carnot concerning the efficiency of a heat engine. Carnot asserts that the efficiency of a reversible heat engine operating between two heat reservoirs is independent of the working substance and of the details of the engine. His ideas can be generalized in two different but related directions. One, it may assume classical equilibrium reservoirs but relax the restriction that no entropy is produced in the system (Lambermont and Lebon 1977). Two, it may analyse a situation in which one of the reservoirs (say that at higher temperature) is in a non-equilibrium steady state, whereas the other one is in an equilibrium state (Jou and Casas-Vázquez 1987). If the engine is endoreversible (i.e. if the only irreversibility is that arising in the heat exchange between the reservoir and the system but not inside the system itself), the efficiency of the engine will be

$$\eta = 1 - \frac{T_2}{\theta_1}. \tag{4.5}$$

Since θ_1 is less than the local-equilibrium temperature T_1, the efficiency of the engine in this situation will be less than that achieved when both reservoirs are at equilibrium, the first being at temperature T_1. In view of (4.2), expression (4.5) may be written explicitly as

$$\eta = 1 - \frac{T_2}{T_1} + T_2 \frac{\partial \alpha}{\partial u} \boldsymbol{q} \cdot \boldsymbol{q}. \tag{4.6}$$

For ideal gases, it may be shown that the derivative in (4.6) is negative (Jou *et al* 2001). Thus, the non-classical term indicates that the reduction in efficiency is related to the entropy

produced when a 'more organized' energy in the non-equilibrium hot reservoir is transferred to the working substance, where it becomes completely 'disorganized' (Jou and Casas-Vázquez 1987). It must be stressed that the use of expression (4.5) is only admissible in the mentioned situation in which the engine is endoreversible. In connection with the Gedanken experiment of figure 1, this would mean that the equilibrium temperature of the working fluid (which plays a role analogous to the equilibrium system Σ_r in figure 1, would be the same as the non-equilibrium temperature of the reservoir (analogous to system Σ_s in figure 1). Since the engine in itself is assumed reversible, (4.5) would be applicable to this situation. Deeper and more general research on this kind of analysis (i.e. assuming that the reservoir is a system in a non-equilibrium steady state rather than an equilibrium state) is needed. Note that this is not an academic situation, because in many actual engines, the reservoirs (such as, for instance, a steam boiler) are continuously fed with energy to keep their temperature at a given steady value, by compensating the heat they supply to the engine.

From a geometrical point of view, the difference between θ and T can be easily understood in terms of the description shown in figure 3 (Casas-Vázquez and Jou 1994, see also Sienituycz and Berry 1991, 1993 for a related presentation). The actual non-equilibrium state is A, the equilibrium state reached by an adiabatic projection is B. The slope of the non-equilibrium entropy at A (corresponding to $1/\theta$) is different from the slope of the equilibrium entropy at B (corresponding to $1/T$). Thus, when one refers to the local-equilibrium temperature T, one is taking as a reference state the accompanying local-equilibrium state B rather than the actual non-equilibrium state A. Note that $\theta^{-1} > T^{-1}$, because the slope of the non-equilibrium entropy is steeper than that of the local-equilibrium entropy. This is a rather general feature because $s(u, \boldsymbol{q}) \leqslant s_{eq}(u)$ and $s(u, \boldsymbol{q}) \to s_{eq}(u)$ when $u \to \infty$ at constant $\boldsymbol{q}$ (this results from the property that the value of αq^2 decreases when u increases at constant q). Therefore, the curve $s(u, \boldsymbol{q})$ will be steeper than $s_{eq}(u)$ and, in general, one will have $\theta \leqslant T$. Since a non-equilibrium steady state is characterized by less entropy than that of corresponding equilibrium state, and is therefore more ordered than the equilibrium state (because entropy may be related to molecular disorder), one could qualitatively interpret $\frac{3}{2}nk_B\theta$ as the 'disordered' part of the internal energy, in analogy to the classical expression for the internal energy of monatomic gases per unit volume, given by $\frac{3}{2}nk_BT$.
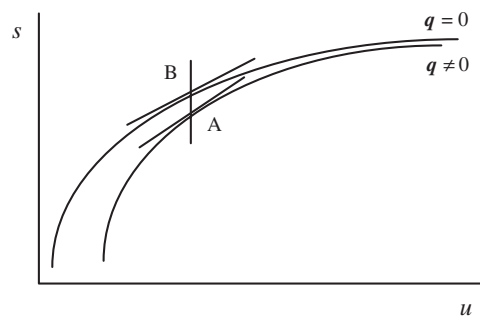
Figure 3. A schematic plot of local-equilibrium entropy (upper line) and non-equilibrium entropy defined by (4.15). Assume that the system is not at equilibrium, in such a way that its state A is defined by a given value of internal energy u and of non-vanishing heat flux $\boldsymbol{q}$. The state B is the projection of A on the equilibrium manifold, at constant internal energy. The slope of s versus u on the non-equilibrium line at point A yields the reciprocal of the generalized non-equilibrium temperature of state A, whereas the slope of the local-equilibrium entropy versus u at point B yields the local-equilibrium temperature at B, i.e. the local equilibrium temperature of state A as adiabatically projected on the equilibrium manifold.

4.3. Extended irreversible thermodynamics

In this section, we give a physical basis for an entropy having the form (4.1), depending on the heat flux as a non-equilibrium variable, and we study the relation between heat flux and temperature gradient, which was needed for the discussion of the Gedanken experiment of figure 1 in section 4.2.1. We present it within the framework of the so-called extended irreversible thermodynamics (EIT), a thermodynamic theory which incorporates the fluxes in the set of basic thermodynamic variables (Jou *et al* 1988, 1999, 2001, Eu 1992, Sieniutycz and Salomon 1992, Müller and Ruggeri 1993).

4.3.1. Entropy and temperature.   Consider a rigid solid or an incompressible perfect fluid at rest, locally characterized by the internal energy density u per unit mass (dependent on position and time, which we omit for the sake of simplicity) and the heat flux vector $\boldsymbol{q}$. The energy balance equation reduces to

$$\rho \frac{\mathrm{d}u}{\mathrm{d}t} = -\nabla \cdot \boldsymbol{q}, \tag{4.7}$$

where, for simplicity, no energy supply has been considered. To obtain an evolution equation for $\boldsymbol{q}$ compatible with the second law, one postulates the existence of a generalized entropy s which depends on u and $\boldsymbol{q}$, and where the total differential is given by

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u - \alpha(u, v)\boldsymbol{q} \cdot \mathrm{d}\boldsymbol{q}, \tag{4.8}$$

where according to (4.2) it has been introduced $\theta^{-1} = (\partial s/\partial u)_{v,\boldsymbol{q}}$ as the generalized non-equilibrium absolute temperature, which clearly is a function of u, v and $\boldsymbol{q}$, that is, of the whole set of basic variables depending, as we recall, on space and time. The time derivative of s may be obtained from (4.8) and written as

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} = -\theta^{-1}\nabla \cdot \boldsymbol{q} - \rho\alpha\boldsymbol{q} \cdot \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t}, \tag{4.9}$$

wherein use has been made of (4.7). The factor θ^{-1} in the first term on the right-hand side may be introduced into the divergence term so that equation (4.9) becomes

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} + \nabla \cdot (\theta^{-1}\boldsymbol{q}) = \boldsymbol{q} \cdot \left(\nabla\theta^{-1} - \rho\alpha\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} \right). \tag{4.10}$$

Comparison with the general form of the entropy balance $\rho\mathrm{d}s/\mathrm{d}t + \nabla \cdot \boldsymbol{J}^s = \sigma^s$ leads us to identify entropy flux $\boldsymbol{J}^s$ and entropy production σ^s as

$$\boldsymbol{J}^s = \theta^{-1}\boldsymbol{q}, \tag{4.11}$$

$$\sigma^s = \boldsymbol{q} \cdot \left(\nabla\theta^{-1} - \rho\alpha\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} \right). \tag{4.12}$$

To formulate an equation for the evolution of $\boldsymbol{q}$ compatible with the required positive definiteness of (4.12), the simplest hypothesis is to assume that

$$\nabla\theta^{-1} - \rho\alpha\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} = \mu\boldsymbol{q}, \tag{4.13}$$

with $\mu \geqslant 0$ being a function to be identified below. For small values of the heat flux, the contribution of the order $\boldsymbol{q} \cdot \boldsymbol{q}$ to the absolute temperature may be neglected so that θ goes over the local-equilibrium temperature T. Then, comparison of (4.13) with the Maxwell–Cattaneo equation (Joseph and Preziosi 1989, 1990, Jou *et al* 2001), namely,

$$\tau \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} = -(\boldsymbol{q} + \lambda\nabla T), \tag{4.14}$$

leads to the identifications $\alpha(u, v) = \tau v (\lambda T^2)^{-1}$, $\mu(u, v) = (\lambda T^2)^{-1}$, where λ is the thermal conductivity and τ a relaxation time of the heat flux defined according to (4.14).

We have written this short summary to emphasize that in this setting it is the generalized absolute temperature θ and not merely the local-equilibrium temperature T that is the relevant quantity appearing in the entropy flux and the evolution equation for the heat flux, according to the thermodynamic requirements imposed by the positiveness of the generalized entropy production (4.12). In view of (4.8) and the former identification of $\alpha(u, v)$, the generalized Gibbs equation takes the form

$$\mathrm{d}s = \theta^{-1}\mathrm{d}u - \frac{\tau}{\rho \lambda T^2}\boldsymbol{q} \cdot \mathrm{d}\boldsymbol{q}. \tag{4.15}$$

The integrability condition of (4.15) leads straightforwardly to expression (4.3).

When non-linear terms in $\boldsymbol{q} \cdot \boldsymbol{q}$ are kept in the expression for θ, the Maxwell–Cattaneo equation (4.14) generalizes as follows:

$$\tau \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} + \boldsymbol{q} = -\lambda \nabla \theta \tag{4.16}$$

and μ and α in (4.13) become $\mu = (\lambda \theta^2)^{-1}$ and $\alpha = \tau v (\lambda \theta^2)^{-1}$, respectively. The linear Maxwell–Cattaneo equation (4.14) is currently used to describe heat waves in solids at low temperatures. For a detailed discussion of this equation and its thermodynamic consequences, the reader is referred to Jou *et al* (1999, 2001). It is important to note that the appearance of θ instead of T in (4.16) is imposed by thermodynamic requirements that are a direct consequence of the use of the generalized entropy (4.15) instead of the local-equilibrium entropy. Some physical consequences of the non-equilibrium temperature on heat transport may be found in Nettleton (1987, 1996b) and in Casas-Vázquez and Jou (1989, 1994). Let us mention that Cimmelli and Kosinsky (1991) have proposed a non-equilibrium semiempirical absolute temperature for the description of materials with thermal relaxation, rather than proposing an evolution equation for the heat flux itself, as the Maxwell–Cattaneo equation.

It is important to stress that the Maxwell–Cattaneo equation is only the simplest transport equation incorporating memory effects. However, in many situations, more general equations are needed, which incorporate non-local effects, such as, for instance, the so-called Guyer–Krumhansl equation describing phonons in solids (for its thermodynamic discussion see Dreyer and Struchtrup (1993) or Jou *et al* (2001, Chapter 10)). In this case, the non-local terms may be described by means of higher-order fluxes, which contribute with additional terms to entropy and entropy flux. These new terms contribute to the complexity of the analysis of temperature in non-equilibrium, as it is briefly illustrated in section 4.3.2, devoted to the relation between entropy flux and temperature.

Another justification of the generalized entropy (4.15) that clarifies its meaning, limitations and domain of applicability is the following: consider a fluid in a non-equilibrium steady state characterized by a heat flux $\boldsymbol{q}$. As in the classical theory, the elementary cell of volume $\mathrm{d}v$ we are considering is assumed so small that within it the spatial variations of pressure and temperature are negligible. It is then asked which entropy may be ascribed to it. To answer this question, the volume element is suddenly isolated and allowed to decay to equilibrium. The decay of $\boldsymbol{q}$ to its final vanishing equilibrium values is accompanied by a production of entropy, so that one may write

$$s_{\mathrm{leq,f}} = s_{\mathrm{neq,i}} + \int_0^\infty \sigma^s \,\mathrm{d}t \,\mathrm{d}v. \tag{4.17}$$

Indices i and f refer to the initial non-equilibrium state and the final equilibrium state respectively, and σ^s is the entropy production. This relation defines a non-equilibrium entropy.

Instead of an adiabatic relaxation, other processes may be imagined, such as, for instance, isothermal or isobaric relaxations.

In (4.17), let $t = 0$ be the instant at which the volume element is isolated. The expression of σ^s, according to (4.12, 13) is given by

$$\sigma^s = \mu \boldsymbol{q} \cdot \boldsymbol{q} = (\lambda T^2)^{-1} \boldsymbol{q} \cdot \boldsymbol{q}. \tag{4.18}$$

If the decay of $\boldsymbol{q}$ is described by means of the Maxwell–Cattaneo equation (4.14), we have

$$\boldsymbol{q}(t) = \boldsymbol{q}(0) \exp(-t/\tau). \tag{4.19}$$

After inserting this expression in (4.17) and integrating, one obtains for the non-equilibrium entropy per unit mass in the steady state

$$s = s_{\text{leq}} - \frac{\tau v}{2\lambda T^2} \boldsymbol{q} \cdot \boldsymbol{q}, \tag{4.20}$$

which is precisely the integrated form of expression (4.15). This derivation gives a physical interpretation of the non-equilibrium contribution to the entropy, being due to internal dissipation during the projection from the true non-equilibrium state (state A in figure 3) to the accompanying local-equilibrium state (state B in figure 3).

4.3.2. Entropy flux and temperature. Another way to explore the meaning of the non-equilibrium temperature is by studying the entropy flow $\boldsymbol{J}^s = \theta^{-1} \boldsymbol{q}$. As noted in section 2.3, temperature is not related only to entropy but also to entropy flux. Analogously, the form of the entropy flux is changed out of equilibrium and the role of absolute temperature in the generalized entropy flux must be carefully considered in the presence of non-local effects requiring the introduction of the flux of the heat flux $\mathbf{Q}$ (a second-order tensor), as a further independent variable. In this case, the equation for the heat flux in the steady state turns out to be

$$\boldsymbol{q} = -\lambda \nabla \theta - \nabla \cdot \mathbf{Q}. \tag{4.21}$$

For instance, in situations where $\mathbf{Q}$ is related to $\nabla \boldsymbol{q}$, expression (4.21), in combination with the energy balance equation (4.7), yields the so-called Guyer–Krumhansl equations mentioned in the previous section, which may be related to higher-order moments of the distribution function for the particles of the system (Dreyer and Struchtrup 1993, Jou *et al* 2001, chapter 10). In the general case of equation (4.21), the generalized entropy flux has the form (Domínguez-Cascante and Jou 1995, 1998)

$$\boldsymbol{J}^s = \theta^{-1} \boldsymbol{q} + \beta \mathbf{Q} \cdot \boldsymbol{q}. \tag{4.22}$$

However, the tensor $\mathbf{Q}$ will have in general a non-linear coupling with the heat flux, of the form $\mathbf{Q} = \gamma(u, v) \boldsymbol{q} \boldsymbol{q}$, with $\gamma(u, v)$ being a phenomenological coefficient. Of course, as mentioned before, $\mathbf{Q}$ could include other terms such as $\nabla \boldsymbol{q}$, which do not affect the present discussion concerning temperature. Thus, the entropy flux becomes in this case

$$\boldsymbol{J}^s = \theta^{-1} \boldsymbol{q} + \beta \gamma q^2 \boldsymbol{q}. \tag{4.23}$$

Then, if we consider the relations between $\boldsymbol{J}^s$ and $\boldsymbol{q}$ in the non-linear domain it is seen that, despite $\boldsymbol{q}$ and $\boldsymbol{J}^s$ being parallel, their proportionality constant is no longer θ^{-1} (as a direct extension of the equilibrium relation $\boldsymbol{J}^s = T^{-1} \boldsymbol{q}$ would suggest), but the form $\theta^{-1} + \beta \gamma q^2$.

4.4. Coldness, contact temperature

In this section, we examine other possibilities to define temperature in non-equilibrium. The first of them emphasizes the role of the entropy flux, whereas the second one tries to build an axiomatic general basis for the definition of temperature in a non-equilibrium system.

4.4.1. Coldness. Müller (1971a,b) introduced a non-equilibrium entropy η depending not only on the empirical temperature θ_e but also on its time derivative (Hutter 1977). Accordingly, he defined the coldness Λ as the derivative of the entropy with respect to internal energy. Such a coldness depends on the empirical temperature and on its time derivative, denoted here by an upper dot, that is to say, $\Lambda = \Lambda(\theta_e, \dot{\theta}_e)$ and it is continuous at a perfect wall, i.e. across surfaces where there is no entropy production. Indeed, energy conservation imposes the continuity of the normal component of the heat flux across the wall and the condition of perfect wall imposes the continuity of the normal component of the entropy flux. Then, if one assumes that $\boldsymbol{J}^s = \Lambda \boldsymbol{q}$, the continuity of heat flux and of entropy flux requires the continuity of Λ across the wall, which guarantees that the Λ indicated by the thermometer will coincide with the Λ corresponding to the system, as it is expected. Batra (1974) generalized the concept of coldness to the case where several higher-order derivatives of temperature play a role as variables of the entropy.

It is thus seen that in Müller's definition, the form of the entropy flux plays a more important role than the differential of the entropy itself. The problem is that when the entropy flux is no longer parallel to the heat flux, as in the presence of a viscous pressure or of non-linear couplings between viscous pressure and heat flux, temperature is no longer continuous across the wall. For steady states, in which the time derivative of the empirical temperature is zero, the coldness reduces to the usual temperature. This point of view may be used with a more general form of the entropy flux, as (4.23), which may be written in a more compact form as $\boldsymbol{J}^s = \phi(u, q)\boldsymbol{q}$ with $\phi \equiv \theta^{-1} + \beta\gamma q^2$. Then, the continuity arguments will lead to the continuity of ϕ rather than the continuity of θ across the perfect wall in such a way that a thermometer would indicate ϕ rather than θ.

4.4.2. Contact temperature. Two internally equilibrated systems are said to be in mutual thermal equilibrium if and only if they do not exchange heat when put in mutual thermal contact. Muschik (1977, 1979a,b) and Muschik and Brunk (1977) generalized this idea by introducing the concept of contact temperature for non-equilibrium systems as the temperature T_{cont} at which an equilibrium environment should be in such a way that if the internally non-equilibrium system is put in contact with the environment, the total heat exchange Q across the boundaries of the system (assumed impervious to work and matter) is zero, in spite of the fact that it is different from zero in several regions of the boundaries. If one requires that the heat flux exchanged between the system and the environment be zero everywhere, the classical version of the zeroth principle is recovered. In greater detail, it is asked not only that the total heat exchange Q is zero but also that the heat exchange has different signs when the values of the temperature T of the environment are higher or lower than the contact temperature T_{cont}, in such a way that

$$\dot{Q}\left(\frac{1}{T_{\text{cont}}} - \frac{1}{T}\right) \geqslant 0. \tag{4.24}$$

The contact temperature depends on the whole contact area and on the state history of the non-equilibrium system, and provides a dynamical analogue of the thermostatic temperature. However, in contrast to the thermostatic temperature, not only does it depend on the internal energy (for V and N constant) but also on some other variables. Indeed, if one considers an isolated non-equilibrium system, internal energy is conserved but the contact temperature is generally a function of time.

The contact temperature defined in this way is thus a global concept, rather than local. It is not given in general by a thermometer applied to the system itself, but rather to the suitable environment. It is not clear, however, up to what point this definition satisfies the transitivity

property implied by the zeroth law. Indeed, if one assumes that non-equilibrium systems A and B have the contact temperature corresponding to a given equilibrium environment C, it is not clear that A and B will not exchange heat among themselves if put in direct thermal contact.

Besides contact temperature, Muschik defines dynamical generalized forces and dynamical partial molar enthalpies, which determine the exchange of work and matter between the system and the environment in a way similar to the contact temperature defines the exchange of heat.

4.5. Rational thermodynamics and entropy-free thermodynamics

Here, we deal with the role of temperature in two other thermodynamic approaches: rational thermodynamics and thermodynamics without entropy, which are less explicit concerning the meaning of this physical quantity.

4.5.1. Rational thermodynamics. Rational thermodynamics (Truesdell 1969, Bataille and Kestin 1979, Silhavy 1997, Wilmanski 1998) proposes a generalized entropy that is not identical to local-equilibrium entropy and takes temperature as a primitive quantity. Maybe because of this primitive character attributed to temperature—which, in fact, is one of the subtler and more difficult concepts in thermodynamics—rational thermodynamics has not contributed much to the understanding of temperature in non-equilibrium situations. Indeed, its proponents have tried to avoid the use of the derivative of the generalized entropy with respect to the internal energy as the reciprocal of temperature, and have restricted their interests to local-equilibrium equations of state, in contrast to their wide generalization of the transport (or constitutive) equations. Thus, in rational thermodynamics, entropy is a quantity for which the role seems limited to imposing restrictions on the transport equations, through the Clausius–Duhem inequality, but it is not used to extract any explicit information concerning non-equilibrium equations of state.

In one interesting modification of the early formalism of rational thermodynamics, Liu (1972) proposed to take into account the restrictions imposed on the processes by the balance equations of mass, momentum and energy by means of Lagrange multipliers. For instance, in the case of heat conduction, it is assumed that there exists an entropy that obeys a balance law with a non-negative production σ^s. To take into account the constraint placed by energy balance, one includes it via a Lagrange multiplier $\Lambda_0(u, \boldsymbol{q})$, so that expression $\rho \mathrm{d}s/\mathrm{d}t + \nabla \cdot \boldsymbol{J}^s \geqslant 0$ takes the form

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} + \nabla \cdot \boldsymbol{J}^s - \Lambda_0 \left(\rho \frac{\mathrm{d}u}{\mathrm{d}t} + \nabla \cdot \boldsymbol{q} \right) \geqslant 0. \tag{4.25}$$

At this stage, s and $\boldsymbol{J}^s$ are unknown functions of u and $\boldsymbol{q}$. By differentiating them with respect to u and $\boldsymbol{q}$, and rearranging the terms one obtains from (4.25)

$$\rho \left(\frac{\partial s}{\partial u} - \Lambda_0 \right) \frac{\mathrm{d}u}{\mathrm{d}t} + \nabla \cdot (\boldsymbol{J}^s - \Lambda_0 \boldsymbol{q}) + \boldsymbol{q} \cdot \nabla \Lambda_0 \geqslant 0. \tag{4.26}$$

Since $\mathrm{d}u/\mathrm{d}t$ can be given independent values, the positiveness of (4.26) requires that

$$\Lambda_0 = \frac{\partial s}{\partial u} \equiv \frac{1}{\theta}, \qquad \boldsymbol{J}^s = \Lambda_0 \boldsymbol{q} = \theta^{-1} \boldsymbol{q}, \qquad -\frac{1}{\theta^2} \boldsymbol{q} \cdot \nabla \theta \geqslant 0. \tag{4.27}$$

Thus, the relation between the Lagrange multiplier Λ_0 and temperature is obtained. Recall that Lagrange multipliers have already been found in section 3.3, in the context of information theory, where they accounted for the restrictions on the averages of some extensive quantities.

In this section, the role of Lagrange multipliers is different, as it is not related to any extremalization procedure, but to the restrictions implied by an evolution equation (here, the energy balance equation). In both situations, it turns out that the Lagrange multiplier conjugated to the energy may be identified as the inverse of an absolute temperature.

4.5.2. Entropy-free thermodynamics and dynamical temperature. In regards to the difficulties of finding a rigorous and unique definition of entropy in non-equilibrium situations, Meixner (1970, 1972, 1974) tried to avoid the use of the entropy formulating an entropy-free thermodynamics. To achieve this goal he used only the Clausius first formulation of the second law, in which for any process from an initial equilibrium state A to a final equilibrium state B the entropy change must satisfy

$$S(\mathrm{B}) - S(\mathrm{A}) \geqslant \int_{\mathrm{A}}^{\mathrm{B}} \frac{\hat{\mathrm{d}}Q}{T}, \tag{4.28}$$

where T is the temperature at which heat transfer occurs. The restriction that A and B must be equilibrium states was later loosened by Clausius simply stating that $\mathrm{d}S \geqslant \hat{\mathrm{d}}Q/T$ for each infinitesimal part of an irreversible process. However, despite his interest in avoiding the use of any non-equilibrium entropy, Meixner was not able to avoid the introduction of a dynamical temperature by means of a kind of entropy flux in the Clausius inequality. No operational definition of the dynamical temperature is given, but only its existence is assumed. The values of the dynamical temperature on the surface of a part of the body are supposed to be given by the temperatures of fictitious heat baths in contact with it. The fundamental inequality of this formulation of thermodynamics is then written in the weak form as

$$\int \mathrm{d}t \left[(T_{\mathrm{eq}}^{-1} - T_{\mathrm{dyn}}^{-1})\dot{u} + \rho^{-1}\boldsymbol{q} \cdot \nabla T_{\mathrm{dyn}}^{-1} \right] \geqslant 0, \tag{4.29}$$

with T_{dyn} the dynamical temperature, which he tentatively identified as the translational temperature of molecules, and T_{eq} the local-equilibrium temperature. Expression (4.29) directly follows from the Clausius inequality, in which $\boldsymbol{q}/T_{\mathrm{dyn}}$ is used as the entropy flux from the equilibrium heat bath to the non-equilibrium system. The difference between T_{dyn} and T_{eq} is expressed by a constitutive relation as a function of u, v, $\dot{u}$, and $\boldsymbol{q}$ but, to our knowledge, explicit expressions for this difference have not been worked out.

5. Microscopic interpretations

The motivations and theoretical bases to go beyond local equilibrium formulations are not only found at the macroscopic level, but also at the microscopic one. Kinetic theory, information theory, stochastic processes and non-equilibrium molecular dynamics have been faced with the problems posed by the interpretation of temperature in non-equilibrium steady states when a non-linear approach to the entropy or the transport equations is required. Here, we review these analyses, with special attention given to temperature.

5.1. Kinetic theory

In 1872, Boltzmann formulated an evolution equation for the single-particle distribution function $f(\boldsymbol{r}, \boldsymbol{c}, t)$, where $\boldsymbol{c}$ is the particle velocity. Such an equation has the form

$$\frac{\partial f}{\partial t} + \boldsymbol{c} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \frac{\boldsymbol{F}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{c}} = \int \mathrm{d}\tilde{\boldsymbol{c}} \int \mathrm{d}\Omega \, |\boldsymbol{c} - \tilde{\boldsymbol{c}}| \, \sigma(\boldsymbol{c} - \tilde{\boldsymbol{c}}, \varphi) \, [f'\tilde{f}' - f\tilde{f}]. \tag{5.1}$$

Here, f, $\tilde{f}$, f' and $\tilde{f}'$ denote $f(\boldsymbol{r}, \boldsymbol{c}, t)$, $f(\boldsymbol{r}, \tilde{\boldsymbol{c}}, t)$, $f(\boldsymbol{r}, \boldsymbol{c}', t)$ and $f(\boldsymbol{r}, \tilde{\boldsymbol{c}}', t)$, respectively; m is the mass of the particles and $\boldsymbol{F}$ the external force acting on the particles; $\sigma(\boldsymbol{c} - \tilde{\boldsymbol{c}}, \varphi)$ is the differential cross-section of the collisions between the particles, one of them with initial velocity $\boldsymbol{c}$ and the other with initial velocity $\tilde{\boldsymbol{c}}$, which give as final velocities after collision $\boldsymbol{c}'$ and $\tilde{\boldsymbol{c}}'$; φ is the angle between $\boldsymbol{c}$ and $\boldsymbol{c}'$, and $\mathrm{d}\Omega$ is the differential solid angle around φ.

Furthermore, Boltzmann showed that according to equation (5.1), the function

$$H(\boldsymbol{r}, t) \equiv \int f(\boldsymbol{r}, \boldsymbol{c}, t) \ln f(\boldsymbol{r}, \boldsymbol{c}, t) \, \mathrm{d}\boldsymbol{c} \tag{5.2}$$

steadily decreases until the system reaches a minimum value, corresponding to an equilibrium state, where $f(\boldsymbol{r}, \boldsymbol{c}, t)$ acquires the form of the Maxwell distribution. This result, known as the H theorem, allows us to define an entropy for the Boltzmann transport theory with a microscopic expression of the form

$$\rho s(\boldsymbol{r}, t) = -k_{\mathrm{B}} \int f(\boldsymbol{r}, \boldsymbol{c}, t) \ln f(\boldsymbol{r}, \boldsymbol{c}, t) \, \mathrm{d}\boldsymbol{c}. \tag{5.3}$$

In fact, the H theorem is not strictly equivalent to the second law of thermodynamics, as the latter deals with purely macroscopic quantities and the former with microscopic functions for a gas of independent single particles. Nevertheless, the importance of the H theorem in the discussions on the microscopic interpretation of the second law has been outstanding. Since the form of f in a non-equilibrium steady state is *a priori* unknown, the same is true for the non-equilibrium entropy. For instance, in a system in a steady state under a heat flux $\boldsymbol{q}$, the distribution function will depend not only on u and v, but also on $\boldsymbol{q}$. Thus, from (5.3) one will have $s = s(u, v, \boldsymbol{q})$. If $s(u, v, \boldsymbol{q})$ is introduced into definition (2.11), one has

$$\theta^{-1}(u, v, \boldsymbol{q}) = \left(\frac{\partial s}{\partial u} \right)_{v, \boldsymbol{q}}, \tag{5.4}$$

which is, formally speaking, one of the equations of state in this entropy representation.

5.1.1. Kinetic definition of temperature and pressure.

In ideal gases the internal energy only depends on T; thus, out of equilibrium, one imposes on the non-equilibrium distribution function the following side conditions, requiring that the first five moments (related to the hydrodynamic variables) have a well-specified value (Grad 1958)

$$\int f \, \mathrm{d}\boldsymbol{c} = \int f_{\mathrm{leq}} \, \mathrm{d}\boldsymbol{c} = n \tag{5.5a}$$

$$\int f \boldsymbol{c} \, \mathrm{d}\boldsymbol{c} = \int f_{\mathrm{leq}} \boldsymbol{c} \, \mathrm{d}\boldsymbol{c} = n\boldsymbol{v} \tag{5.5b}$$

$$\int \frac{1}{2} m c^2 f \, \mathrm{d}\boldsymbol{c} = \int \frac{1}{2} m c^2 f_{\mathrm{leq}} \, \mathrm{d}\boldsymbol{c} = \frac{3}{2} n k_{\mathrm{B}} T \tag{5.5c}$$

with f_{leq} the local-equilibrium Maxwellian distribution function corresponding to the number density n, internal energy u and barycentric velocity $\boldsymbol{v}$. In contrast, the higher-order moments of f, corresponding to non-conserved quantities (viscous pressure tensor, heat flux and other higher-order fluxes), will in general differ from the corresponding moments of f_{leq}.

From a practical point of view the calculation of T according to (5.5c) is very simple, as it is directly related to the mean translational kinetic energy, a quantity which is well defined either in equilibrium or out of equilibrium. This definition of temperature is consistent with the local-equilibrium hypothesis, which postulates that out of equilibrium the entropy may be defined locally by identifying the entropy of small parts of the system with a given energy u and specific volume v with the entropy $s(u, v)$ of the system in an equilibrium state characterized

by the same values of u and v. However, the assumption that T is the temperature measured by a thermometer implies the hypothesis that T acts as a potential for heat transport, i.e. that heat flows according to ∇T^{-1}; this hypothesis is consistent within the framework of the local-equilibrium theory, but must be revised in a more general context, where non-linear terms are taken into account. As a consequence of (5.5), θ defined by (5.4) cannot be equal to T defined by (5.5) in non-equilibrium states. In this paper, we will call θ a non-equilibrium absolute temperature and T the local-equilibrium absolute temperature.

We also comment on the definition of pressure in non-equilibrium, since it is helpful to clarify some aspects of temperature. Though pressure has a rather immediate mechanical interpretation, which seems to make it a more accessible quantity than temperature from the microscopic point of view, its macroscopic definition out of equilibrium also requires subtle considerations. For instance, pressure becomes a tensor rather than a scalar or diagonal tensor in non-equilibrium situations, where the presence of the flows introduces an anisotropy in otherwise isotropic equilibrium situations.

It must be recalled that entropy is a characteristic function of the system on the condition that it is expressed in terms of extensive variables (Callen 1960). Therefore, rather than the fluxes themselves, one should use their product times the volume, such as, for instance, $v\boldsymbol{q}$, as independent variables. Indeed, these variables are extensive in the following sense: if one has two systems of volumes V_1 and V_2 crossed by the same heat flux $\boldsymbol{q}$, the variable $V\boldsymbol{q}$ is additive, i.e. $V_{\text{tot}}\boldsymbol{q} = V_1\boldsymbol{q} + V_2\boldsymbol{q}$ although $\boldsymbol{q}$ itself is not additive. The consequence of this choice will be reflected in the definition of non-equilibrium pressure, which is obtained as the derivative of the entropy with respect to the volume at constant $v\boldsymbol{q}$ rather than at constant $\boldsymbol{q}$. Since temperature is related to the derivative of the entropy with respect to the internal energy at constant v, the fact that $v\boldsymbol{q}$ or $\boldsymbol{q}$ are kept constant does not modify the results.

The most suitable definition for the non-equilibrium pressure π is then

$$\pi\theta^{-1} = \left(\frac{\partial s}{\partial v}\right)_{u,v\boldsymbol{q}}. \tag{5.6}$$

However, a conceptual problem now arises, because in an ideal gas the equilibrium pressure is defined as one-third of the trace of the pressure tensor. Since for an ideal gas $p = \frac{2}{3}\rho u$ and since u is independent of the fluxes because of the condition (5.5c), it seems that we are faced with a contradiction, because the pressure defined in (5.6) does depend on the fluxes. To see that this contradiction is only apparent, consider an ideal gas submitted to a heat flux and assume that the pressure tensor has the form

$$\mathbf{P} = \pi\mathbf{U} + \alpha\boldsymbol{qq}, \tag{5.7}$$

where $\mathbf{U}$ denotes the unit rank-two tensor. Since the pressure tensor must satisfy $\text{Tr}\,\mathbf{P} = 3p$, it is required that the coefficient α in (5.7) has to obey the condition $\text{Tr}\mathbf{P} = 3\pi + \alpha\boldsymbol{qq} = 3p$. This result makes clear that although the derivative of the entropy with respect to the volume depends on $\boldsymbol{q}$, it is not in contradiction with the property that the trace of the tensor is not dependent on the flux. Let us add that expression (5.7) is supported by other approaches, such as microscopic analyses of electromagnetic radiation (Domínguez and Jou 1995, Domínguez-Cascante and Faraudo 1996), and Hamiltonian methods in polymer solutions (Grmela and Öttinger 1997) and radiation (Grmela et al 1998).

Let us explicitly write $\mathbf{P}$ in a simple situation, namely, when heat flux has the y direction, so that

$$\mathbf{P} = \begin{pmatrix} \pi & 0 & 0 \\ 0 & \pi & 0 \\ 0 & 0 & \pi \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & \alpha q_y^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{5.8}$$

This expression implies that the work of compression or expansion will depend on the relative direction between the axis of compression and the heat flux. This has been found in some computer simulations, where the thermodynamic pressure is seen to be equal to the minimum eigenvalue of the pressure tensor (Evans and Morriss 1990). This is indeed the situation found in (5.8), because $\pi < p$ and therefore $\alpha q^2 > 0$. A Gedanken experiment analogous to that in figure 1 could be devised for the non-equilibrium pressure, by replacing the rigid conducting rod connecting the systems in figure 1 by a mobile piston.

Note that for an ideal gas under a heat flux, definition (5.6) taken at $v\boldsymbol{q}$ constant yields $\pi/\theta = p/T$. Indeed, according to (4.15), one has

$$\frac{\pi}{\theta} = \left(\frac{\partial s}{\partial v}\right)_{u,v\boldsymbol{q}} = \left(\frac{\partial s_{\text{leq}}}{\partial v}\right)_u - \frac{1}{2}\frac{\partial}{\partial v}\left(\frac{\tau}{v\lambda T^2}\right) v\boldsymbol{q}\cdot v\boldsymbol{q}. \tag{5.9}$$

However, according to kinetic theory the thermal conductivity is $\lambda = \frac{5}{2}(nk_B T^2/m)\tau$, and therefore $\tau/v\lambda$ is independent of v, as the specific volume (the reciprocal of the mass density) is $v = 1/nm$. Therefore, the second term on the right-hand side in (5.9) vanishes and it is found that

$$\frac{\pi}{\theta} = \left(\frac{\partial s_{\text{leq}}}{\partial v}\right)_u = \frac{p}{T} = nk_B. \tag{5.10}$$

Note that the result would have been different if the derivative was performed at constant $\boldsymbol{q}$. Let us return to expression (5.8) for the pressure tensor; since $\theta < T$, as seen explicitly below, it is easy to see that $P_{xx} = P_{zz} = \pi < p$, and $P_{yy} = 3p - 2\pi > p$. Since for an ideal gas the components of the pressure tensor are related to the second moments of the velocity, we have

$$\left\langle \tfrac{1}{2}mv_x v_x\right\rangle = \left\langle \tfrac{1}{2}mv_z v_z\right\rangle = \tfrac{1}{2}k_B\theta < \tfrac{1}{2}k_B T, \tag{5.11a}$$

$$\left\langle \tfrac{1}{2}mv_y v_y\right\rangle = \tfrac{1}{2}k_B(3T - 2\theta) > \tfrac{1}{2}k_B T. \tag{5.11b}$$

Three points are worth noting: (1) the average molecular kinetic energy $\langle \tfrac{1}{2}mv^2\rangle$ is given by $\frac{3}{2}k_B T$, in agreement with definition (5.5c) of T; (2) out of equilibrium, the equipartition theorem, implying that the average kinetic energy along the three axes is the same, is no longer valid: the average energy is lower in the directions orthogonal to the heat flux; (3) note, finally, that $k_B\theta$ is the part of the energy which is distributed isotropically, whereas $\frac{1}{2}k_B(3T - 2\theta)$ is distributed exclusively along the y axis. Thus, in this situation, the idea that $\frac{3}{2}k_B T$ is the total internal energy and $\frac{3}{2}k_B\theta$ is the 'disordered' part of the internal energy is verified.

5.1.2. Microscopic analysis of the proposed Gedanken experiment. Here, we try to give a microscopic interpretation of the Gedanken experiment proposed in section 4.2. Thus, we suppose that the two systems in figure 1 consist of an ideal monatomic gas, and study the power delivered to both ends of the connecting rod. If the power arriving at one side is higher than the power arriving at the other, it may be expected that heat will flow from the first end to the second, unless the bar is insulating. We will qualitatively show that even if both ends of the rod are at the same local-equilibrium temperature, the end corresponding to the non-equilibrium system is receiving less power than the end at equilibrium. As a consequence, heat will flow from the latter system to the former, confirming the macroscopic prediction of section 4.2.

Consider the kinetic energy transferred to the wall due to collisions of particles for which the trajectory makes an angle $\pm\phi$ with the normal to the surface of the wall (figure 4). A fraction of this energy will be delivered to the rod if it is heat conducting. The energy arriving to the wall will be proportional to $a(\phi)[n_+ T_+\sqrt{T_+} + n_- T_-\sqrt{T_-}]$, where $a(\phi)$ is a geometrical factor depending on ϕ and on the energy transfer coefficient between the molecules and the rod;

Figure 4. Microscopic interpretation of the Gedanken experiment presented in figure 1. The power delivered through molecular collisions with the ends of the rod is less in the non-equilibrium system in the presence of the heat flux q_y than in the equilibrium system.

n_+, n_- and T_+, T_- are the number densities of particles and the temperatures at the positions shown in figure 4. Indeed, $n\sqrt{T}$ is proportional to the flow of particles colliding with the wall (density times speed), whereas T is the temperature measuring the mean energy carried per particle. Thus, $nT\sqrt{T}$ is the flow of energy carried by the particles colliding with the wall.

At equilibrium, n and T do not depend on the position, so that $n_+ = n_- = n$ and $T_+ = T_- = T$. In the non-equilibrium system, $n(y)$ and $T(y)$ depend on the position, but the product $n(y)T(y)$ must be independent of y, in order to avoid convective motion (constant pressure condition); thus, $n_+T_+ = n_-T_-$, with $T_+ = T + \delta T$, $T_- = T - \delta T$, and $\delta T \approx \ell \nabla T \sin \phi$, ℓ being the mean free path. Thus, the energy transferred to the wall per unit time will be, in the equilibrium system, and for a given angle ϕ,

$$J_u^{\text{eq}}(\phi) = 2a(\phi)nT\sqrt{T}. \tag{5.12}$$

In the non-equilibrium system it is given by

$$J_u^{\text{neq}}(\phi) = a(\phi)nT\sqrt{T}\left\{\left[1 + \left(\frac{\delta T}{T}\right)\right]^{1/2} + \left[1 - \left(\frac{\delta T}{T}\right)\right]^{1/2}\right\}. \tag{5.13}$$

The net energy flow may be found by integrating (5.13) for $-\pi \leqslant \phi \leqslant \pi$, so that, up to second order in $\delta T/T$, one gets

$$\Delta J_u = J_u^{\text{neq}} - J_u^{\text{eq}} = -\tfrac{1}{4}A\ell^2(\nabla \ln T)^2, \tag{5.14}$$

with

$$A = nT\sqrt{T}\int_{-\pi}^{\pi} a(\phi)\sin^2 \phi \, \mathrm{d}\phi. \tag{5.15}$$

Thus, $J_u^{\text{neq}}(\phi) < J_u^{\text{eq}}(\phi)$ shows that the energy per unit time arriving at the end of the rod from the system at equilibrium is higher than at the other end, in spite of the fact that both systems are at the same local-equilibrium temperature, i.e. they are characterized by the same average molecular energy.

This interpretation reveals that a non-equilibrium temperature θ is not contradictory with the concept of local-equilibrium temperature. The latter is related to the internal energy of the ideal gas, but it is not exactly the temperature measured by a thermometer, because, as we have seen in this section, two systems at the same T, but one in equilibrium and the other out of equilibrium undergo a net exchange of heat. The difference between θ and T is of second order in $\ell \nabla \ln T$, so that T and θ are identical in a first-order theory, i.e. in usual hydrodynamics and in classical irreversible thermodynamics. However, the difference between both concepts is of interest in second- and higher-order developments of the kinetic theory of gases as, for instance, in the Burnett and super-Burnett approximations (Grad 1958, Keizer 1987).

5.1.3. Evaluation of non-equilibrium temperature. In this section, an estimate of the order of magnitude of the difference $T - \theta$ is carried out by starting from (4.15). For a monatomic ideal gas one has, according to the kinetic theory of gases (Grad 1958), $\lambda = \frac{5}{2}(k_B^2 T n/m)\tau$, so that $(\tau v/\lambda T^2) = 2/(5p^2 T)$, with $p = nk_B T$. Then, by integrating relation (4.15), the expression for the entropy up to second order in $\boldsymbol{q}$ is

$$s(u, \boldsymbol{q}) = s_{\text{leq}}(u) - \left[\frac{1}{5p^2 T}\right] \boldsymbol{q} \cdot \boldsymbol{q}. \tag{5.16}$$

For a metallic conductor, heat is carried out by electrons, and $\lambda = \frac{1}{3}(\pi^2 k_B^2 T^3 n/m)\tau$ from which follows $(\tau v/\lambda T^2) = 3/(\pi^2 k_B^2 T^3 n^2)$, so that the entropy is

$$s(u, \boldsymbol{q}) = s_{\text{leq}}(u) - \left[\frac{3}{2\pi^2 k_B^2 T^3 n^2}\right] \boldsymbol{q} \cdot \boldsymbol{q}. \tag{5.17}$$

Taking the derivatives of (5.16) and (5.17) with respect to u at constant $\boldsymbol{q}$ and bearing in mind that $du = c_v dT$ with c_v being the specific heat ($c_v = \frac{3}{2}k_B/m$ for monatomic gases and $c_v = (\pi^2 k_B T/2m^*\varepsilon_F)$ for an electron gas in metals, with m^* the effective electron mass and ε_F the Fermi energy of the metal), one obtains, respectively, the explicit expressions of the generalized temperature, namely

$$\theta^{-1} = T^{-1} + \frac{2}{5}\left(\frac{m}{n^2 k_B^3 T^4}\right) \boldsymbol{q} \cdot \boldsymbol{q}, \tag{5.18}$$

$$\theta^{-1} = T^{-1} + \left(\frac{9}{\pi^4}\right)\left(\frac{m\varepsilon_F}{n^2 k_B^4 T^5}\right) \boldsymbol{q} \cdot \boldsymbol{q}. \tag{5.19}$$

To estimate $T - \theta$, assume, for instance, that the system is composed of CO_2 at 300 K and 0.1 atm. Then, $m = 4 \times 10^{-26}$ kg and $n = 2.6 \times 10^{24}$ particles m^{-3} and we have from (5.18) $T - \theta = 9.6 \times 10^{-12} q_s^2$, with q_s being expressed in W m^{-2}K^{-1}. Thus, for q_s of the order of 10^5 W m^{-2}K^{-1}, the effective temperature difference $T - \theta$ would be of the order of 9.6×10^{-2} K. If the subsystem is made of copper for which $n = 8.45 \times 10^{22}$ cm^{-3}, $T_F = \varepsilon_F/k_B = 8.12 \times 10^4$ K and $m^* = 9.1 \times 10^{-31}$ kg, the difference $T - \theta$ for a temperature gradient in the y direction of the order of 10^4 K m^{-1} would be as calculated from (5.19) of the order of 2×10^{-3} K, less than for the gas of the previous example.

5.1.4. Non-ideal gases: temperature and bulk viscosity. The definition of temperature in kinetic theory has also been widely discussed in the case of dense gases with intermolecular interactions (Wang-Chang *et al* 1964, Ernst 1966, García-Colín and Green 1966, van Beijeren *et al* 1988). Two definitions of temperature are generally used: the first one expresses it in terms of the total molecular energy, whereas the second one relates it to the molecular kinetic translational energy. These definitions are related to two possible formulations of the one-particle distribution function, namely $f_I(\boldsymbol{r}|n, \boldsymbol{c}, \varepsilon)$ and $f_{II}(\boldsymbol{r}|n, \boldsymbol{c}, T)$ with ε the total-energy density and T the local-kinetic temperature. The temperature in these distribution functions is respectively obtained by requiring the following conditions on the energy average

$$\varepsilon = \int \frac{p^2}{2m} f_I(\boldsymbol{r}_1|n, \boldsymbol{c}, \varepsilon) \, d\boldsymbol{c} + \frac{1}{2}\int \phi(r) f_2(\boldsymbol{r}_1, \boldsymbol{r}_2 \,|\, f_1(\boldsymbol{r}_1|n, \boldsymbol{c}, \varepsilon)) \, d\boldsymbol{c} \, d\boldsymbol{r}_2, \quad (5.20)$$

where $\phi(\boldsymbol{r})$ is the intermolecular pair potential and f_2 the pair distribution function, and

$$\frac{3}{2}nk_B T + \frac{1}{2}nmv^2 = \int \frac{p^2}{2m} f_{II}(\boldsymbol{r}|n, \boldsymbol{c}, T) \, d\boldsymbol{c}. \tag{5.21}$$

Near equilibrium, f_I and f_{II} take a Maxwellian form, but with respective temperatures T' and T. In equilibrium, T and T' have the same value but, out of equilibrium, they have been found to differ in a quantity proportional to the divergence of the barycentric velocity. Thus, these distribution functions give different predictions for the value of the bulk viscosity: in both

methods, bulk viscosities are zero in first and second order in the density, but both of them are non-zero in third order and differ in terms proportional to the divergence of the velocity. This is disturbing, because it seems to indicate that an apparently well-defined fluid property has a value that depends on the means of calculating it. The explanation is that both methods lead to different macroscopic equations of motion, and that one must be careful to use in each of them the transport properties and the temperature of the corresponding approach.

García-Colín and Green (1966) consider that the definition related to the total-energy density should be preferred from a macroscopic point of view, because this is the one appearing in the Navier–Stokes–Fourier formulation of hydrodynamics, built from a purely macroscopic point of view prior to microscopic interpretations of the kinetic meaning of the involved quantities. Furthermore, concerning the problem of which quantity T or T' or a combination of both is indicated by a thermometer in a non-equilibrium state, they state that 'in spite of the fact that the thermometer is calibrated to read equilibrium temperature, the reading in non-equilibrium will depend on the structure and the nature of its interaction with the system'. This is precisely the point of view we mentioned in discussing the generalization of the zeroth principle to non-equilibrium situations.

5.1.5. Grad's expansion. In this paragraph we show that expression (4.15) of entropy is confirmed by the kinetic theory of gases in the 13-moment Grad approximation (Grad 1958). The expression for $s(u, \boldsymbol{q})$ may be derived from the kinetic theory of gases as follows. In Grad's approach, the non-equilibrium distribution function under a heat flux $\boldsymbol{q}$ is given by

$$f(\boldsymbol{r}, \boldsymbol{c}, t) = f_{\text{leq}}(\boldsymbol{r}, \boldsymbol{c}, t) \left[1 + \frac{2m}{5pk_{\text{B}}^2 T^2} \left(\frac{1}{2}mc^2 - \frac{5}{2}k_{\text{B}}T \right) \boldsymbol{c} \cdot \boldsymbol{q} \right]. \tag{5.22}$$

Introduction of this expression into the Boltzmann formula (5.3) for the entropy yields

$$\rho s = \rho s_{\text{leq}} - \frac{m}{5pk_{\text{B}}T^2} \boldsymbol{q} \cdot \boldsymbol{q}. \tag{5.23}$$

Thus, it is seen that T defined in terms of the average kinetic energy does not coincide with the inverse of the derivative of s with respect to u. Therefore, the meaning of temperature in kinetic theory is also worth examination in greater detail. We may ask another question: what is the energy u^* of a gas in equilibrium which corresponds to the same entropy as a gas with energy u but subject to a heat flux $\boldsymbol{q}$; i.e. in other words, we seek for an energy u^* such that

$$s_{\text{leq}}(u^*) = s(u, \boldsymbol{q}) = s_{\text{leq}}(u) - \tfrac{1}{2}\alpha \, \boldsymbol{q} \cdot \boldsymbol{q}. \tag{5.24}$$

Expanding $s_{\text{eq}}(u^*)$ up to the first order in $u^* - u$, one obtains

$$s_{\text{leq}}(u^*) = s_{\text{leq}}(u) + \left(\frac{\partial s_{\text{eq}}}{\partial u} \right)_{u=u^*} (u^* - u) + \cdots \tag{5.25}$$

and after comparing with expression (5.24), it follows that

$$u^* = u - \tfrac{1}{2}T\alpha \boldsymbol{q} \cdot \boldsymbol{q}, \tag{5.26}$$

with $T = 1/(\partial s_{\text{eq}}/\partial u)_{u=u^*}$. Since for a monatomic gas, energy density per unit mass u and temperature T are related according to expression $u = \frac{3}{2}(k_{\text{B}}/m)T$, the relation between u^* and u can be formulated in terms of the respective temperatures as

$$T^* = T \left(1 - \frac{m}{3k_{\text{B}}} \alpha \, \boldsymbol{q} \cdot \boldsymbol{q} \right). \tag{5.27}$$

The meaning of the temperature T^* is the following one. In a non-equilibrium state with energy u and heat flux $\boldsymbol{q}$, the gas has less entropy and more order than in equilibrium with

the same energy. Thus, not all the energy u contributes to the molecular disorder; the fraction of u contributing to the molecular disorder is precisely u^*, so that θ/T expresses the fraction of internal energy that actually contributes to the molecular disorder. The temperature T^* is not exactly equal to the absolute non-equilibrium temperature θ, which is given by $\theta^{-1} = T^{-1}[1 + (m/k_\mathrm{B})\alpha \boldsymbol{q} \cdot \boldsymbol{q}]$.

The value of the generalized temperature depends on the constraints acting on the system. For instance, the value calculated at constant heat flux $\boldsymbol{q}$ is different from the value obtained at a constant temperature gradient. To be explicit, consider a monatomic ideal gas with a repulsive power-law potential. For this system, one has $\tau = aT^{-b}$, with a a constant and $0 < b < \frac{1}{2}$, the limiting values $b = 0$ and $\frac{1}{2}$ corresponding, respectively, to Maxwell molecules and to hard spheres. The entropy (5.23) in the steady state takes the form

$$s = s_\mathrm{leq} - \frac{a}{2\rho\lambda T^{2+b}}\boldsymbol{q} \cdot \boldsymbol{q} = s_\mathrm{leq} - \frac{a\lambda}{2\rho T^{2+b}}\nabla T \cdot \nabla T. \qquad (5.28)$$

Now, we consider two alternative definitions of the generalized temperature, namely

$$\theta^{-1} = \left(\frac{\partial s}{\partial u}\right)_{\boldsymbol{q}}, \qquad (\theta^*)^{-1} = \left(\frac{\partial s}{\partial u}\right)_{\nabla T} \qquad (5.29)$$

that correspond to two different choices of independent variables. Recalling that $\lambda = \frac{5}{2}(k_\mathrm{B}^2 Tn/m)\tau$, expression (5.28) reads as

$$s = s_\mathrm{leq} - (5n^2 k_\mathrm{B}^2 T^3)^{-1}\boldsymbol{q} \cdot \boldsymbol{q} = s_\mathrm{leq} - \frac{5}{4}\left(\frac{k_\mathrm{B}^2}{m^2}\right)a^2 T^{-(1+2b)}\nabla T \cdot \nabla T. \qquad (5.30)$$

Observe that when s is written in terms of $\boldsymbol{q}$ it does not depend explicitly on τ and, as a consequence, it is independent of the particular form of the intermolecular potential. In contrast, expression $s(u, \nabla T)$ is related to the intermolecular potential through the parameter b. By differentiating $s(u, \nabla T)$ with respect to u at constant ∇T we obtain

$$(\theta^*)^{-1} = T^{-1} + (1 + 2b)\left(\frac{\tau\lambda}{2\rho c_v T^3}\right)\nabla T \cdot \nabla T. \qquad (5.31)$$

Similar remarks can be repeated concerning the definition of non-equilibrium temperature in systems under shear, for which the EIT entropy is (Jou *et al* 2000, 2001)

$$s = s_\mathrm{leq} - \left(\frac{\tau}{2\eta T\rho}\right)(P_{12}^v)^2 = s_\mathrm{leq} - \left(\frac{\tau\eta}{2T\rho}\right)\dot{\gamma}^2, \qquad (5.32)$$

where P_{12}^v is the shear viscous pressure and $\dot{\gamma}$ the shear rate, related to P_{12}^v by $P_{12}^v = \eta\dot{\gamma}$, with η the shear viscosity. In a monatomic gas, one has $\eta = nk_\mathrm{B}T\tau$, so that

$$s = s_\mathrm{leq} - (2n^2 k_\mathrm{B}T^2 m)^{-1}(P_{12}^v)^2 = s_\mathrm{leq} - \left(\frac{k_\mathrm{B}\tau^2}{2m}\right)\dot{\gamma}^2. \qquad (5.33)$$

The corresponding temperature defined at constant P_{12}^v is

$$\theta^{-1} = \left(\frac{\partial s}{\partial u}\right)_{P_{12}^v} = T^{-1} + (n^2 k_\mathrm{B}T^3 mc_v)^{-1}(P_{12}^v)^2, \qquad (5.34)$$

whatever the form of the intermolecular potential is. In contrast, at constant $\dot{\gamma}$ one has

$$(\theta^*)^{-1} = \left(\frac{\partial s}{\partial u}\right)_{\dot{\gamma}} = T^{-1} + \frac{bk_\mathrm{B}\tau^2}{c_v Tm}\dot{\gamma}^2, \qquad (5.35)$$

so that $\theta^* = T$ for Maxwell molecules, but $\theta^* < T$ for hard spheres. In their analysis concerning the influence of the shear rate on the non-equilibrium temperature, Brey and Santos (1992) used the temperature defined at constant $\dot{\gamma}$.

A third alternative has been proposed by Banach and Pierarski (1992, 1993a), Banach and Larecki (2001), Eu and García-Colín (1997) and Bhalekar and García-Colín (1998), which consists of keeping the Grad fluxes constant, as, for example, $[\tau/(\rho\lambda T^2)]^{1/2}\boldsymbol{q}$ rather than the fluxes themselves. In this case, the generalized temperature is equal to the local equilibrium one. The physical problem is that this is not the Grad flux that appears in the balance equations, but the heat flux itself, and therefore the physical meaning of the derivative keeping this generalized flux constant is not clear.

5.2. Information theory: non-equilibrium ensembles

Informational statistical techniques may also be used out of equilibrium (Zubarev 1974, Zubarev *et al* 1996, Luzzi *et al* 2001, 2002a). The assumption of maximum entropy in steady states is not in contradiction with the fact that the entropy is maximum at equilibrium, since the entropy corresponding to a steady state is always less than (or at most equal to) the entropy corresponding to the equilibrium state with the same internal energy, volume and number of particles as the steady state, because the latter one is submitted to a wider set of constraints than the equilibrium state. These techniques provide a useful basis for macroscopic formalisms, in particular, that of EIT when the selected variables are the fluxes (Nettleton 1988, 1990a,b, Luzzi *et al* 1991, 2001, García-Colín *et al* 1994, Eu 1998). As has been seen in section 3.3, in information theory, the Lagrange multiplier conjugated to the energy plays the role of the reciprocal of absolute temperature. Thus, to explore the meaning of temperature in non-equilibrium it is interesting to analyse how this Lagrange multiplier is affected in some non-equilibrium situations. Early applications of this formalism to heat conduction were carried out by Robertson (1966, 1967), in which the Lagrange multiplier conjugated to internal energy was seen to play the role of the reciprocal of temperature, in analogy to what has been shown macroscopically in (4.16). However, he did not give explicit expressions for such non-equilibrium temperature.

Here, we will present two simple examples, an ideal gas in shear flow and a harmonic lattice under an energy flow. Other situations may be found in Jou *et al* (2001). In both examples, it turns out that the Lagrange multiplier conjugated to the energy is different from the inverse of the local-equilibrium temperature, since it depends not only on the internal energy but also on the viscous pressure or the heat flux, respectively.

First, we discuss an ideal gas under shear flow, in such a way that the restrictions imposed on it are the kinetic energy and the pressure tensor (Banach and Pierarski 1993c, Bidar *et al* 1996, Jou *et al* 2000, 2001, Jou and Criado-Sancho 2001). The maximum-entropy distribution under these constraints has the form

$$f_N(\boldsymbol{r}, \boldsymbol{C}) = Z^{-1}(\boldsymbol{r}) \exp\left[-\frac{1}{2}\left(\beta(\boldsymbol{r})\sum_i mC_i^2 + \lambda_{ij}(\boldsymbol{r})\sum_{i,j} mC_iC_j\right)\right], \quad (5.36)$$

where Z is the partition function and β and λ the Lagrange multipliers related to the restrictions on the total kinetic energy and on the pressure tensor. Note that the second Lagrange multiplier has no analogues in classical equilibrium statistical mechanics. Since the particles are independent, one may write this distribution function in terms of the one-particle distribution function

$$f(\boldsymbol{r}, \boldsymbol{C}) = z^{-1}(\boldsymbol{r}) \exp\left(-\tfrac{1}{2}\mathbf{M}(\boldsymbol{r}) : m\boldsymbol{C}\boldsymbol{C}\right), \quad (5.37)$$

with **M** a matrix related to the Lagrange multipliers through

$$\mathbf{M} = \begin{pmatrix} \beta + 2\lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \beta + 2\lambda_{22} & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \beta + 2\lambda_{33} \end{pmatrix}. \tag{5.38}$$

Now, restricting our attention to the case of a plane Couette flow, the non-vanishing Lagrange multipliers are β and λ_{12}, which are found to have the form (Bidar *et al* 1996, Jou *et al* 2001)

$$\beta = \frac{1-y}{2[R^2 + (1-y)]} \frac{N}{U}, \qquad \lambda = \frac{3R^2 + 2(1-y)}{2R[R^2 + (1-y)]} \frac{N}{U}, \tag{5.39}$$

where $R = V P_{12}^v / U$ and $y = (1 + 3R^2)^{1/2}$. Note that near equilibrium, when viscous pressure is negligible, β tends to $\beta = \frac{3}{2}(N/U) = (k_B T)^{-1}$, the Lagrange multiplier λ becomes negligible and (5.37) reduces to the Maxwell–Boltzmann distribution function. Far from equilibrium, instead, the Lagrange multiplier β is different from the reciprocal of the local equilibrium temperature. The corresponding non-equilibrium entropy has the form

$$S = S_{\text{leq}} + \frac{Nk_B}{2} \ln \frac{27R^2[R^2 + (1-y)]^2}{2(y-1)^3}. \tag{5.40}$$

The second situation we analyse is a linear harmonic chain under a heat flow (Miller and Larson 1979, Jou *et al* 2001). In order to avoid difficulties related to boundary conditions, it is assumed that the chain is closed on itself, forming a ring. In the harmonic chain, the mean free path of phonons diverges, and therefore both energy and energy flux are conserved homogeneous quantities. If one imposes restrictions on their average value, namely $\langle H \rangle = \varepsilon$ and $\langle J \rangle = Q$, the distribution function per particle, after diagonalization of the Hamiltonian, is

$$f = z^{-1} \exp(-\beta H - \gamma \cdot J). \tag{5.41}$$

Here, H and J are the microscopic operators for the energy and the energy flux, and β and γ are the respective Lagrange multipliers conjugated to the constraints on the average value of the energy per particle ε and the average contribution per particle to the heat flux Q. The values for the mass of the particles and the elastic constant of the strings are taken as unity. It follows that the Lagrange multipliers are

$$\beta = \frac{1 + x^2}{\varepsilon(1 - x^2)}, \qquad y = -\frac{2x}{1 - x^2}, \tag{5.42}$$

where x is the dimensionless heat flux $x = Q/\varepsilon$ (recall that the speed of waves, which should appear in the denominator, is unity, because of the mentioned selection of the values of mass and the elastic constant of the strings). Since the equilibrium temperature is related to the energy per particle as $\varepsilon = k_B T$, it is clear from (5.42) that out of equilibrium the Lagrange multiplier β is different from the reciprocal of the local-equilibrium temperature. The entropy s per particle is

$$S = S_{\text{leq}} + Nk_B \ln(1 - x^2). \tag{5.43}$$

Thus, in both situations, the entropy is different from the local-equilibrium entropy; near equilibrium, when viscous pressure or heat flux are small, these expressions may be expanded up to second-order in the fluxes and one obtains for the entropy expressions such as that proposed in (4.1).

Some points to be noted are that the coefficient β diverges (i.e. non-equilibrium temperature tends to zero) when the heat flux or the viscous pressure tends to some critical value. A generalized form of the third law may be stated (Camacho 1995a,b) because it turns out that the specific heat tends to zero when the generalized non-equilibrium temperature tends to zero, in analogy to what happens in equilibrium when temperature tends to zero. In fact,

when a quantum distribution function instead of a classical distribution function is used, the entropy tends to a finite constant when the generalized temperature tends to zero.

5.3. Stochastic theories

Expressions related to fluctuations and fluctuation–dissipation theorems have been used to define generalized non-equilibrium temperatures. We consider here three proposals: Keizer's one is rather comprehensive, because it tries to relate generalized thermodynamic potentials with the fluctuations in non-equilibrium situations; the two other proposals are more concrete, and are directly related to the fluctuation–dissipation theorem and to the Einstein relation between diffusion coefficient and mobility.

5.3.1. Keizer's approach: fluctuations in non-equilibrium steady states.

Keizer's approach (1976, 1985, 1987) starts from the analysis of molecular fluctuations in non-equilibrium steady states. He notes that molecular fluctuations at equilibrium are well described in terms of thermodynamics through the Boltzmann–Planck postulate that relates the entropy to the number of molecular states of the system, namely

$$W(\delta \boldsymbol{n}) \approx \exp\left(\frac{\Delta S}{k_B}\right) \sim \exp\left(\frac{\delta^2 S}{2k_B}\right), \tag{5.44}$$

where $\delta \boldsymbol{n}$ denotes the fluctuations of the extensive quantities with respect to their corresponding steady-state value (namely $\boldsymbol{n}(r, t) \equiv \boldsymbol{n}(r, t) - \boldsymbol{n}_{ss}(r) \equiv (\delta u, \delta n_1, \dots, \delta n_r)$, n_i being the number of particles of component i and W the probability that a fluctuation has the set of values $\boldsymbol{n}$. Again, we omit for simplicity the position dependence of the quantities. Relation (5.44) was used by Einstein in 1905 to develop a theory of equilibrium fluctuations and by Onsager in 1931 to obtain the reciprocity relations in linear non-equilibrium thermodynamics. Keizer argues that molecular fluctuations far from equilibrium may be different from the local-equilibrium ones, but that the formal analysis is similar. Thus, he assumes that the probability of fluctuations in a non-equilibrium steady state may be written as

$$W(\boldsymbol{n}) = \left[(2\pi)^{-k} \det \boldsymbol{\sigma}^{-1}\right] \exp\left[-\tfrac{1}{2}(\boldsymbol{n} - \boldsymbol{n}_{ss})^T \cdot \boldsymbol{\sigma}^{-1} \cdot (\boldsymbol{n} - \boldsymbol{n}_{ss})\right], \tag{5.45}$$

where $\boldsymbol{n}_{ss}$ are the average values of the corresponding quantities in the steady state and $\boldsymbol{\sigma}$ the covariance matrix of the fluctuations of the corresponding quantities, namely

$$\boldsymbol{\sigma} \equiv \langle (\boldsymbol{n} - \boldsymbol{n}_{ss})(\boldsymbol{n} - \boldsymbol{n}_{ss}) \rangle_{ss}. \tag{5.46}$$

Then, Keizer defines the generalized entropy S as that satisfying (Keizer 1976, 1987)

$$\frac{\partial^2 S}{\partial n_i \partial n_j} \equiv -k_B(\boldsymbol{\sigma}^{-1})_{ij}. \tag{5.47}$$

At equilibrium, $\boldsymbol{\sigma}$ reduces to the equilibrium covariance matrix and S identifies with the classical entropy. In analogy to classical thermodynamics, Keizer introduces the corresponding intensive parameters as

$$\phi_i \equiv \frac{\partial S}{\partial n_i}, \tag{5.48}$$

which shows that

$$\sum_j \boldsymbol{\phi} \cdot \frac{\mathrm{d}\boldsymbol{n}}{\mathrm{d}t} \geqslant \sum_j \boldsymbol{\phi}_{ss} \cdot \frac{\mathrm{d}\boldsymbol{n}}{\mathrm{d}t}. \tag{5.49}$$

On the left-hand side, $\boldsymbol{\phi}$ denotes the instantaneous values of the intensive parameters, whereas on the right-hand side, $\boldsymbol{\phi}_{ss}$ denotes average values in the steady state. Keizer (1985) named

this relation a generalized Clausius inequality, because for an equilibrium system in contact with a thermal reservoir at temperature T_R it becomes

$$T_R \frac{dS}{dt} \geqslant \frac{dQ}{dt}. \tag{5.50}$$

Thus, in Keizer's theory, the fluctuations in the extensive variables generate the non-mechanical state functions of thermodynamics, which leads to a local definition of the generalized entropy S. Since the non-equilibrium steady state must be maintained through some fluxes f_i (of the corresponding extensive quantities n, namely energy, mass, etc) exchanged with a set of reservoirs (heat reservoirs, mass reservoirs, etc), Keizer assumes that S will depend on the classical extensive variables n, the fluxes f and, in principle, on the intensive variables R characterizing the reservoirs. One may thus write

$$S(\boldsymbol{n}; \boldsymbol{f}, \boldsymbol{R}) = S_{\mathrm{eq}}(\boldsymbol{n}) + \sum_j \boldsymbol{f}_j \cdot \boldsymbol{\nu}_j(\boldsymbol{n}; \boldsymbol{f}, \boldsymbol{R}), \tag{5.51}$$

where $\boldsymbol{\nu}_j$ are the corresponding quantities conjugated to the fluxes f_i. In particular, the intensive variable conjugated to the internal energy is

$$\frac{1}{T} = \frac{1}{T_{\mathrm{leq}}} + \sum_j \boldsymbol{f}_j \cdot \frac{\partial \boldsymbol{\nu}_j}{\partial u}. \tag{5.52}$$

Thus, in this formalism, as well as in extended irreversible thermodynamics, the intensive variable conjugated to the internal energy is not the reciprocal of the local-equilibrium absolute temperature T, but it contains additional terms depending on the fluxes.

Alternatively, one may write the generalized entropy in terms of fluctuations as

$$S(\boldsymbol{n}; \boldsymbol{f}, \boldsymbol{R}) = S_{\mathrm{eq}}(\boldsymbol{n}) + \frac{1}{2} \sum_{i,j} n_i n_j B_{ij}(\boldsymbol{f}, \boldsymbol{R}), \tag{5.53}$$

where $i = 0$ corresponds to the internal energy, and the coefficients B_{ij} are given by

$$B_{ij} \equiv -k_B \left(\boldsymbol{\sigma}^{-1} - \boldsymbol{\sigma}_{\mathrm{eq}}^{-1} \right)_{ij}, \tag{5.54}$$

and consequently

$$\frac{1}{T} = \frac{1}{T_{\mathrm{leq}}} + \sum_j n_j B_{j0}(\boldsymbol{f}, \boldsymbol{R}). \tag{5.55}$$

In principle, the difference between both temperatures could be found by experimentally measuring the fluctuations in a non-equilibrium steady state. Note that one of the differences between Keizer's approach and extended irreversible thermodynamics is that in the latter the fluxes are considered as independent variables, instead of taking them as constant parameters, as it is done in Keizer's theory.

To underline the possible connections between the non-equilibrium temperature in Keizer's approach and that in EIT, let us say that it follows from the latter that

$$\langle \delta u \delta u \rangle = \langle \delta u \delta u \rangle_{\mathrm{leq}} + \alpha' q^2, \tag{5.56}$$

δu being the fluctuations of the internal energy with respect to its steady-state average and α' a coefficient, the explicit form of which is given in Jou *et al* (2001). Thus, one may write q as

$$q^2 = \left[\langle \delta u \delta u \rangle - \langle \delta u \delta u \rangle_{\mathrm{leq}} \right] (\alpha')^{-1} \tag{5.57}$$

and then, (4.2) may be rewritten as

$$\theta^{-1} = T^{-1} - \frac{1}{2\alpha'} \frac{\partial \alpha'}{\partial u} \left[\langle \delta u \delta u \rangle - \langle \delta u \delta u \rangle_{\mathrm{leq}} \right]. \tag{5.58}$$

This is analogous to Keizer's expression (5.55) but with a coefficient well defined *a priori*. Then, when the fluctuations depart from their local-equilibrium value, temperature may be different from that of local equilibrium, a feature that is common to Keizer's theory and to extended irreversible thermodynamics. Analogous modifications to the chemical potential follow from the same considerations and are corroborated experimentally, confirming that the intensive thermodynamic parameters depend on the second moments of fluctuations or, alternatively, on the fluxes present in the system.

5.3.2. Fluctuation-based definitions. Other ways of defining non-equilibrium effective temperatures rely on generalizations of the fluctuation–dissipation theorem. This theorem relates the fluctuations of a variable with the response function of such a variable with respect to external solicitations, and is one of the cornerstones of modern non-equilibrium statistical mechanics. Here, we will give a simplified approach, which will be presented with more generality in section 7.3. Assume that m is some variable (or set of variables) and that in equilibrium the entropy differential is given by

$$\mathrm{d}s = T^{-1}\mathrm{d}u + T^{-1}h(m)\,\mathrm{d}m, \tag{5.59}$$

where $h(m)$ is the thermodynamic variable conjugate to m. In equilibrium, the second moments of the fluctuations of m are given by

$$\langle(m - \langle m\rangle^2)\rangle \equiv \langle(\delta m)^2\rangle = k_\mathrm{B}T\left(\frac{\partial m}{\partial h}\right)_T. \tag{5.60}$$

Out of equilibrium, (5.60) will be modified; thus, in some situations it is proposed that we define an effective non-equilibrium temperature T_eff in analogy to (5.60) as

$$\langle(\delta m)^2\rangle = k_\mathrm{B}T_\mathrm{eff}\left(\frac{\partial m}{\partial h}\right)_T. \tag{5.61}$$

For instance, density fluctuations (i.e. taking m as the density) have been used to study temperature in granular media or in glasses (Nowak *et al* 1998). Relation (5.61), applied to energy fluctuations, i.e. written as $\langle(\delta U)^2\rangle = k_\mathrm{B}T_\mathrm{eff}^2(\partial U/\partial T_\mathrm{eff})_V$, has been used by Carati and Galgani (2000) to define an effective temperature for a classical system of harmonic oscillators colliding with point particles in situations very far from equilibrium.

Relation (5.61) is often formulated in a more general form, in which a memory function or generalized susceptibility $R(t, t')$ is introduced through the expression

$$m(t) = \int_{-\infty}^{t} R(t, t')h(t')\,\mathrm{d}t', \tag{5.62}$$

and the double-time correlation function of the fluctuations of m is used instead of the one-time second moments. In this way, (5.61) is generalized to

$$-\frac{\partial}{\partial t}\langle\delta m(t)\delta m(t')\rangle = k_\mathrm{B}T\left(\frac{\partial m(t)}{\partial h(t')}\right) = k_\mathrm{B}TR(t, t'). \tag{5.63}$$

In section 7.3, we will see how this expression or closely related ones are used to define effective non-equilibrium temperatures in glasses, powders and sheared fluids (Cugliandolo *et al* 1997, Cugliandolo and Kurchan 1999, Barrat and Berthier 2001, Berthier and Barrat 2002a,b). In these expressions, all non-equilibrium contributions are attributed to non-equilibrium temperature, but there could be explicit contributions stemming from non-linear generalizations of the fluctuation–dissipation theorem (Stratonovich 1992), which could have a different origin than a temperature.

However, these definitions of effective temperature, although useful in some situations, are not completely consistent with the temperature defined as the derivative of the entropy. Assume, for instance, that q is a non-equilibrium variable, in such a way that the entropy in non-equilibrium may be written in the form (4.1), namely $s = s_{eq}(u, m) - \alpha(u, m)q^2$. Then, the differential relation for the entropy in non-equilibrium becomes

$$ds = \theta^{-1}du + \theta^{-1}H(m)\,dm, \qquad (5.64)$$

with θ and H given by

$$\theta^{-1} \equiv T^{-1} - \left(\frac{\partial \alpha}{\partial u}\right)q^2, \qquad \text{and} \qquad \theta^{-1}H \equiv T^{-1}h - \left(\frac{\partial \alpha}{\partial m}\right)q^2. \quad (5.65)$$

Then, taking into account the explicit expression for H, the second moments of the fluctuations of m will be given in terms of the derivative of m with respect to h (the conjugate of m in equilibrium) by

$$\langle(\delta m)^2\rangle = k_B\theta\left(\frac{\partial m}{\partial H}\right)_\theta = \frac{k_B\theta}{1 - (\partial^2\alpha/\partial m^2)(\partial m/\partial h)\,q^2}\left(\frac{\partial m}{\partial h}\right)_\theta \equiv k_B T_{eff}\left(\frac{\partial m}{\partial h}\right)_\theta. \quad (5.66)$$

Hence, the ratio between the second moments of the fluctuations and $(\partial m/\partial h)$ defining $k_B T_{eff}$ is not strictly proportional to the non-equilibrium temperature θ but is connected to it by the relation derived from the last equality in (5.66). Anyway, as long as the denominator has a well-defined sign, heat will flow from higher to lower values of T_{eff} because this direction will coincide with the direction corresponding to the decrease of θ, and thus T_{eff} will be useful as a temperature in many circumstances. This example illustrates the fact that effective temperatures, useful as they may be for some purposes, are not always related to a thermodynamic first principles definition of temperature, and cannot be considered as truly fundamental.

Let us finally note that Landauer (1978) also assigned a relevant role to fluctuations in thermodynamics of non-linear electrical circuits, and showed that the relation $\hat{d}Q = T\,dS$ may remain valid far from equilibrium in slowly modulated dissipative steady states in fluctuating circuits provided that heat and temperature are conveniently related to fluctuations. In particular, he showed that $\hat{d}Q = \hat{d}Q_0 + \hat{d}Q_r = \hat{d}Q_0 + T_N\,dS$, $\hat{d}Q_0$ being the irreversible heat flow, calculated macroscopically by multiplying the ensemble averages of currents and voltages in the dissipative elements, and $\hat{d}Q_r$ a reversible heat flow associated with the dispersion in the ensemble of fluctuating circuits. The temperature T_N can be very different from the ambient temperature, and characterizes the fluctuations in the circuit, and entropy is obtained in terms of the probability distribution function of fluctuations. Landauer (1978) applied his formalism to study the divergence of heat flux near second-order transitions in the circuits.

5.3.3. Generalizations of Einstein's relation.   Another procedure to define non-equilibrium effective temperatures is through an extrapolation of the Einstein relation between the diffusion coefficient D and the mobility μ' in the linear regime around equilibrium, which states that

$$D = k_B T\mu'. \qquad (5.67)$$

The mobility coefficient relates the steady velocity v of the particles and the external force F as $v = \mu'F$. Thus, if one considers small 'tracer' particles immersed in a fluid, D and μ' will be strongly dependent on the tracer size and shape. However, their ratio will be independent of the tracer particles and will be common to all the different kinds of particles and equal to the temperature of the fluid, provided that we are in equilibrium. Thus, the fact that D/μ' is independent of the characteristics of the particles may be considered as evidence for thermalization in the system.

Since v may be obtained in terms of the displacements x of the particles as $v = \langle x \rangle / t$ and the diffusion coefficient as $D = \lim_{t \to \infty} \langle x^2 \rangle / 2t$, one may obtain the temperature in terms of the displacement of the particles as

$$k_{\mathrm{B}} T = \frac{D}{\mu'} = \lim_{t \to \infty} \frac{\langle x^2 \rangle}{2 \langle x \rangle} F. \tag{5.68}$$

It is to be understood that the average in the numerator is taken in absence of the force, whereas that of the denominator is evaluated in the presence of the force in the stated condition of being in a linear regime around equilibrium. This expression has been used, for instance, in the evaluation of temperature in granular systems (Makse and Kurchan 2002), to define effective temperatures in glasses (Cugliandolo *et al* 1997) or in supercooled colloidal fluids (Bonn and Kegel 2003).

However, from a thermodynamic point of view, the Einstein relation cannot be safely extrapolated to non-equilibrium situations. Indeed, (5.67) is a particular form of the more general expression (Hope *et al* 1981)

$$\frac{D}{\mu'} = n \left(\frac{\partial \mu}{\partial n} \right)_T, \tag{5.69}$$

when the chemical potential μ is given by $\mu = \mu^0(T) + k_{\mathrm{B}} T \ln n$. Thus, relation (5.67) would be more closely related to the non-equilibrium generalization of the chemical potential than to the generalization of temperature itself. To illustrate the situation, note that if a relation such as (4.1) is assumed to be out of equilibrium, one would have for the chemical potential

$$\theta^{-1} \mu = \left(\frac{\partial s}{\partial n} \right) = T^{-1} \mu_{\mathrm{leq}} + \left(\frac{\partial \alpha}{\partial n} \right) q^2, \tag{5.70}$$

where the non-equilibrium variable q could be related to the external force (for instance, electrical field). Thus, one would have as a generalization of the Einstein relation (5.69)

$$\frac{D}{\mu'} = k_{\mathrm{B}} \theta + n \left(\frac{\partial^2 \alpha}{\partial n^2} \right) q^2 \equiv k_{\mathrm{B}} T'_{\mathrm{eff}}. \tag{5.71}$$

In this case, the ratio between the diffusion coefficient and the mobility would not strictly coincide with the non-equilibrium temperature θ derived from the entropy. Furthermore, it is interesting to note that the effective temperature defined through the Einstein relation (5.67) would be also different (to second order in the non-equilibrium quantities) from the effective temperature (5.61) defined through the second moments of the fluctuations, as it is seen by comparing (5.66) and (5.71).

Thus, it turns out that a thermodynamic analysis shows that extrapolations of different equilibrium relations to non-equilibrium are not expected to give strictly the same non-equilibrium effective temperature, but quantities differing in second-order terms in non-equilibrium variables.

5.4. Non-equilibrium molecular dynamics

Based on molecular dynamics, numerical simulations have become useful grounds on which to evaluate transport coefficients and other quantities of interest in non-equilibrium situations (Evans and Morriss 1990, Hoover 1991, 1999). Though, in general, most of the practitioners have taken the usual kinetic definition as temperature until now, increasing interest is being paid to theoretical ideas on non-equilibrium temperature and non-equilibrium pressure.

From this perspective, the pioneering approach to the analysis of non-equilibrium temperature was made by Evans (1989). This author computed explicitly the entropy of a

system of soft discs under shear flow and compared the thermodynamic temperature, defined as the reciprocal of the derivative of the entropy with respect to internal energy, with the kinetic temperature. Here, we review this line of thought and its main results.

The non-equilibrium behaviour in a flow along the x-axis under a shear rate $\dot{\gamma}$ directed along the y-axis is usually modelled through the following system of equations of motion for the particles of the system (Evans and Morriss 1990):

$$\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} = \frac{\boldsymbol{p}_i}{m} + \dot{\gamma}\, y \boldsymbol{e}_x, \tag{5.72a}$$

$$\frac{\mathrm{d}\boldsymbol{p}_i}{\mathrm{d}t} = \boldsymbol{F}_i - \dot{\gamma}\, p_{yi}\, \boldsymbol{e}_x - \alpha \boldsymbol{p}_i, \tag{5.72b}$$

where $\boldsymbol{r}_i$ is the position of the ith particle, $\boldsymbol{p}_i$ its momentum and $\boldsymbol{F}_i$ the intermolecular force, which is derived from an intermolecular potential, subscript i refers to the ith particle, $\boldsymbol{e}_x$ is the unit vector along the x-axis, and α is a thermostatting multiplier given by the Nosé–Hoover feedback formula (Nosé 1984, Hoover 1985), in such a way that the total kinetic energy of the system stays constant. This is an artificial way of removing the heat produced in the system through viscous dissipation. In actual fact, heat is removed not locally at each point, but through a flux going from the hotter to the colder parts of the fluid. In the Nosé–Hoover formalism, one wants to reproduce the canonical phase–space distribution function, so that the total kinetic energy may fluctuate with an adequate distribution function. The simulation involving shear is only feasible if the available simulation time is significantly longer than $\dot{\gamma}^{-1}$; thus, many of the simulations are carried out at very high values of the shear rate, so that its comparison with phenomenological results obtained for small values of the shear rate is not immediate.

Another non-equilibrium situation studied by means of NEMD (non-equilibrium molecular dynamics) is the so-called colour flow, namely, a situation where the system is globally at rest but there is a flow of some tagged or 'coloured' particles, which allows one to simulate a diffusion flux or an electric flux. In this case, the algorithm used to describe the motion of the particles is

$$\frac{\mathrm{d}\boldsymbol{q}_i}{\mathrm{d}t} = \frac{\boldsymbol{p}_i}{m}, \qquad \frac{\mathrm{d}\boldsymbol{p}_i}{\mathrm{d}t} = \boldsymbol{F}_i + c_i F \boldsymbol{e}_x - \alpha(\boldsymbol{p}_i - c_i J \boldsymbol{e}_x), \tag{5.73}$$

where $\boldsymbol{F}_i$ is the colour field (namely, the force setting the tagged particles in motion), c_i the colour charge (a number indicating whether particle i is coloured or not) and J the colour current, describing the flow of coloured particles, defined as $\boldsymbol{J} \equiv (1/N) \sum_i c_i \dot{\boldsymbol{r}}_i$. Thus, NEMD provides at least two interesting situations to compare (with the due cautions) with the phenomenological results, namely, a fluid under shear flow and a fluid with a vectorial current of particles.

First of all, we will consider fluids under shear. In his early works on this topic, Evans (1989) considered a system of soft discs interacting through a potential of the form $\phi(r) = \varepsilon(\sigma/r)^{12}$, truncated at $r = 1.5\,\sigma$ and calculated the entropy for an isoenergetic planar Couette flow by using the expression

$$\frac{S}{N} = 1 - k_B \ln\left(\frac{n}{2\pi m k_B T}\right) - \frac{1}{2} n k_B \int g(r_{12}) \ln g(r_{12})\, \mathrm{d}r_{12}, \tag{5.74}$$

with $g(r_{12})$ being the radial distribution function. In this expression, the momentum distribution function has been assumed to be very close to the local-equilibrium one and has been integrated in the second term, in such a way that the relevant non-equilibrium effects are attributed to the non-equilibrium distortion of the radial distribution function. The entropy is obtained by calculating the radial distribution function from numerical experiments, introducing it in (5.74)

Table 1. Values for non-equilibrium entropy, kinetic temperature T and thermodynamic temperature θ at energy $u = 2.134$ at different densities and different values of the shear rate $\dot{\gamma}$. All quantities are expressed in units of the parameters of the molecular potential ε, σ and of k_B (Evans and Morriss 1990). The uncertainties in the values of the entropy are ± 0.005 and those in temperature 0.004.

ρ	$\dot{\gamma}$	s	T	θ
0.100	0.0	5.917	2.175	2.126
0.100	0.5	5.653	2.171	2.048
0.100	1.0	5.392	2.169	1.963
0.075	0.0	6.213		
0.075	0.5	5.852	2.190	2.088
0.075	1.0	5.499	2.188	1.902

Table 2. Values of local-equilibrium pressure p and non-equilibrium pressure π at energy $u = 2.134$ and density $\rho = 0.100$ for different values of the shear rate $\dot{\gamma}$ (Evans and Morriss 1990).

$\dot{\gamma}$	p	π
0.0	0.244	0.215
0.5	0.245	0.145
1.0	0.247	0.085

and performing the integration. After such a calculation is performed, Evans obtained the (reciprocal of) thermodynamic temperature by differentiating the entropy with respect to the internal energy. Table 1 shows some of his results that make evident the difference between the kinetic (local-equilibrium) temperature T and the (non-equilibrium) thermodynamic temperature θ defined as the derivative of internal energy with respect to entropy.

Furthermore, Evans (1989) calculated the non-equilibrium pressure, defined as $\pi = -(\partial U/\partial V)_{\dot{\gamma}}$, and compared it with the kinetic pressure p obtained from the trace of the pressure tensor. Some of his results are reproduced in table 2.

It is evident from these results that there are significant differences between the values of θ and T and between those of π and p in presence of shear rates. Note, furthermore, that $\theta < T$ and $\pi < p$ as discussed in section 5.1.1. Evans (1989) noted that the numerical data for the thermodynamic pressure π agree with the minimum eigenvalue of the pressure tensor, and conjectured that this is a general feature by arguing that if entropy is related to the minimum reversible work to accomplish a virtual change, in a non-equilibrium steady state the minimum work which changes the volume in dV will be that carried out by moving the wall perpendicular to the direction corresponding to the minimum eigenvalue of the pressure tensor. We have found in (5.8) a similar result for a gas submitted to a heat flux, where the pressure is lower in the directions perpendicular to the heat vector.

A second effort in the analysis of temperature in non-equilibrium situations in fluids under flow was the study, by Evans and co-workers, of the Poiseuille flow of a fluid (Baranyai *et al* 1992, Todd and Evans 1995) and of the non-homogeneous shear flow produced by a sinusoidal transverse force (Todd *et al* 1995). The purpose was to study the conditions of thermal 'equilibrium' between different parts of the system in a non-equilibrium steady state in mutual thermal and mechanical contact but submitted to different values of shear rate. One interesting result is the occurrence of a heat flow between different parts of the system even when they are at the same kinetic (i.e. local-equilibrium) temperature. This reinforces the arguments presented in section 5.1, in which it was claimed that heat flux is related to the gradient of the temperature θ rather than to the gradient of the local-equilibrium temperature T. Here, instead of a heat flux, the non-equilibrium parameter is the shear rate. The results of Todd and Evans

(1995) confirm that layers with identical kinetic temperatures may have shear-rate dependent thermodynamic temperatures, since they exchange heat.

However, thermodynamic temperature is expected to decrease with increasing shear rates. In contrast, Todd and Evans (1995) obtained a heat flux in the opposite sense, i.e. from the layers with higher shear rate to those with lower shear rate. They modellized these findings by proposing an *ad hoc* constitutive equation for the heat flux of the form

$$\boldsymbol{q} = -\lambda \nabla T - \xi \nabla \big[(\nabla \boldsymbol{v}) : (\nabla \boldsymbol{v})^T \big], \tag{5.75}$$

where λ is the usual thermal conductivity and ξ a coupling coefficient which describes the 'isothermal' generation of a heat flux due to a velocity gradient between parallel plates located at $y = 0$ and $y = d$.

A renewed interest in the comprehension of temperature has been launched by the geometrical and dynamical Rugh's proposal, presented in section 3.2.1, which allows one to define configurational temperature. In this context, Ayton *et al* (1999) have shown that kinetic temperature does not correctly describe the heat flux through Fourier's law but that Rugh's configurational temperature must be used. In the presence of shear flows, the configurational temperature is higher than the kinetic one and it was found that the difference in configurational non-equilibrium temperatures was driving heat in the sense observed in the simulations without need of assumption (5.75). Configurational temperatures may be related not only to positional degrees of freedom but also to orientational ones, which have much importance in some materials and on which much information may be gathered from x-ray, electron or neutron scattering spectra. Chialvo *et al* (2001) have derived explicit relations to determine orientational configurational temperature in simulations of classical molecular liquids.

Now we turn our attention to the second situation where NEMD provides a wealth of results, namely, that of systems under a colour flow, described by (5.73). Baranyai (1996, 2000a,b) has worked out in detail the topic of a non-equilibrium temperature, both in the situation under shear as under a colour current. He has noted that in both models (which are clearly anisotropic) the kinetic temperature shows strong direction dependence, as reported in table 3.

Typically, the smallest value of the temperature is that of T_{Kz}, i.e. the kinetic temperature along the z direction, perpendicular to the shear plane; in colour conductivity, the anisotropy of the kinetic temperature is less pronounced, and the smallest value is still that in the directions perpendicular to the colour flow. By extending Rugh's formalism to non-equilibrium situation, Baranyai (2000a) defines a configurational temperature T_{Cx} along the x-axis as

$$\frac{1}{k_B T_{Cx}} \equiv \frac{\left\langle 2 \sum_{ij} X_{ij} \right\rangle}{\left\langle \sum_i F_{ix}^2 \right\rangle}, \tag{5.76}$$

with $X_{ij} \equiv \mathrm{d}F_{ijx}/\mathrm{d}(x_i - x_j)$, F_{ij} being the force between particles i and j. Though configurational temperature is very difficult to constrain, Baranyai has shown that in shear flows the values of configurational temperatures are always larger than the corresponding kinetic ones, whereas in colour flow the configurational temperature is smaller than the kinetic

Table 3. Transversal and longitudinal kinetic temperatures and operational temperatures as defined by Baranyai (2000b). The precision of the results is indicated in parentheses.

Colour current, J_x	$T_y = T_z$	T_x	$T_{op}(m_s = 0.1)$	$T_{op}(m_s = 0.2)$
0.000	1.000	1.000	1.01(3)	1.02(3)
0.097(3)	0.989(4)	1.023(3)	1.02(3)	1.03(3)
0.298(20)	0.924(10)	1.140(20)	0.93(3)	0.93(3)

one. The difference between kinetic and configurational temperatures may be due in NEMD to the fact that heat is removed instantaneously from the kinetic degrees of freedom and there is no time for the configuration to follow the instantaneous removal of kinetic energy. This may justify the fact that, in general, the configurational temperature will be higher than the kinetic one in NEMD models. In dense fluids, the configurational part is the most important; in more realistic models with slow heat removal, the difference between configurational and kinetic temperatures may be smaller than in the NEMD calculations. This is another point where comparison of experiments with computer simulations must be done in a very careful way.

To understand the operational temperature, which is measured by a given thermometer, one must consider in detail the interaction between the system and the thermometer. In general, it is not possible to predict which temperature (kinetic or configurational) will be closer to the operational one, because this requires detailed knowledge of the relative contributions of both temperatures to the heat exchange between system and thermometer, which is probably non-universal, but a specific feature. Baranyai (2000b) has proposed an operational thermometer composed by a spherical piece of solid crystal, which behaves as one of the fluid particles in order to do not disturb the homogeneity of the system. Temperature is identified with the random kinetic energy of the particles of the thermometer, which is seen to be in internal equilibrium despite being in contact with the far-from-equilibrium environment. He has considered two different non-equilibrium situations: a 'colour' current and a shear stress. In the presence of a colour current this author concludes that the kinetic temperature along the direction transversal to the current is lower than the longitudinal temperature, as it follows from the thermodynamic analysis made in (5.11), and as corroborated in a different situation by the results of Morriss and Rondoni (1999) mentioned below. Second, the operational temperature T_{op} (which is reported in table 3 for two different masses of the solid particles) exhibits a strange behaviour: it becomes higher than the total kinetic temperature at intermediate colour currents, and it approaches the transversal kinetic temperature for high colour currents. In situations with shear flow, kinetic and configurational temperatures may be very different when heat is not instantaneously and locally removed, but when it flows in a realistic way from the regions where energy is being dissipated towards the boundaries.

Morriss and Rondoni (1999) have combined the dynamical definition of temperature, proposed by Rugh (1997) for Hamiltonian dynamical systems, with the Hamiltonian representation of a non-equilibrium isokinetic steady state in which the forces may be derived from a potential, which allows one to use Rugh's definition of temperature, and have obtained an expression for temperature away from equilibrium. In numerical simulations of two-dimensional systems of soft spheres, they have observed a strong correlation between the dynamical non-equilibrium temperature and the kinetic temperature transversal to the colour flux present in the system. This is a partial support to the comment made in section 5.1.1, where we noted that, in the presence of a heat flux, thermodynamic temperature may be interpreted as the kinetic transversal temperature. The proximity between the dynamical non-equilibrium temperature and the transversal kinetic temperature increases when the number of particles increases, as shown in table 4.

Table 4. Kinetic transversal temperature, dynamical temperature and total kinetic temperature (Morriss and Rondoni 1999).

Number of particles, N	$T_{kin\ trans}$	T_{dyn}	$T_{kin\ tot}$
56	1.994	2.07	2.000
224	1.966	1.98	2.000
896	1.954	1.93	2.000

Thus, we have seen that the analysis of non-equilibrium temperature is being actively developed in the context of non-equilibrium molecular simulations. This interest is fully justified, because if one tries to compare numerical predictions with experimental measurements, it is necessary to know what the thermometer is measuring. As has been seen, this is still not clear, because it depends on the relative direction and, furthermore, because kinetic and configurational temperatures may contribute in different ways to the measured temperature, according to the kind of thermometer being used.

To mention still another possibility for an operational thermometer in systems under shear flow, we note that Berthier and Barrat (2002a) have proposed the use of tracer particles with a mass much larger than that of the particles of the fluid. The thermometer measures an effective temperature different from the kinetic temperature of the particles, because the heavy particles have a much slower oscillation frequency and their dynamics is coupled to the slow fluctuations of the system. In their numerical simulations, Berthier and Barrat find that the average kinetic energy of the light fluid particles and that of the heavy tracer particles follow equipartition but with different temperatures, the effective or operational one for heavy ones and the bath or kinetic one for the light particles. They do not consider, however, the behaviour of the different components of the velocity, but only that of the total kinetic energy of the particles.

C. Non-equilibrium situations: illustrations and practical applications

In this section, we illustrate some differences between temperature defined from the non-equilibrium entropy and local-equilibrium temperature in several systems: monatomic ideal gases, harmonic oscillators, electromagnetic radiation and photo-injected plasma in semiconductors. The aim is to outline that the above discussions concerning non-equilibrium temperature are not only conceptual but are on the experimental consequences that could be checked.

6. Possible experiments

6.1. Harmonic oscillators and chains and monatomic gases under a heat flux or a viscous pressure

Simple harmonic oscillators in a thermal bath and coupled to some external force are probably the simplest systems where the behaviour of temperature out of equilibrium may be discussed (Hatano and Sasa 2000). By computing the average kinetic and potential energy of a forced harmonic oscillator in a thermal bath, Hatano and Jou (2003) have found that these averages take different values, thus showing that kinetic temperature and potential (or configurational) temperature are different from each other in this system. Depending on the parameters of the oscillator and of the frequency of the force, either the kinetic or the configurational temperature may be higher. To define an operational temperature, they have studied the heat flow between one forced oscillator in a bath and an unforced oscillator in a different bath. This provides a situation that is analogous to that presented in figure 1. The operational temperature of the forced oscillator is identified with the temperature of the bath in which the unforced oscillator is placed, when no energy flows between both oscillators. It is found that the operational temperature coincides neither with the kinetic nor the configurational temperatures of the forced oscillator, thus providing a clear illustration of the complexity of the definition of temperature in systems out of equilibrium.

Monatomic ideal gases are the most thoroughly studied systems; thus, though we have referred to them in many occasions throughout this paper, it is still convenient to outline some

of the non-conventional results that could be probably checked experimentally in a relatively simple way. With this aim in mind, let us return to expression (5.8) for the pressure tensor when q is directed along the y-axis and where it was seen that $P_{xx} = P_{zz} = \pi < p$, and $P_{yy} = 3p - 2\pi > p$. It was found that

$$
\begin{aligned}
\left\langle \tfrac{1}{2} m v_x v_x \right\rangle &= \left\langle \tfrac{1}{2} m v_z v_z \right\rangle = \tfrac{1}{2} k_B \theta < \tfrac{1}{2} k_B T, \\
\left\langle \tfrac{1}{2} m v_y v_y \right\rangle &= \tfrac{1}{2} k_B (3T - 2\theta) > \tfrac{1}{2} k_B T.
\end{aligned}
\tag{6.1}
$$

This consequence could, in principle, be checked, for instance, by exciting a small region of a rarefied gas with two crossed laser beams and analysing the Doppler broadening of emission lines from the excited region along the direction of the heat flux and perpendicularly to it (Camacho and Jou 1995). This could provide a direct test for prediction which in some sense has been already supported from molecular dynamics but in the case of colour current instead of heat flux, as mentioned in section 5.4.

Another situation of much interest is provided by one-dimensional heat-conducting systems. The main problem under consideration in this context concerns the conditions of validity of Fourier's law of heat transport. The systems studied are one-dimensional 'gases' (i.e. successions of N particles with several different kinds of interaction potentials) or of lattices of N particles, connected by springs (harmonic or anharmonic). Two different temperatures, e.g. T and $T + \Delta T$, are imposed on the boundaries of the system. Then the heat flow is computed as a function of ΔT and of the length L, which is proportional to N. Surprisingly, it follows that Fourier's law, with $q \propto \Delta T/L \propto \Delta T/N$, is an exception rather than the rule. In general, it is found that $q \propto \Delta T/N^\alpha$ with α a fractional exponent where the value depends on the system considered. The breaking of equipartition exhibited in (6.1) makes us suspect that it could be also broken in these systems. With this aim, we considered one-dimensional systems composed of two alternating kinds of particles of masses m_1 and m_2, respectively. By means of information-theoretical techniques, the average energies u_1 and u_2 in both kinds of particles were computed in non-equilibrium steady states characterized by a heat flux q. It was found that (Kato and Jou 2001)

$$
\frac{u_1}{u_2} = \frac{1 + 2m_1 \beta^3 (L_1/N_1)^2 q^2}{1 + 2m_2 \beta^3 (L_2/N_2)^2 q^2} \qquad \text{(gases)},
\tag{6.2}
$$

$$
\frac{u_1}{u_2} = \frac{1 + 2m_1 \beta^2 \kappa^{-1} q^2}{1 + 2m_2 \beta^2 \kappa^{-1} q^2} \qquad \text{(harmonic chains)},
\tag{6.3}
$$

where β is the Lagrange multiplier conjugated to the total energy, L_i the length of the system occupied by particles i in their motion and κ the stiffness of the Hookean springs connecting the particles. In both expressions, equipartition is found in equilibrium (i.e. for $q = 0$), whereas in the steady state it is no longer satisfied.

Aoki and Kuznesov (2003) have studied the breakdown of local equilibrium and linear response in classical lattice models with heat flow. In their analysis, the role of a non-equilibrium temperature is taken into consideration and it is found to be relevant in the exploration of these topics. As a possible microscopic definition of temperature they propose $T_{\text{eff}} = (\langle p^4 \rangle / 3m)^{1/2})$, which may incorporate non-equilibrium effects, and it has been useful to describe the deviations observed by these authors in their numerical simulations. This definition is in clear contrast to the usual kinetic definition (3.1), namely $T = \langle p^2 \rangle / 2m$, which does not change under the presence of a heat flux, because of restriction (5.5c).

It would also be of interest to incorporate the configurational temperature in those analyses, which until now have used only the kinetic definition of temperature. Because of their

relative simplicity, this kind of one-dimensional system could be helpful in understanding the configurational and the kinetic contributions to the whole heat flux.

6.2. Electromagnetic radiation

The determination of temperature of radiation is very important in astrophysics, cosmology and in technological applications of solar energy (Landsberg and Tonge 1980, Essex et al 2003). The temperature of electromagnetic radiation in equilibrium or blackbody radiation may be determined in three different ways: (i) from the internal energy density given by $U/V = aT^4$, a being a universal constant, related to the Stefan–Boltzmann constant σ by $a = 4\sigma/c$ (see (3.33)); (ii) using the wavelength $\lambda_{\max}$ corresponding to maximum power emission, by starting from Wien's displacement law (3.32), which states that $\lambda_{\max}$ is related to temperature as $(k_B T)^{-1} = 2.823(\lambda_{\max}/hc)$; (iii) finally, from the whole spectrum of radiation, by fitting it to Planck's distribution function (3.31). In equilibrium, the values of the temperature obtained by these three methods coincide. Furthermore, they also coincide with the temperature derived from the relation $T^{-1} = (\partial S/\partial U)_V$. Here, we will consider non-equilibrium radiation under a non-vanishing energy flux.

Effective non-equilibrium temperature for radiation not being in equilibrium in frequency distribution (for instance, monochromatic radiation) or in directional distribution of propagation (for instance, a unidirectional beam of light) is of special interest. It was defined already by Landau and Lifshitz (1985) in terms of the energy density $u(\nu, \boldsymbol{n})$, with ν the frequency and $\boldsymbol{n}$ the direction of the beam, as

$$T(\nu, \boldsymbol{n}) = \frac{h\nu}{\ln\left[1 + (h\nu^3/\pi c^3)(1/u(\nu, \boldsymbol{n}))\right]}. \qquad (6.4a)$$

This is the temperature of a blackbody that would correspond to the same energy density of radiation in a narrow frequency range around ν as the monochromatic radiation being considered, according to Planck's distribution. An alternative possibility is to define the effective temperature for monochromatic radiation of frequency ν_0, (Landsberg and Tonge 1980) in terms of n_{ν_0}, the number of photons having frequency ν_0 as

$$\frac{1}{T_{\text{bright}}} = \frac{k_B}{h\nu_0} \ln(1 + n_{\nu_0}^{-1}). \qquad (6.4b)$$

This is called the brightness temperature and corresponds to the temperature of a blackbody that would emit the same intensity of radiation in the same narrow frequency range between ν_0 and $\nu_0 + d\nu$ as the monochromatic radiation being considered, according to Planck's distribution. Another situation of practical interest in the study of solar energy is the so-called diluted blackbody radiation (Landsberg and Tonge 1980), a broadband radiation, where the contribution of each frequency ν is diluted by a factor of $\varepsilon(\nu)$ (for instance, radiation of different frequencies arriving to the atmosphere may be absorbed by molecules in a way dependent on the frequency). Then, the corresponding spectrum for the occupation number is

$$n(\nu) = \frac{\varepsilon(\nu)}{\exp(h\nu/k_B T) - 1}. \qquad (6.5a)$$

One defines the effective temperature $T_{\text{eff}}(\nu)$ through

$$\frac{1}{\exp[h\nu/k_B T_{\text{eff}}(\nu)] - 1} = \frac{\varepsilon(\nu)}{\exp(h\nu/k_B T) - 1}. \qquad (6.5b)$$

This effective temperature is independent of the frequency only when $\varepsilon = 1$, i.e. for blackbody radiation, where there is thermal equilibrium between radiation of different frequencies. The

effective temperatures defined in the above expressions are of practical interest in the discussion of radiation in astrophysics and in solar energy. A further definition of non-equilibrium effective temperature, found in astrophysics and cosmology (Weinberg 1972), is by relating the absorption rate coefficient $\Lambda(v, T)$ and the stimulated emission coefficient $\Omega(v, T)$ through an extension of the Einstein formula, namely

$$\exp\left[-\frac{hv}{k_B T_{\text{eff}}(v)}\right] = \frac{\Omega(v)}{\Lambda(v)}. \tag{6.6}$$

In equilibrium, the effective temperature is strictly equal to the absolute temperature, and does not depend on the frequency of the radiation. Out of equilibrium, effective temperature may become negative, in media with population inversion in which light may be amplified.

To get a deeper insight onto temperature, beyond these practical definitions, we will discuss here non-equilibrium radiation by the methods of entropy maximization presented in section 3.3. To study electromagnetic radiation one must take into account that the relevant statistics is that of Bose–Einstein and therefore one should maximize

$$S = -k_B(h^{3N} N!)^{-1} \int [f \ln f - (1 + f) \ln(1 + f)] \, d\Gamma, \tag{6.7}$$

under convenient constraints on the energy and, in our case, on the energy flux, which are expressed in terms of momentum p as $E = hv = pc$ and $J = pcc$. This yields for the maximum-entropy distribution function

$$f = \left[\exp(\beta pc + \gamma \cdot pcc) - 1\right]^{-1}, \tag{6.8}$$

where β and γ are the respective Lagrange multipliers conjugated to these constraints. Note that when $\gamma = 0$, (6.8) reduces to the Planck distribution, when normalization is taken into account. The calculation of β and γ is rather cumbersome (Larecki 1993) and the final results are

$$\beta = \frac{1}{2k_B}\left(\frac{aV}{U}\right)^{1/4} \frac{(y+2)^{1/2}}{(y-1)^{3/4}} \tag{6.9a}$$

and

$$\gamma = -\frac{3}{4}\left(\frac{a}{V}\right)^{1/4} \frac{Vq}{c^2 U^2} \frac{1}{(y+2)^{1/2}(y-1)^{3/4}}, \tag{6.9b}$$

where y denotes

$$y = \left[4 - 3\left(\frac{Vq}{cU}\right)^2\right]^{1/2}. \tag{6.10}$$

One could consider β as the reciprocal of non-equilibrium temperature or, alternatively, one could also interpret $\beta + \gamma \cdot c$ as the reciprocal of a quasi-temperature depending on the direction. We will comment the second possibility in section 7.7. The corresponding entropy obtained by introducing (6.4)–(6.9) into (6.7) is

$$\frac{S}{V} = \frac{2}{3}a^{1/4}\left(\frac{U}{V}\right)^{3/4}(y-1)^{1/4}(y+2)^{1/2}, \tag{6.11}$$

which tends to the expected value $S/V = \frac{4}{3}aT^3$ at equilibrium ($Vq = 0$) and vanishes for $V^2 q^2 \to c^2 U^2$, which is the maximum flux corresponding to the motion of all photons in the same direction. This vanishing of entropy corresponds to zero non-equilibrium temperature, as defined from the reciprocal of the Lagrange multiplier (6.9a) and it may be considered as an extension of the third law to non-equilibrium situations.

Expanding (6.7) up to the second order in the heat flux, it follows for $\theta^{-1} \equiv k_B \beta$

$$\theta^{-1} = T^{-1} \left(1 + \tfrac{15}{32} c^{-2} U^{-2} V^2 \boldsymbol{q}^2\right). \tag{6.12}$$

To evaluate the non-equilibrium temperature θ we can assume, for example, that at the surface of a star the radiation flux is given $q = \tfrac{1}{4} c(U/V)$ with U/V given by $U/V = aT^4$, and then expression (6.12) yields $\theta^{-1} = 1.031 \, T^{-1}$. Thus, the modification in the temperature in this region is of the order of 3%.

Fort and Llebot (1998) and Fort *et al* (1998, 1999a,b) have examined in greater detail some of the problems related to the measurement of temperature in non-equilibrium states. By using information theory for the description of radiation under a given temperature gradient, they find for the intensity distribution function in terms of the wavelength (Fort *et al* 1998)

$$i(\lambda, T) = i_{\text{Planck}}(\lambda, T)[1 + \phi_1(\lambda, T)\varepsilon + \phi_2(\lambda, T)\varepsilon^2], \tag{6.13}$$

with $\varepsilon \equiv (\ell/T)\nabla T$, ℓ being the photon mean free path, and ϕ_i the first- and second-order corrections to the equilibrium Planck distribution function i_{Planck}, with

$$
\begin{aligned}
i_{\text{Planck}}(\lambda, T) &= \frac{2\pi c^2 h}{\lambda^5} \frac{1}{\exp(hc/k_B T\lambda) - 1}, \\
\phi_1(\lambda, T) &= \frac{2}{3} \frac{ch}{k_B T\lambda} \frac{\exp(hc/k_B T\lambda)}{[\exp(hc/k_B T\lambda) - 1]^2}, \\
\phi_2(\lambda, T) &= \frac{1}{4} \left(\frac{ch}{k_B \lambda T}\right)^2 \frac{[\exp(hc/k_B \lambda T) + 1]\exp(hc/k_B \lambda T)}{[\exp(hc/k_B \lambda T) + 1]^2}.
\end{aligned}
\tag{6.14}
$$

Note, from here, that Wien's law for the wavelength corresponding to the maximum intensity of radiation is modified. If one denotes $x_{\max} \equiv hc(k_B T\lambda_{\max})^{-1}$, Planck's distribution yields the classical result

$$\left(1 - \tfrac{1}{5} x_{\max}\right) e^{x_{\max}} = 1, \tag{6.15}$$

whereas the first-order correction in the heat flow is

$$5 + (x_{\max} - 5)\exp(x_{\max}) = 2\varepsilon \frac{x_{\max} \exp(x_{\max})}{\exp(x_{\max}) - 1}, \tag{6.16}$$

as given by Fort *et al* (1997), who also provided the explicit expression for the equation up to the second order in the gradient, and reported the results for $T = 2000\,\text{K}$, $dT/dz = 10\,\text{K m}^{-1}$, $\ell = 10\,\text{m}$ (which corresponds to $\varepsilon = 0.05$). These results are $\lambda_{\max} = 1.4489\,\mu\text{m}$ (Wien's result), $\lambda_{\max} = 1.4076\,\mu\text{m}$ (first-order result) and $\lambda_{\max} = 1.4004\,\mu\text{m}$ (second-order result). Thus, the difference between the classical and first-order results for $\lambda_{\max}$ is 2.9% and the difference between classical and second-order results is 3.5%. In other terms, if Wien's law is used to obtain the temperature of this system for which $\lambda_{\max} = 1.4004\,\mu\text{m}$, the researcher would obtain $T = 2069\,\text{K}$ instead of the actual value $T = 2000\,\text{K}$, which is obtained when the first- and second-order corrections to Wien's law are taken into account.

A more detailed analysis of thermodynamics of non-equilibrium radiation based on information theory and incorporating higher-order fluxes (i.e. higher-order moments of the distribution function) (Vasconcellos *et al* 2001a,b) is able to yield an effective temperature for each mode of radiation in terms of the total energy and the fluxes present in the system. An alternative treatment is provided by kinetic theory of particles and photons, which provides a hierarchy of evolution equations for the several higher-order moments of the distribution function (Oxenius 1985).

6.3. Photoexcited plasma in semiconductors

Information statistical thermodynamics, discussed in section 5.2, allows us to analyse some experiments that can provide a measurement of quasi-temperatures, based on modulation optical spectroscopy. In particular, the dependence on the dissipative fluxes of the temperature of photoinjected carriers in a highly excited plasma in semi-conductors (HEPS) has been examined by Luzzi and co-workers (Luzzi *et al* 1997a,b). In a typical experiment, an intense laser light pulse produces a concentration N of photoinjected carriers (electrons and holes), and a constant electric field of intensity E is applied to the system. We choose as basic macroscopic variables for the system: (a) for the carriers, the energy $E(t)$; the particle numbers $N_a(t)$; the linear momenta $\mathbf{P}_a(t)$, and the energy fluxes $\mathbf{I}_a(t)$, where $a = e$ for electrons and $a = h$ for holes; and (b) the phonon populations $\nu_{q\gamma}(t)$ in mode $\mathbf{q}$ of branch γ. The corresponding intensive thermodynamic variables (the Lagrange multipliers) to which we call, respectively, $\beta(t)$, the reciprocal quasi-temperature (or effective temperature) of the carriers, $-\beta(t)\mu_a(t)$ with μ an effective chemical potential, $-\beta(t)\mathbf{v}_a(t)$ with $\mathbf{v}_a$ a drift velocity; $-\beta(t)\boldsymbol{\alpha}_a(t)$ that associated with the energy flux and, finally, $F_{q\gamma}(t)$ are those associated with the phonon populations. Because of Coulomb interaction, the carriers are internally thermalized in the subpicosecond timescale. As a consequence, $\beta(t)$ is the same for electrons and holes, while μ, $\mathbf{v}$, $\boldsymbol{\alpha}$ differ for the two types of carriers because of the difference in their effective masses.

In IST the informational entropy for this choice of variables is given by

$$\bar{S}(t) = \phi(t) + \beta(t)E(t) - \sum_a \beta(t) \left[\mu_a(t)N_a(t) + \mathbf{v}_a(t) \cdot \mathbf{P}_a(t) + \boldsymbol{\alpha}_a(t) \cdot \mathbf{I}_a(t) \right]$$
$$+ \sum_{\vec{q}\gamma} F_{\vec{q}\gamma}(t)\nu_{\vec{q}\gamma}(t), \tag{6.17}$$

where $\phi(t)$ is the logarithm of a non-equilibrium partition function. The associated generalized Gibbs equation has the form

$$k_B \Theta_c \mathrm{d}\bar{S} = \mathrm{d}E - \sum_a \left[\mu_a \mathrm{d}N_a + \mathbf{v}_a \cdot \mathrm{d}\mathbf{P}_a + \boldsymbol{\alpha}_a \cdot \mathrm{d}\mathbf{I}_a \right], \tag{6.18}$$

with $\Theta_c(t)$ the effective temperature or quasi-temperature of the carriers, defined as

$$\frac{\partial \bar{S}(t)}{\partial E(t)} = \beta(t) = \frac{1}{k_B \Theta_c(t)}. \tag{6.19}$$

We look for the dependence of $\Theta_c(t)$ on the fluxes $\mathbf{P}(t)$ and $\mathbf{I}(t)$. We write

$$\Theta_c(E(t), N_a(t), \mathbf{P}_a(t), \mathbf{I}_a(t)) = T_c^*(E(t), N_a(t), \mathbf{P}_a(t))$$
$$- \Delta\Theta_c(E(t), N_a(t), \mathbf{P}_a(t), \mathbf{I}_a(t)). \tag{6.20}$$

Here, T_c^* is the carrier quasi-temperature in the thermodynamic description that does not include the energy flux $\mathbf{I}$ as a state variable and $\Delta\Theta_c$ denotes the difference that includes the energy flux $\mathbf{I}$ as a basic variable. Up to lowest order in α, $\Delta\Theta_c$ is given by

$$\Delta\Theta_c(t) = \sum_a \Lambda_a \mathbf{v}_a \cdot \boldsymbol{\alpha}_a, \tag{6.21}$$

where Λ_a is a function of $T_c^*(t)$, $N_a(t)$ and $\mathbf{v}_a(t)$, which is positive and, for the sake of brevity, we omit its lengthy expression (see Luzzi *et al* 1997a,b).

So far we have characterized the carrier quasi-temperature in the formulation that retains the energy fluxes as basic variables. Next stands the question of the measurement of Θ_c, what

can be done in experiments of photoluminescence, from the intensity of radiative recombination (Luzzi and Vasconcellos 1980, 1990) which has the form

$$I(\omega, t) = g(\omega, t) \exp \left[-\frac{\hbar\omega - E_G}{k_B \Theta_c(t)} \right], \tag{6.22}$$

where $g(\omega, t)$ is the absorption coefficient, E_G the energy gap and ω the photon frequency. Then, from the high-frequency side of the spectrum, where $g(\omega, t)$ is very weakly dependent on ω, we obtain

$$k_B \Theta_c(t) = -\hbar \left[\frac{d \ln I(\omega, t)}{d\omega} \right]^{-1}, \tag{6.23}$$

which gives the quasi-temperature Θ_c in terms of the logarithm of the intensity of the luminescence spectrum on the high-frequency band. Experiments of photoluminescence in an external electric field are available in the case of modulation spectroscopy in semiconductor heterostructures. From the experimental data reported by Méndez *et al* (1988) for GaAs lattices, we obtain through the use of (6.19) the dependence of Θ_c with the electric field shown on the right ordinate of figure 5. Points are derived from the experimental data and the curve is obtained by polynomial interpolation.

To demonstrate the expected influence of the energy flux on Θ_c, we note that in the weak-field regime the dependence of T_c^*, on the right of (6.20), with E arising out of the dependence of E and P with E is of the form

$$T_c^*(E, N_a, P_a) = T_0^*(E^0, N_a) + \phi(E^0, N_a)E^2, \tag{6.24}$$

where T_0^* is the photoexcited carriers' quasi-temperature at zero electric field and ϕ is field intensity independent (E^0 is the energy at zero field). Hence, for vanishing $\Delta\Theta_c$ in (6.19) (i.e. neglecting the dependence on the energy flux), there follows that $(\Theta_c - T_0^*)/E^2 = \phi(E^0, N_a)$ is field independent and therefore a departure of this behaviour should be ascribed to $\Delta\Theta_c$.
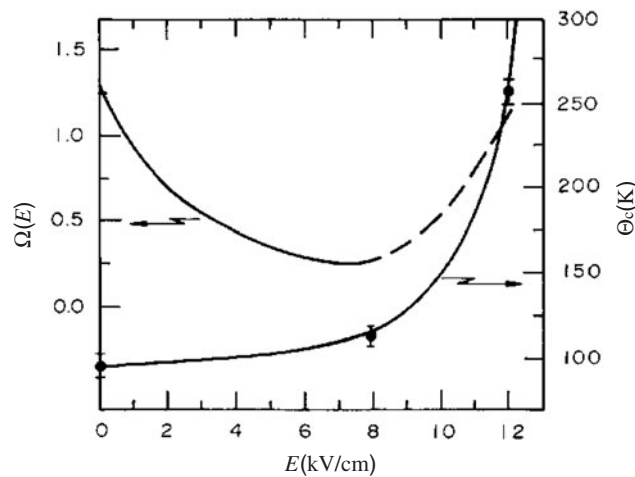

Figure 5. The carrier non-equilibrium temperature Θ_c (6.19) (right ordinate) and the function Ω of equation (6.25) (left ordinate) as a function of the electric field intensity (Luzzi *et al* 1997), obtained from photoluminiscence modulation spectroscopy in a laser-induced highly excited plasma in a GaAs lattice in the presence of an external electric field which produces an electric current in the plasma.

Introducing the function

$$\Omega(E) = \frac{\Theta_c(E) - T_0^*}{E^2} = \phi(E, N) - \frac{\Delta \Theta_c(\boldsymbol{I})}{E^2} \qquad (6.25)$$

we find that, according to experiments, it takes the values given on the left ordinate of figure 5, where it is evident that Ω is not a constant but a decreasing function of E. This is taken as an indication of the influence of the flux-dependent $\Delta \Theta_c$. Indeed, in the truncated description that neglects this flux, Ω is a near constant at low fields but the inclusion of the energy-flux-dependent $\Delta \Theta_c$ changes this behaviour making Ω at low to intermediate fields a monotonically decreasing function of E, as it is detected in the experiments. The corresponding non-equilibrium temperature Θ_c of the carrier is shown on the right ordinate of figure 5.

7. Non-equilibrium temperature in several systems

In this last section we discuss temperature in several practical situations where it is defined in a rather *ad hoc* form, which is useful, however, to describe, compare and systematize information in the particular domain of study. The definitions of such effective temperatures may be rather different, being based, for instance, on microscopic concepts (relative populations of microstates, average kinetic energies) or on semimicroscopic relations (fluctuation–dissipation relations) or on macroscopic grounds (equations of state, transport coefficients, etc). This section, thus, provides explicit illustrations of the ideas discussed in section 5 and, furthermore, it hints at the practical importance of definitions of effective temperature and the need to relate all of them in a coherent framework.

7.1. Two-temperature systems

In many situations, the systems under study are composed of two classes of particles or of subsystems, in which case, if the energy exchange between both subsystems is sufficiently slow, one may attribute its own temperature to each subsystem. A classical example of such a system is found in plasma physics (Ichimaru 1973, Krall and Trivelpiece 1975, Bobylev *et al* 1997, Rat *et al* 2001). Here, electrons and ions may have very different kinetic energies, and the energy exchange through collisions is very slow, because of the disparity of the masses of both kinds of particles. Another example is metallic conductors subjected to fast laser heating (Qiu and Tien 1993), which mainly heats the electrons, which slowly transmit their energy to the lattice, or hot electrons in semiconductor devices, which do not thermalize with the lattice. In contrast, systems under strong gravitational forces, as in accretion disks around black holes, proton temperature may be much higher than electron temperature (Mahadevan *et al* 1997, Mahadevan 1998). Still another example is radiation and matter: the exchange between matter and radiation is fast in ionized matter but it is slow when matter is neutral. The measurement of temperature in these non-equilibrium systems depends very much on the procedure: some probes are only sensitive to electrons, others are mainly sensitive to ions, and so on. Other examples are found in climatic situations (Peixoto and Oort 1984), traffic flow models (Larraga *et al* 2002), shock waves (Uribe *et al* 1998) and many other situations. One of the recent most active topics of research in these fields is the analysis of transport laws and transport coefficients.

To give an illustration we consider, for instance, a metal under the action of a fast laser pulse (Qiu and Tien 1993, Tzou 1997). The electrons and the lattice will have a very different response, because the former ones will immediately be heated and therefore the electron temperature is much higher than the lattice temperature for a short time. This situation may

be described by the following evolution equations for the electron and lattice temperatures T_e and T_l, respectively:

$$c_e \frac{\partial T_e}{\partial t} = \nabla \cdot (\lambda \nabla T_e) - C(T_e - T_l), \tag{7.1}$$

$$c_l \frac{\partial T_l}{\partial t} = C(T_e - T_l). \tag{7.2}$$

The constant C describes the electron–phonon coupling, which accounts for the energy transfer from the electrons to the lattice, and c_e and c_l are the specific heats of the electrons and lattice per unit volume, respectively. When the solution of equation (7.2), namely, $T_e = T_l + (c_l/C)\partial T_l/\partial t$, is introduced into (7.1), one is led to

$$\nabla^2 T_l + \frac{c_l}{C} \frac{\partial \nabla^2 T_l}{\partial t} = \frac{c_l + c_e}{\lambda} \frac{\partial T_l}{\partial t} + \frac{c_e c_l}{\lambda C} \frac{\partial^2 T_l}{\partial t^2}. \tag{7.3}$$

Thus, the time evolution of a system with two temperatures is more complicated than simple diffusion behaviour and shows, with respect to it, some delays related to the energy transfer between several degrees of freedom.

A two-temperature description is appropriate for other systems such as heterogeneous systems, where liquid and solid phases are at different temperatures, polyatomic gases, to which one can ascribe different temperatures for translational and internal degrees of freedom, and also the liquid helium II, where different temperatures may be assigned to the normal and superconductor fluids. These situations, and the derivation of the suitable generalized equations for heat transfer, have been thoroughly reviewed by Tzou (1997) within the framework of the dual-phase-lag formalism.

7.2. Temperature in nuclear physics

The temperature concept was introduced in nuclear physics by Bethe (1937) though, since nuclei are very small systems which are not in the thermodynamic limit, the temperature in the different ensembles (microcanonical, canonical and grandcanonical) does not coincide. The use of temperature as a relevant parameter was enhanced by different kinds of problems. In the 1960s, the interest was focused on the emission of nucleons and nuclear fragments in nuclear collisions between heavy nuclei, where one wants to describe and understand the main features of the mass yields, the isotopic yields and the kinetic energy spectra. The use of thermal models was stimulated by the fireball model (Hagedorn 1968, Hagedorn and Ranft 1968, Westfall *et al* 1976, Gosset *et al* 1978), which assumed a hot quasi-equilibrated expanding nucleon gas to predict kinetic energy spectra of emitted nucleons or of excited state populations. In the 1980s, interest was raised further, in discussions concerning the possibility of a transition from liquid phase to gas phase in finite nuclear matter after sudden expansion in a collision (Jaqaman 1984). Finally, in the 1990s, interest was focused on the possibility of reaching a transition from nuclear matter to quark-gluon plasma in ultrarelativistic collisions of heavy nuclei.

The temperature of nuclei is measured by studying the properties of the outgoing particles. The three usual methods of measurement are based on (Morrissey *et al* 1994): (i) the kinetic spectra of the emitted particles; (ii) the relative numbers of particles; and (iii) the excited state populations. These three methods do not always yield the same results. The rationale behind them is to assume that the system is thermalized in such a way that some equilibrium distribution function (the canonical one, for instance) may be used, in which the populations

with energy E_i are related through

$$\frac{N(E_2)}{N(E_1)} = \frac{g_2}{g_1} \exp\left(-\frac{E_2 - E_1}{k_B T}\right), \tag{7.4}$$

g_i being the corresponding degeneracy factors. In this way, the temperature T turns out to be given by

$$k_B T = (E_1 - E_2) \ln\left[\frac{N(E_2)g_1}{N(E_1)g_2}\right]. \tag{7.6}$$

In the three methods mentioned, E_i may refer to kinetic energy of the emitted particles, or the energies of excited states, and $N(E_i)$ to the number of different particles emitted, or to the relative populations in excited states.

Several comments are in order. These relations, or similar ones, are used as operational definitions of effective temperatures both in equilibrium and non-equilibrium systems. Second, the use of the Maxwell–Boltzmann factor instead of more detailed quantum statistics is justified if $\exp(\mu/k_B) \ll 1$, μ being the chemical potential; indeed, in many of the situations analysed, it turns out that $\exp(\mu/k_B T) \ll 0.05$, and therefore the classical approximation is meaningful. Many of these measurements, however, are complicated by different factors, such as, for instance, sequential feeding from higher-lying particle unstable states, which may lead to different apparent emission temperatures; or the zero-point motion of nucleons in the nuclei, which may contribute to the kinetic spectra with high energy tails.

There are various definitions of nuclear temperatures, according to the method of measurement: kinetic, isotope (or chemical), and population temperatures. The main characteristics are the following.

7.2.1. Kinetic temperatures, T_s. The most widely used method to determine the temperature of nuclei is based on measurements of kinetic energy spectra of emitted particles: a nucleus in thermal equilibrium evaporates particles with an energy distribution of Boltzmann type

$$N(E_k) = C(E_k - V_C) \exp[-(E_k - V_C)/k_B T_s], \tag{7.7}$$

where E_k is the kinetic energy of the emitted particle, V_C the Coulomb barrier, C a constant and T_s the temperature of the source. The main problem in this method is the experimental identification of the source (Boal 1984, Hirsch *et al* 1984, Bauer 1995). Furthermore, the interpretation of kinetic spectra is complicated by their sensitivity to collective motions, the temporal evolution of the emitting system, the sequential decay of highly excited primary fragments and fluctuations of the Coulomb barrier (Pochodzalla *et al* 1987).

7.2.2. Double isotopic ratio, T_r^0. This method (Albergo *et al* 1985, Machner 1985, Louvet *et al* 1993, Sokolov *et al* 1993, Sauvestre *et al* 1994, Coujeaud *et al* 1999) assumes that the emitters are in thermal and chemical equilibrium. The ratio between the yields of two isotopes (isotones) differing by one proton (neutron) depends only on the temperature and on the free proton (neutron) density. In the ratio, the proton (neutron) density cancels out and the ratio depends only on temperature through the formula

$$k_B T_r^0 = \frac{(B_2 - B_1) - (B_4 - B_3)}{\ln\left(s(Y_1/Y_2)/(Y_3/Y_4)\right)}, \tag{7.8}$$

where Y_i are the yields of the isotopes, s depends on the spins and B are the binding energies. At temperatures above a few megaelectron volt, the population of excited states should be taken into account. The larger the value of B, the higher the sensitivity of T_r^0. Therefore, one usually studies cases where the pair of isotopes at the denominator is ^{3}He–^{4}He.

7.2.3. Relative population of excited states, T_{pop}. The principle of this method (Morrissey *et al* 1985, Pochodzalla *et al* 1985) relies on the assumption that a nucleus in thermal equilibrium contains clusters in ground and excited states. The relative populations of these states are distributed accordingly as a probability proportional to the Boltzmann factor, in such a way that the ratio between the number of clusters emitted in two different states is

$$\frac{N_{gs}}{N} = \frac{2J_{gs} + 1}{2J + 1} \exp\left(-\frac{\Delta E^*}{k_B T_{pop}}\right),$$ (7.9)

where N_{gs} and N are the number of fragments emitted in ground state and excited states, respectively, J their corresponding spins, $\Delta E^* = E_1^* - E_2^*$ the energy difference between both states and T_{pop} the temperature of the source. From this equation, the population temperature is given by

$$k_B T_{pop} = \frac{\Delta E^*}{\ln\left(2J_{gs} + 1/2J + 1\right)(N_{gs}/N)}.$$ (7.10)

This method is sensitive only when the value of ΔE^* is much larger than the temperature at the point at which the particles leave the equilibrated system. Furthermore, it requires that the emitting subsystem be not only close to kinetic equilibrium but also to chemical equilibrium.

These different methods may lead to rather different values for the temperature of the nuclei. For instance, the emission temperature may be a factor of 3 lower than the temperature parameter that determines the kinetic spectra (Morrissey *et al* 1985, Pochodzalla *et al* 1987). These differences are interpreted as an indication that the degrees of freedom, associated with translational motion and the internal excitation, are not in mutual equilibrium. Furthermore, kinetic spectra may be deformed by collective flow effects and, in particular, by a fast expansion of the system in which the temperature may substantially drop. It has been suggested (Pochodzalla *et al* 1987) that the kinetic energy spectra indicate the initial temperature of the system (even if collective flows arise during an expansion phase), whereas the temperatures obtained from the relative populations of excited states correspond to the temperature at the point of emission. Thus, the emission of fragments from a collision could be prior to the attainment of a statistical equilibrium of the compound nucleus (Fields 1984). It is worth considering that there is not enough time to reach any kind of equilibration and that temperature is a meaningless concept after all. Indeed, nuclear collisions are rather fast and it is difficult to think of a non-equilibrium steady state.

7.3. Glasses and sheared fluids

The question about whether there is a useful concept of temperature in out-of-equilibrium systems appears naturally in supercooled liquids and glasses. In these systems there are several dynamical scales (fast and slow), which may imply that the same system can be at equilibrium on one scale and out of equilibrium on another or that it can be in equilibrium on two scales at once but exhibit different properties in them. Typical examples are a piece of glass kept at room temperature for months; the glass is not itself in equilibrium so that one cannot strictly talk about its temperature, but it is assumed that a thermometer in contact with it will indicate the room temperature. A thermodynamic description of glasses requires at least one more parameter than the description of the same system in the liquid equilibrium state, because of the breakdown of time-translation invariance of the ageing phenomenon.

Possible candidates for such an extra parameter are, for instance, the age of the glass or the cooling rate at which it was formed. In some approaches, one introduces, instead, a fictitious or effective temperature, the use of which goes back to the 1940s and which provides nowadays a first step towards the formulation of a non-equilibrium statistical thermodynamics

of glasses. These temperatures are defined in terms of some quantity of interest (for instance, enthalpy, thermal expansion coefficient, refraction index, etc) and are useful for modelling the slow relaxation of liquid and glass structures as it affects this particular physical property. On the other hand, the different fictitious temperatures defined from different physical quantities do not necessarily coincide, neither they are related to molecular structures. They have been developed since the 1950s (Jäckle 1986, Scherer 1990, Hodge 1994). The evolution of such fictitious temperatures is usually described by phenomenological equations of the form

$$\frac{\mathrm{d}T_\mathrm{f}}{\mathrm{d}t} = -\frac{T_\mathrm{f} - T}{\tau(T_\mathrm{f}, T)}, \tag{7.11}$$

T being the temperature of the heat bath and τ a suitable relaxation time depending on the state of the system.

Nieuwenhuizen (1998, 2000) formalized in greater detail the concept of effective temperature by writing

$$\hat{\mathrm{d}}Q = T\,\mathrm{d}S_\mathrm{eq} + T_\mathrm{eff}\,\mathrm{d}S_\mathrm{c}', \tag{7.12}$$

where S_eq is the entropy of the degrees of freedom which have reached equilibrium (because of a fast dynamics), whereas S_c' is the entropy of the slow configurational degrees of freedom which still remain out of equilibrium. One writes S_c' instead of S_c because the latter denotes the configurational entropy of the glass, namely, the total entropy of the glass minus the entropy of the fast vibrational modes, whereas, in contrast, S_c' is the part of the configurational entropy related to slow modes, i.e. excluding some configurational modes (like, for example, short-distance rearrangements) which are relatively fast. The temperatures T and T_eff are the usual room temperature and the effective temperature associated with the slow modes, respectively. In the presence of several different timescales, several temperatures related to different timescales could be introduced.

It is expected, and is so in several theoretical models of glasses, that this effective temperature is useful to match the behaviour of internal energy of the system, as $U(t, H) = U_\mathrm{eq}(T_\mathrm{eff}(t), H)$, or the magnetization M as $M(t, H) = M_\mathrm{eq}(T_\mathrm{eff}(t), H)$, where the subscript eq means the equilibrium equation of state and H is the magnetic field.

Recently, much attention has been paid to fluctuation–dissipation expressions relating the time-correlation functions of the variables with the respective response functions. Indeed, Cugliandolo *et al* (1997) have shown that in non-equilibrium systems with small energy flows there exists a timescale-dependent effective temperature that plays the same role as the thermodynamic temperature from two aspects: it controls the direction of heat flow and it acts as a criterion for thermalization. They also study stationary systems with weak stirring and glassy systems that age after cooling and show that they exhibit a similar behaviour, provided that time dependences are expressed in terms of correlation functions. More recently, the question has been addressed on the breaking of the fluctuation–dissipation theorem, which has been used to define effective temperatures (Cugliandolo *et al* 1997, Bellon *et al* 2001, Sellito 2001, Fielding and Sollich 2002). Theoretical generalizations of such theorems have been proposed for supercooled systems and experimental measurements confirming them have been reported for colloidal glasses (Bellon *et al* 2001), structural glasses (Grigera and Israeloff 1999, Di Leonardo *et al* 2000) and in non-equilibrium driven systems, such as, for instance, sheared complex fluids (Exartier and Peliti 2000, Barrat and Berthier 2001, Sciortino and Tartaglia 2001, Berthier and Barrat 2002a,b, Ono *et al* 2002).

We summarize the general ideas of this approach in the following way. Consider a variable m and define its time correlation function as

$$C(t, t_\mathrm{w}) \equiv \langle m(t)m(t_\mathrm{w})\rangle - \langle m(t)\rangle\,\langle m(t_\mathrm{w})\rangle, \tag{7.13}$$

t_{w} being the age of the system or waiting time, i.e. the time spent by the system in the glassy state after having been quenched suddenly into it, and let

$$R(t, t_{\mathrm{w}}) \equiv \frac{\delta \langle m(t) \rangle}{\delta h(t_{\mathrm{w}})} \tag{7.14}$$

be the linear response of $m(t)$ to a small change in its conjugate field h at time t_{w}. In glassy systems, in which some modes relax extremely slowly, the fluctuation–dissipation theorem is violated and one describes the departure with respect to the fluctuation–dissipation theorem in terms of an effective temperature T_{eff} defined as (Cugliandolo *et al* 1997)

$$R(t, t_{\mathrm{w}}) = \frac{1}{T_{\mathrm{eff}}} \frac{\partial C(t, t_{\mathrm{w}})}{\partial t_{\mathrm{w}}}. \tag{7.15}$$

In fact, if the system is supplied energy externally (such as, for instance, by shaking, tapping or shearing), fast motions may be non-thermal but slow modes may have a generalized temperature. The correlation and response functions may be split as

$$
\begin{aligned}
C_{\mathrm{AB}}(t, t_{\mathrm{w}}) &= C_{\mathrm{AB}}^{\mathrm{fast}}(t, t') + C_{\mathrm{AB}}^{\mathrm{slow}}(t, t_{\mathrm{w}}), \\
R_{\mathrm{AB}}(t, t_{\mathrm{w}}) &= R_{\mathrm{AB}}^{\mathrm{fast}}(t, t') + R_{\mathrm{AB}}^{\mathrm{slow}}(t, t_{\mathrm{w}}),
\end{aligned}
\tag{7.16}
$$

and one has

$$R_{\mathrm{AB}}(t, t_{\mathrm{w}}) = R_{\mathrm{AB}}^{\mathrm{fast}}(t, t') + \frac{1}{T_{\mathrm{eff}}} \frac{\partial C_{\mathrm{AB}}^{\mathrm{slow}}(t, t_{\mathrm{w}})}{\partial t_{\mathrm{w}}}, \tag{7.17}$$

where the fast response $R_{\mathrm{AB}}^{\mathrm{fast}}(t, t')$ has no general relation with the fast part of the correlation $C_{\mathrm{AB}}^{\mathrm{fast}}(t, t')$ (Kurchan 2000). Recall that due to extremely slow relaxation, glassy systems exhibit ageing, i.e. time translational invariance breaks down, in such a way that $R(t, t_{\mathrm{w}})$ and $C(t, t_{\mathrm{w}})$ cannot be written as $R(t - t_{\mathrm{w}})$ and $C(t - t_{\mathrm{w}})$. The derivative with respect to t_{w} has a more direct physical sense than the derivative with respect to t, because t_{w} corresponds to the time where the conjugate field h is perturbed externally. Temperature is found by plotting susceptibility $\chi(t, t_{\mathrm{w}}) \equiv \int_{t_{\mathrm{w}}}^{t} R(t, t') \, \mathrm{d}t'$ versus $C(t, t_{\mathrm{w}})$ with t fixed and t_{w} being used as a parameter. If there is only one ageing time (such as, for instance, in the spherical p-spin model), the plot consists of two intersecting straight lines, one giving T_{eff} at short times and T (room temperature) at long times (see figure 6 for the representation of an analogous situation). Instead, in models with an infinite hierarchy of timescales, the plot is a continuous curve with different slopes (and hence different effective temperatures) at different timescales.

   The effective temperature defined in (7.15) is higher than the room temperature and decreases with increasing age of the system and it is a decreasing function of the frequency of the perturbation, which means that the low-frequency modes relax to equilibrium much more slowly than the high-frequency modes. This timescale-dependent non-equilibrium temperature has been shown to have several properties associated with a thermodynamic temperature (Cugliandolo *et al* 1997). Furthermore, by considering two or more degrees of freedom, they have shown that the effective temperature determines the direction in which the heat flows. This temperature seems to be independent of the observable m under consideration, and it is applicable to the glassy material as a whole, instead of being purely local. Though these features are established in mean field models, Fielding and Sollich (2002) have pointed out that its status in non-mean field models is much less obvious. By starting from a trap model for glassy dynamics, they have shown that the limiting plot of the fluctuation–dissipation theorem may depend on the observable, in such a way that the mean-field concept of an effective temperature derived from a fluctuation–dissipation theorem cannot be in general univocally applied.

Barrat and Berthier (2001) and Berthier and Barrat (2002a,b) have used this formalism to analyse fluids in shear flow; in contrast to the unstable ageing behaviour of glasses, the fluids may be set into a non-equilibrium steady state with time-translation invariance. In this case, both $R(t, t_w)$ and $C(t, t_w)$ may be written as $R(t - t_w)$ and $C(t - t_w)$ and, therefore, $\partial/\partial t_w$ in (7.15) may be replaced by $-\partial/\partial t$, which yields the expression being used by these authors to define effective temperature. In sheared fluids, the shear rate $\dot{\gamma}$ rather than the waiting time t_w becomes the control parameter; when $\dot{\gamma}^{-1}$ becomes comparable or smaller than the relaxation time of the fluid, interesting new features appear. A further advantage of these systems with respect to conventional glasses is that the usual glass transition is very difficult to investigate experimentally, because of its very high viscosity, whereas these soft systems are not so viscous at the transition. Berthier and Barrat (2002a,b) take (7.15) for the definition of the effective temperature T_{eff}. They have simulated a mixture of particles A and B interacting through a Lennard-Jones potential and submitted to a shear flow, simulated on the basis of the equations of motion (5.72) mentioned in section 5. They have considered several variables, for instance: the single-particle density fluctuations, the self-part of the intermediate scattering function for different wavevectors, the stress fluctuations, the self-diffusion of tagged particles, and they have explored their behaviour at different values of the composition.

Their results show that the equilibrium fluctuation–dissipation theorem is obeyed only at short times (or for fast variables), whereas it is violated for long times (slow variables). The parametric plot of susceptibility $\chi(t) \equiv \int_0^t R(t') \, dt'$ versus the correlation function $C(t)$ may be described rather well by two straight lines of slopes $-1/T_{eff}$ for short times and $-1/T$ for long times (figure 6), with $T_{eff} > T$, in agreement with theoretical predictions (Berthier *et al* 2000). These authors have seen that the value of T_{eff} for different variables is the same, the only
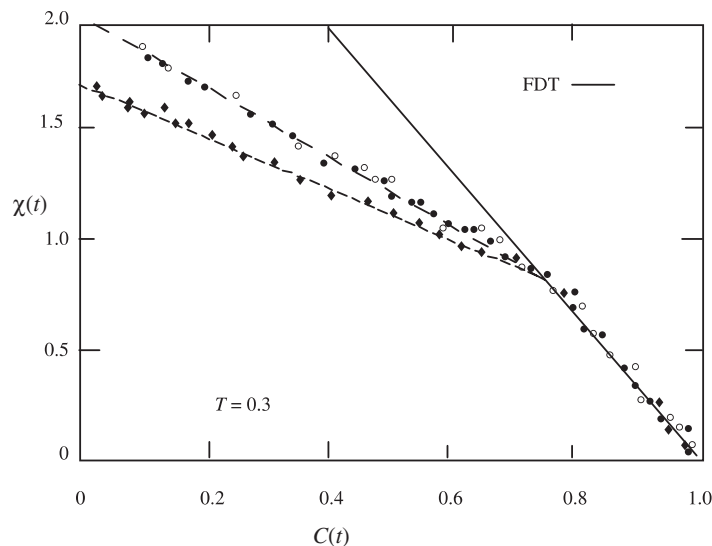

Figure 6. Schematic representation of a typical parametric plot of the susceptibility $\chi(t)$ in terms of the corresponding correlation function $C(t)$. The full straight line corresponds to the equilibrium fluctuation–dissipation theorem, with slope $-1/T$, T being the equilibrium room temperature. The dashed lines yield $-1/T_{eff}$ for two different observables, T_{eff} being the corresponding effective temperature, which is higher than the room temperature T. The line with diamonds is farther from equilibrium than the line with round symbols. Precise values may be found in Berthier and Barrat (2000) where the points correspond to the results of molecular simulations of single-particle density fluctuations in a fluid under shear flow, at different values of the shear rate.

difference being the value of the shear rate at which the crossover from T_{eff} to T is observed in the mentioned parametric plot. They have studied the system at different values of the shear rate. As expected, when $\dot{\gamma}$ is reduced, the effective temperature reduces to the bath temperature T, for T higher than the transition temperature; instead, if $T < T_c$, T_{eff} decreases with decreasing $\dot{\gamma}$ but its final saturation value does not reach the bath temperature T but remains higher than it, as predicted by Berthier *et al* (2000). This difference is physically interpreted from the fact that at low temperature the near-equilibrium regime does not exist because the relaxation time is very long (Cugliandolo and Kurchan 1999). From an experimental point of view it is difficult to reproduce these results because although the correlation functions may be obtained directly from light scattering, it is much more difficult to obtain the response functions, as one should externally manipulate the particles at the same wavevector used in the light-scattering experiment (Berthier and Barrat 2002a,b).

Another analysis of complex systems under shear is that by Ono *et al* (2002), who have studied fluctuations in a model of sheared foam. They have analysed five different quantities, all of them functions of the shear rate, and found their effective temperatures, which reduce to the equilibrium temperature in the quiescent state.

7.4. Granular systems

Granular materials, foams and colloids are very active topics of research (Jaeger *et al* 1996, Duran 1998). These systems exhibit also a slow dynamics, in similarity with glasses. Indeed, the slow settling of grains and powders in gently tapped jars has some analogies with the ageing of glassy systems. These systems may also have faster dynamics when they are submitted to external forces, such as, for instance, when they are shaken or sheared. The problem of temperature has different aspects in slow and the fast dynamics.

In spite of the fact that granular systems rapidly dissipate energy in collisions between particles, and thus ordinary techniques of statistical mechanics which rely on energy conservation break down, there have been several attempts to assign them some effective temperature. The simplest idea of relating temperature to the average kinetic energy is used in the context of externally shaken granular media but it is not satisfactory in general. Indeed, in the absence of such shaking mechanisms, it turns out that in typical granular systems (for instance, sand, powders, rice, wheat, etc), the thermal kinetic energy of each particle $k_B T$ is irrelevant in comparison with the kinetic energy of drift of each grain (Jaeger *et al* 1996). For example, the 'kinetic temperature' corresponding to translation velocities of $1\,\mathrm{cm\,s^{-1}}$ of small beads in typical silicate glass is 11 orders of magnitude higher than room temperature. Another argument that shows the negligible role of room temperature is to compare it with the typical energy needed to raise a grain of mass m over a height equal to its diameter d under the Earth gravity g; the value of mgd is more than 10^{12} times $k_B T$, at room temperature T. Thus, at first sight, ordinary thermodynamic arguments seem to be irrelevant in these situations.

However, Edwards and collaborators (Edwards and Oakeshott 1989, Edwards and Mounfield 1994, Edwards and Grinev 1998) have pointed out the existence of interesting and deep analogies between granular systems and classical statistical systems. They have proposed to compute the entropy of dense, slowly moving (gently sheared, tapped or vibrated) granular systems as $S_{Edw} = k_B \ln \Omega_{Edw}(E, V)$, where Ω_{Edw} is the number of blocked configurations of the system (i.e. in which every grain is unable to move) at given E and V rather than the number of all possible configurations, which should be considered strictly in Boltzmann–Gibbs statistics. Thus, all blocked configurations are assigned the same statistical weight, in analogy to the microcanonical ensemble of classical systems. This hypothesis is, of course, not evident, and it has been checked by means of numerical simulations. However,

the ensemble of blocked configurations is ill-defined, because tangential forces and sliding friction may or may not block some configuration (Makse and Kurchan 2002).

According to Edwards and Oakeshott (1989), the total volume occupied by the material could play a role analogous to that of the internal energy of the system (which is not conserved) in the thermodynamic formalism for granular systems. In this way, the microcanonical ensemble would be composed of all stable configurations that occupy a total given volume, instead of at a given constant energy, as in the classical microcanonical ensemble. Thus, the microcanonical relation

$$f = e^{-S/k_B} \delta(H - E) \qquad (7.18)$$

is replaced by

$$f = e^{-S/\lambda} \delta(W - V), \qquad (7.19)$$

where λ is a suitable constant and $\delta(x)$ is Dirac's delta function. Here, W is a function of the coordinates and the orientations of the grains, which gives the volume occupied by such a configuration; this function would play in this formalism a role analogous to the Hamiltonian in the classical case. Instead of asking that $H = E$, one imposes that only the configurations where the volume W is equal to the available fixed volume V are considered.

Thus, it seems logical in this analogy to explore the physical meaning of the derivatives of the entropy with respect to the energy and the volume, namely

$$T_{Edw}^{-1} = \frac{\partial S}{\partial E}, \qquad X_{Edw}^{-1} = \frac{\partial S}{\partial V}, \qquad (7.20)$$

where X is called the compactivity, because it is the reciprocal of the compaction of the system. Indeed, $X = 0$ corresponds to the most compact situation, whereas $X = \infty$ is the less compact one. Note that the compactivity cannot be identified strictly with temperature, because in a usual thermodynamic system one has $(\partial V/\partial S)_E = T/p$, but in granular systems the thermal temperature T and the pressure p are negligible. Compactivity has been used to study equilibrium situations in powders. Indeed, if two initial states of identical systems with different compactivity are shaken, they tend to a final state with the same common compactivity. This theory may be worked out computationally in model systems (Monasson and Pouliquen 1997), and it is found that it is able to describe compaction (Prados *et al* 2000) and segregation (Mehta and Edwards 1989) in granular systems.

Moreover, it is not easy to test Edwards' theory directly in real materials, because usually the rate of energy input and the density—the key control parameters—are non-uniform. Furthermore, Edwards' proposal is based on an analogy rather than being a direct consequence of first principles. The energy exchange between the system and the surroundings is characterized by external driving and inelastic dissipation, in contrast to the exchange with usual heat baths, so that for the moment it has not been widely accepted. However, it turns out that the value of the compactivity defined through (7.20) may be related to other different measurements of temperature, as those based on the breaking of the fluctuation–dissipation theorem (Grigera and Israelot 1999, Bellon *et al* 2001, Sellito 2001), which have already been introduced in the context of glasses. Another mechanical analogue of temperature has recently been proposed by Ngan (2003), to describe the contact force distribution amongst particles by a variational principle, minimizing energy at a constant value for the entropy.

Another measurement of temperature, which also leads to numerical results coincident with the compactivity, is based on the Einstein relation between diffusivity and mobility, as was discussed in section 5.3. Barrat *et al* (2000) carried out a numerical simulation in a microscopic model (Kob–Anderson model), which is not a mean field one, and they found that the dynamical temperature obtained from the Einstein relation agrees well with the Edwards

temperature obtained from the analysis of blocked configurations. More recently, Makse and Kurchan (2002) have carried out a numerical model of a granular system of spherical particles of different sizes, subject to slow shearing, with uniform rate of energy input and uniform density. They have obtained the temperature from the Einstein relation (5.67), in terms of averages of the displacements of tracer particles. Their results show that this temperature is identical for different size particles and that its value is consistent with that predicted for the Edwards temperature. The agreement between dynamical and Edwards temperatures, however, gets worse when the rate of energy input through tapping or shearing increases (Barrat *et al* 2000).

The opposite regime is found in granular systems that are vigorously shaken. In this case, the erratic motion of the particles is similar to the thermal motion of molecules in a normal gas and therefore it is possible to introduce the concept of granular temperature as

$$\tfrac{3}{2}k_B T_{gr} = \tfrac{1}{2}m\big(\langle c^2 \rangle - \langle c \rangle^2\big), \tag{7.21}$$

c being the speed of the particles and $\langle \cdots \rangle$ denoting the average. When the system receives a high-energy input, it approaches the behaviour of gases, and thus some generalizations of the Boltzmann equation have been applied to their study in such situations (Brey *et al* 2000, 2001). When the degree of shaking of the system is low, this kinetic definition of temperature has less interest, and it is only a way to describe qualitatively this degree of shaking, rather than being a true temperature (Jaeger *et al* 1989, Mehta *et al* 1992, Barrat *et al* 2000). Jaeger *et al* (1989) have studied the avalanches in a shaken sand pile as a function of the angle ϕ between the horizontal and the free surface of the sand pile by assuming a simple model where an effective temperature T_{eff} is introduced, which is directly related to the intensity of the mechanical vibrations. They obtained for the rate of change of such angle that

$$\frac{d\phi}{dt} = -A\theta \exp\left[\xi(\phi - \phi_r)\right], \tag{7.22}$$

where ϕ_r is the angle at rest, $A \equiv A_0 \exp(-U_1/k_B T_{eff})$, $\xi \equiv U_1/k_B T_{eff}$, with A_0 being a constant and U_0 and U_1 constants related to the expansion of an effective barrier height $U(\phi)$ for the fall of the particles taken as $U(\phi) = U_0 + U_1(\phi_r - \phi)$. According to these authors, this equation reproduces reasonably well the observed evolution of ϕ. However, they note that when this temperature becomes smaller than U, the assumption that mechanical vibrations mimic an effective temperature fails; indeed, in contrast to thermal fluctuations, mechanical energy distribution is expected to be cut off sharply above a finite value corresponding to the maximum vibration intensity. Thus, though in some conditions the identification of the intensity of vibration as temperature is useful and satisfactory, it has some limitations.

Feitosa and Menon (2002) and Wildman and Parker (2002) have studied granular temperature in binary vibrated systems with particles of two different masses. Given the kinetic definition of T, they find that the two types of grains do not reach the same temperature, but their temperature ratio is constant in the bulk, independent of number fraction or vibration velocity, but sensitive to the ratio of mass densities. This is in contrast to usual belief that a single temperature describes the mixture of gases. This breaking was observed early by Garzó and Dufty (1999) in a theoretical analysis of cooling of a binary granular mixture.

7.5. Disordered semiconductors

High-field transport in disordered semiconductors is another area where effective temperatures have been proposed to describe strong non-linearities in the field in several quantities as carrier drift mobility, dark conductivity and photoconductivity. It was observed (Grünewald and

Movaghar 1989, Shklovskii *et al* 1990) that in some aspects of hopping conductivity of carriers the electric field plays a role similar to that of temperature, in the sense that the field enlarges the number of states available for the particles. Indeed, in the presence of high fields the electrons no longer follow the Fermi statistics but the energy distribution has long tails that may be described approximately as

$$f(\varepsilon) = \exp\left(-\frac{\varepsilon - \varepsilon_F}{k_B T_{\text{eff}}}\right), \tag{7.23}$$

with T_{eff} being an effective temperature. It is worth noticing that in a certain range of values of electric field E and room temperature T, some physical parameters, such as the electrical conductivity, are found to depend on T and E in a well-defined way, as if this quantity depended on an effective temperature T_{eff}, which is a combination of both T and E, i.e. $\sigma(T, E) = \sigma(T_{\text{eff}})$. Such a $T_{\text{eff}}(T, E)$ is the same that appears in the distribution function (7.23), in such a way that the value of T_{eff} is obtained by comparing conductivity data and equating T_{eff} to the room temperature for which the low-field conductivity is the same as the observed high-field conductivity.

Several expressions for such an effective temperature have been proposed, such as, for instance (Cleve *et al* 1991),

$$k_B T_{\text{eff}}(T, E) = k_B T + eE\langle R \rangle, \tag{7.24}$$

with $\langle R \rangle$ being the mean jump distance in the field direction and e the electron charge, or (Nebel 1991)

$$k_B T_{\text{eff}}(T, E) = k_B T + \tfrac{1}{2}eE\alpha, \tag{7.25}$$

with α the localization length of carriers in the tail states, or (Esipov 1991)

$$T_{\text{eff}}(T, E) = \max\left(T, \tfrac{1}{2}eE\alpha\right), \tag{7.26}$$

or (Marianer and Shklovskii 1992, Nebel *et al* 1992, Baranoskii *et al* 1993)

$$(k_B T_{\text{eff}})^2 = (k_B T)^2 + A(eE\alpha)^2, \tag{7.27}$$

with $A \approx 0.67$. These expressions may be used either for electrons (with $\alpha_e \approx 1$ nm) as for holes (with $\alpha_h \approx 0.5$ nm), the agreement for hole conductivity being better than that for electron conductivity. The linear expressions do not account for the details of the experimental data for the dark conductivity and field mobility, which is well accounted for by the last, non-linear definition. However, this definition, which is helpful from a practical point of view, does not yet have a physical interpretation.

The fact that the effective temperature is higher than T, both in glasses and in amorphous semiconductors, could seem to be a contradiction with the results indicated in section 4.3, where the absolute temperature derived from the non-equilibrium entropy turned out to be smaller than the local-equilibrium temperature. Indeed, in sections 7.3 and 7.4, T indicates the room temperature, which is not the temperature that would correspond to the system if this was suddenly isolated and allowed to reach internal equilibrium. Therefore, it is important not to be confused concerning the different equilibrium reference temperatures. In general, the temperature of a non-equilibrium system is higher than the ambient temperature, because energy is being dissipated in the system.

7.6. Turbulence

The description of fully developed turbulence is also very attractive from the point of view of non-equilibrium statistical mechanics and thermodynamics. The most obvious idea is

to define the temperature of turbulence as the average kinetic energy associated with the turbulent fluctuations of the macroscopic velocity, in analogy to the definition of temperature in kinetic theory, related to the microscopic kinetic energy of the particles. Another definition of temperature arises in relation to some form of probability distribution function and entropy. For instance, one may work with a probability distribution function for the macroscopic velocity fluctuations, incorporating higher-order moments of the distribution function as independent variables. This is analogous to Grad's development in kinetic theory of gases or extended irreversible thermodynamics (Sancho and Llebot 1994, Sadiki and Hutter 2000), or in information theory taking the several Fourier components of the velocity fluctuations (Brown 1982). Castaign (1989, 1994) has proposed another possibility by defining an effective temperature as

$$\frac{1}{T_{\text{eff}}} = \frac{\partial \ln \text{Pr}(r_1', r_2', v_2/v_1)}{\partial \ln(v_2/v_1)},\tag{7.28}$$

where Pr denotes the probability of finding a vortex of spatial scale $r_2' \equiv r_2/\eta$ (with η being the shear viscosity) with characteristic velocity v_2 if it is known that vortices at spatial scale r_1' have characteristic speed v_1. This temperature depends on the Reynolds number, and it becomes independent of the spatial scale at steady state.

The concept of temperature for turbulence has been used, especially in the domain of two-dimensional turbulence. In contrast to three-dimensional flows, two-dimensional flows conserve the quantities of the form $I_n = \int \omega^n \, dA$, where ω is the vorticity, defined as the rotational of the velocity field, i.e. $\omega = \nabla \times v$. In particular, the integral I_n for $n = 2$ is called the enstrophy, which, together with the kinetic energy, are the two quadratic conserved quantities of the flow. Then, some authors (Kraichnan 1975, Kraichnan and Montogomery 1980) have proposed to describe some aspects of two-dimensional turbulence by using a distribution function of the canonical form

$$f = Z^{-1} \exp(-\beta E - \alpha \Omega)\tag{7.29a}$$

with E being the kinetic energy, Ω the enstrophy and β and α Lagrange multipliers related to the 'energy temperature' and 'enstrophy temperature'. These parameters may become negative in some circumstances, as we have already commented at the end of section 3.4. From the above distribution function, it follows that the average values of the energy and the enstrophy for the nth Fourier mode are given by

$$\langle E_n \rangle = \frac{1}{2} \frac{1}{\beta + 2(\alpha/\rho)\lambda_n^2}, \qquad \langle \Omega_n \rangle = \frac{1}{\rho} \frac{\lambda_n^2}{\beta + 2(\alpha/\rho)\lambda_n^2}\tag{7.29b}$$

with λ_n being the wavevector of the corresponding Fourier mode. When $\alpha = 0$ one has energy equipartition and for $\beta = 0$, enstrophy equipartition. Seyler *et al* (1975) made a numerical test of the analytical theory of two-dimensional turbulent equilibria for inviscid Navier–Stokes equation, and demonstrated that a good fit for the energy per Fourier mode is predicted by the two-temperature canonical ensemble of Kraichnan. Dynamical ensembles for the non-equilibrium statistical mechanics of turbulence have been proposed in a more abstract and general setting by Gallavotti and Cohen (1995), following initial ideas proposed by Ruelle (1978). Still a third possibility of defining temperature in some parametric turbulent systems is through the breaking of the fluctuation–dissipation theorem (Hohenberg and Shrainan 1989) in analogy to what has been discussed in the context of glasses and granular systems.

7.7. Temperature transformations in relativistic systems

The analysis of the different meanings of temperature in non-equilibrium situations may be helpful to clarify the apparent inconsistencies amongst different proposals of relativistic

transformations of temperature. Indeed, it has been seen throughout this review that several possible definitions of temperature, which all yield the same result in equilibrium situations, instead yield different results out of equilibrium. This is not a logical inconsistency, but reflects the fact that different measurements of temperature, related to the different definitions adopted, will lead to different results. This is not surprising because different degrees of freedom may be preferentially involved in different kinds of measurement. When two systems, each one in internal equilibrium, are moving with respect to each other, each system sees the other one under the presence of an energy flux, due to the relative motion between them. Thus, it is logical to ask whether this flux may make different definitions and measurements of temperature yield different results. A general updated view of the relativistic transformations of the different quantities starts from the invariance of the full energy–momentum–stress tensor, from which stem the transformation properties of energy density, pressure, heat flux and traceless pressure tensor (Maartens 1998, Maartens *et al* 1998, 1999). However, here we take a historical overview of the most well-known proposals for the transformation of temperature. This is sufficient to indicate that, in spite of their apparently conflicting character, they are not mutually incompatible, because they arise from different operational definitions of temperature, which coincide in equilibrium but not in the presence of an energy flux, as that arising from the relative motion of the systems.

Let us recall some of the different relativistic transformation laws of temperature. Planck and Einstein proposed

$$T = T_0 \left(1 - \frac{v^2}{c^2} \right)^{1/2} \equiv \gamma^{-1} T_0, \tag{7.30}$$

with T_0 the temperature at rest and T the temperature measured by an observer moving with speed v with respect to the system. In this setting, a moving body appears colder than the body at rest, and temperature loses its meaning as a criterion of thermal equilibrium. This result may be understood from the thermal equation of state of ideal gases. Indeed, an ideal gas obeys in the rest frame K_0 the equation $pV_0 = Nk_B T_0$; since the pressure and number of particles are seen as invariant, whereas the volume is contracted in a Lorentz transformation as $V = \gamma^{-1} V_0$, it follows from the invariance of the thermal equation of state that $T = \gamma^{-1} T_0$. (In fact, from the invariance of the full energy–momentum–stress tensor it follows that pressure is not invariant; therefore, this argument used by the original authors cannot be considered as definitive, and a deeper analysis should be undertaken.)

This point of view prevailed for half a century, until, in the 1960s, Ott (1963), Arzeliès (1965) and others proposed that

$$T = T_0 \left(1 - \frac{v^2}{c^2} \right)^{-1/2} \equiv \gamma T_0. \tag{7.31}$$

In this other setting, the moving body appears hotter than in the rest frame. This result can also be understood on the basis of the ideal gas, but now one starts from the caloric equation of state rather than from the thermal equation of state. Indeed, if one takes into account that for an ideal gas $E_0 = \alpha N k_B T_0$, with α being a numerical constant, and if one considers that the energy transforms as $E = \gamma E_0$ because it is the time component of the energy–momentum 4-vector, Ott's result (7.31) is obtained.

The contradiction between (7.30) and (7.31) would imply that temperature is not related to the zeroth law, because according to one criterion the moving system would be colder and according to the other one hotter than the system at rest. To relate temperature to thermal equilibrium, Landsberg and Johns (1970) and Callen and Horwitz (1971) proposed defining temperature as the temperature at the rest frame and to require that it is an invariant quantity by definition. This is the most widely accepted attitude nowadays (Neugebauer 1980).

Note that different transformation laws arise from taking different definitions of temperature, such as, for instance, that coming from the thermal equation of state, or from the caloric equation of state, or from the zeroth law of thermodynamics, or from the derivative of the entropy with respect to the energy, or from the kinetic definition. All these possibilities coincide in equilibrium and each of them could be taken in principle for the formulation of temperature in relativistic system. The important point, noted by Domínguez-Cascante (1997), is that out of equilibrium these different definitions differ, and therefore it is logical that they do not coincide in relativistic transformations, in the presence of a convective energy flux. Thus, the fact is that these several transformations do not refer to the same meaning of temperature, and their different transformations laws are not inconsistent, but rather, they are based on different operational definitions of temperature, and obtained through different kinds of measurements.

To illustrate this, Domínguez-Cascante worked out the example of blackbody radiation. In the rest frame K_0 at temperature T_0, the distribution function for the number density $n(\omega_0)$ of photons with frequency ω_0 observed in the rest frame has the Planck form

$$n(\omega_0) = \frac{2}{\exp(\beta_0 \hbar \omega_0) - 1}, \tag{7.32}$$

where $\beta_0 \equiv (k_B T_0)^{-1}$ and the factor 2 takes into account the two possible polarization states of photons. From a macroscopic point of view, the gas is described by the fundamental thermodynamic equation $S_0 = \frac{4}{3} a^{1/4} V_0^{1/4} U_0^{3/4}$, where a is related to the radiation constant of the Stefan–Boltzmann law as in (6.2); the caloric and thermal equations of state are $U_0 = a V_0 T_0^4$; $p_0 = (1/3)(U_0/V_0)$.

Assume now an inertial frame K in relative motion with respect to the frame K_0 with a relative velocity—v. An observer in K will measure for a photon moving in a direction forming an angle θ with respect to v the energy $e = \hbar \omega$, with ω related to ω_0 according to the Doppler relation

$$\omega_0 = \gamma \omega \left(1 - \frac{v}{c} \cos \theta\right). \tag{7.33}$$

Accordingly, the distribution function will be changed to

$$n(\omega) = \frac{2}{\exp[\beta_0 \hbar \gamma \omega (1 - (v/c) \cos \theta] - 1}. \tag{7.34}$$

Note that this distribution function is not isotropic. The distribution function (7.34) can be expressed in terms of the momentum p by noting that $p = \hbar \omega / c$. Defining the so-called coldness 4-vector $(\beta, I/c)$ where $\beta \equiv \gamma \beta_0$ and $I = -\beta v$, (7.34) is rewritten as

$$n(p) = \frac{2}{\exp(\beta p c + I \cdot p) - 1}. \tag{7.35}$$

Note also that (7.34) may be seen as a Planckian distribution with an effective temperature T_{eff} given by $(k_B \beta_{\text{eff}})^{-1}$ with

$$\beta_{\text{eff}} \equiv \beta \left(1 - \frac{v}{c} \cos \theta\right) = \beta + \frac{I}{c} \cos \theta. \tag{7.36}$$

It is worth noting that from the statistical point of view (7.34) is not strictly a Planckian distribution characterized by one single temperature; thus, neither Einstein's nor Ott's temperatures are temperatures in the statistical sense, in that they do not characterize a Planckian spectrum. The only temperature that can be defined in this way is the rest frame temperature. This seems to support Landsberg and Johns' point of view (1970).

However, Domínguez-Cascante has noted that depending on the adopted definition of temperature one can recover both Einstein's and Ott's temperatures, which however, do not

represent thermal equilibrium between systems in relative motion. Indeed, note that the effective temperature (7.36) depends on the direction. Averaging (7.35) over the distribution function one obtains

$$\langle \beta_{\text{eff}} \rangle = \frac{\int (2(\beta - I \cos \theta))/(\exp(\beta pc + \boldsymbol{I} \cdot \boldsymbol{p}) - 1) \mathrm{d}\boldsymbol{p}}{\int (2/\exp(\beta pc + \boldsymbol{I} \cdot \boldsymbol{p}) - 1) \mathrm{d}\boldsymbol{p}} = \beta \left(1 - \frac{I^2}{c^2 \beta^2} \right) = \gamma^{-1} \beta_0 \qquad (7.37)$$

and it is possible to define the average temperature that an isotropic detector would measure $T_{\text{eff}} \equiv (k_{\text{B}} \langle \beta_{\text{eff}} \rangle)^{-1} = \gamma T_0$. This is the temperature that follows Ott's transformation law. Alternatively, instead of averaging β_{eff}, one may define an effective temperature as $T_{\text{eff}} \equiv (k_{\text{B}} \beta_{\text{eff}})^{-1}$ and average it over the angular distribution. This yields

$$T_{\text{eff}} = T_0 \gamma^{-1} (4\pi)^{-1} \int \left[1 - \left(\frac{v}{c} \right) \cos \theta \right]^{-1} \mathrm{d}\Omega \approx T_0 \left[1 - \frac{1}{6} \left(\frac{v^2}{c^2} \right) \right] + \mathrm{O} \left(\frac{v^4}{c^4} \right). \qquad (7.38)$$

On the other hand, one may obtain the Einstein temperature by defining it in terms of the derivative of the entropy, namely, if one defines temperature as in (2.11), namely $T^{-1} = (\partial S / \partial E)_V$. Taking into account that, according to (6.11), the entropy of the moving radiation system is

$$S(E, V, \boldsymbol{P}) = S_0(E, V) \tfrac{1}{2} (x + 2)^{1/2} (x - 1)^{1/4}, \qquad (7.39)$$

with x defined (see (6.10)) as

$$x \equiv \left(4 - 3 \frac{c^2 P^2}{E^2} \right)^{1/2}, \qquad (7.40)$$

it follows (see (6.9a)) that

$$T = \left(\frac{E}{aV} \right)^{1/4} \frac{2(x - 1)^{1/4}}{(2 + x)^{1/2}} = \gamma^{-1} T_0. \qquad (7.41)$$

This is just Planck's and Einstein's transformation for the temperature (7.30). Thus, it is seen that the apparent inconsistency between different transformation laws is removed once one becomes aware that the way the average is performed (this depends on the way in which the experiment is performed or on the kind of detector being used) determines the transformation law. This is in contrast with the usual point of view, according to which only one of these transformation laws may be correct, the other ones being incompatible with it. We emphasize, however, that a more updated analysis of temperature transformations would be to start from the transformation laws of the energy–momentum–stress tensor (Maartens *et al* 1998, 1999). However, this does not avoid the need to define temperature by relating it to different quantities such as, for instance, pressure or energy density, which appear explicitly in the mentioned tensor. As well as in the present analysis, different definitions of temperature, all of them equivalent in equilibrium, will yield different transformation laws for observers in motion.

8. Conclusions

In the present review, we have emphasized the need for further discussion and additional research for a comprehensive and satisfactory formulation of the concept of temperature in non-equilibrium situations. We have reviewed several different proposals of effective temperatures for non-equilibrium systems, which have interest in their own context, but that require some careful analysis allowing them to be connected and compared to each other. It turns out that this topic is not merely academic, but this diversity of proposals in different fields makes it clear that the concept of temperature is useful and necessary in many situations. These different definitions have been used basically as a practical convenience in the study

of particular problems, where the concept of temperature is not yet sufficiently well defined and understood. Indeed, after all, thermometers are used in non-equilibrium situations, and it is important to know what kind of information they are giving on the system. The different definitions presented show the relevance of the methods of measurement of temperature. It could be considered that since in non-equilibrium situations different methods may lead to different results for temperature, this concept must be abandoned. However, we think that this multiplicity is not an insurmountable problem, but that one should understand the relation between the different effective temperatures. This would allow one to predict, from one given measurement of temperature, the results obtained by other methods, and also to realize the connection of these different temperatures with the underlying microscopic descriptions of the system under analysis.

There seems to remain a wide gap between theoretical formulations of non-equilibrium thermodynamics beyond the local equilibrium, where the meaning of entropy and temperature are central topics, and the phenomenological definitions of effective temperatures. These definitions are directly referred to applications, where not much attention is paid to general macroscopic principles, and where entropy is often ignored. Another example of this lack of communication is found in the several microscopic or semi-microscopic definitions of temperature, which do not make much effort to compare with each other. This fragmentation of proposals is also found at the macroscopic level in the different approaches beyond the local equilibrium. This is understandable, because the physical situations under which the proposals are based, are rather different from each other, but it seems logical to expect that a higher degree of interaction could be mutually rewarding. To stimulate this interaction and to cover the gap between different fields, we have presented several kinds of perspectives and different systems in this review. We summarize in table B the essential conclusions regarding the challenges and limitations relating to the several definitions, along the lines anticipated in table A.

We have noted that the general laws related to the fundamental definition of temperature, namely, the zeroth and second laws, must be dealt with very carefully in non-equilibrium situations. Indeed, concerning the zeroth law, the fact that different degrees of freedom may have different operational temperatures implies that the transitivity of mutual thermal equilibrium is restricted to situations where the interaction between the systems is related to a well-specified set of degrees of freedom. With reference to the second law, its classical statements refer to global behaviour of processes between equilibrium states, but not between non-equilibrium states, and entropy is not well defined out of equilibrium, in such a way that it does not provide, for the moment, a clear-cut response to the concept of temperature. However, these two fundamental laws, though in a more restricted form than in equilibrium, still indicate the most basic features of non-equilibrium temperature. These are the fact that heat flows from higher to lower values of temperature and that a net zero heat balance between some degrees of freedom in two systems is related to the equality of the effective temperature of those degrees of freedom in both systems.

We have outlined three usual kinds of definitions of temperature. The first one contains the concept of entropy or of entropy flux. In our opinion, it is the most fundamental level of enquiry, but it has the drawback that entropy is not clearly defined in non-equilibrium situations. Thus, it seems that in this perspective both entropy and temperature should be studied simultaneously. The belief that temperature is a more primitive concept than entropy and which is clearly defined, whereas entropy is a more problematic quantity, is not completely realistic, because, as has been commented in the previous paragraphs, the ideas of zeroth and second laws must be reformulated in non-equilibrium situations.

Second, we have referred to definitions based on extrapolations of macroscopic equilibrium equations of state. For example, those for internal energy, pressure or

Table B. General overview of the definitions of non-equilibrium effective temperatures.

Definitions from fundamental laws (zeroth and second laws)

Zeroth law: empirical temperature	Problem: temperature depends on interaction between thermometer and system
	Use: contact temperature
Carnot theorem	Problem: heat reservoirs are assumed to be equilibrium systems

Definitions containing entropy or entropy flux

Gibbs relation	Problem: entropy is not clearly defined out of equilibrium
	Use: extended thermodynamics, rational thermodynamics
Entropy flux	Problem: entropy flux is not clearly defined out of equilibrium
	Use: coldness, radiation

Effective definitions from macroscopic quantities

Equations of state: internal energy, magnetization, etc	Problem: different reference quantities may lead to different temperatures
Transport quantities: electrical conductivity	Problem: different reference quantities may lead to different temperatures
	Use: glasses, amorphous semiconductors under electric fields
Einstein relation	Problem: possible superposition of non-equilibrium effects coming from temperature and from chemical potential
	Use: granular matter, sheared suspensions

Semi-microscopic or microscopic definitions

Fluctuation theory	Problem: non-equilibrium effects may arise either in temperature itself as in non-linear corrections to the response functions
	Use: glasses
Fluctuation–dissipation relations	Problem: non-equilibrium corrections may be attributed either to non-equilibrium temperature or to a non-linear generalization of the fluctuation–dissipation theorem
	Use: glasses, sheared fluids
Kinetic theory	Problem: average kinetic energy is always defined, even in situations where temperature does not have a physical meaning
	Use: kinetic theory, computer simulations
Statistical mechanics	Problem: distribution functions out of equilibrium are scarcely known in the non-linear regime; non-linear effects may be attributed either to a non-equilibrium temperature or, for instance, to higher-order moments

magnetization (or their derived quantities such as compressibility or magnetic susceptibility) or of transport coefficients (e.g. thermal or electrical conductivity) or relations amongst them (such as, for instance, the Einstein relation between diffusion coefficient and mobility). From this perspective, one defines some effective temperature T_{eff}, which depends both on room temperature T and some external field X (electric field, velocity gradient, temperature gradient, shaking intensity and so on) in such a way that the observed values of the corresponding quantities are given by the equilibrium equations of state (or transport quantities) with T_{eff} replacing T. For instance, one assumes that the internal energy U (or some other quantity) out of equilibrium may be written as $U(T, H, X) = U_{\text{eq}}(T_{\text{eff}}, H)$ with $T_{\text{eff}}(T, X)$. If such a relation is satisfied, the effective temperature has a practical relevance. In order for T_{eff} to be consistent as a true temperature from a practical point of view, three conditions are necessary: (i) thermal equilibrium between two analogous systems requires the equality of T_{eff} in both of them; (ii) heat flows from higher values of T_{eff} to lower values of T_{eff}; and (iii) it would be necessary that all the different variables yield the same effective temperature. This last condition is convenient if the fundamental thermodynamic equation remains the same out of equilibrium as in equilibrium; if this is not satisfied, this is an indication that the form of the fundamental equation for the entropy or the free energy must be generalized

somehow, but it cannot be always expected because, as has been said, different degrees of freedom have in general different effective temperatures. The problem with this approach is that it is not clear that the equations of state must retain their equilibrium form in non-equilibrium situations. Thus, it could, for example, be that $U(T, H, X)$ is given as $U(T, H, X) = U_{eq}(T, H) + \Delta U(T, H)X^2 \neq U_{eq}(T_{eff}, H)$, i.e. that the non-equilibrium parameter X cannot be incorporated exclusively through an effective temperature.

The third perspective relies on semi-microscopic or microscopic grounds. From the semi-microscopic point of view, one may be interested in the second moments of fluctuations of some quantities or, in greater detail, on the fluctuation–dissipation theorem relating the time-correlation function of some quantities with their respective response functions. From a more microscopic point of view, one could have the whole (exact or approximate) non-equilibrium distribution function, obtained either experimentally, or as the solution of some kinetic equation, or from information-theoretical methods. The problem in this case is that an arbitrary distribution function does not give by itself any indication concerning temperature, in contrast to the equilibrium distribution functions, where temperature plays a very precise role. Information-theoretic methods may be useful to identify temperature (or quasi-temperature) through non-equilibrium Lagrange multipliers conjugated to the energy, whereas in usual kinetic theory one simply identifies temperature with the average translational kinetic energy.

Here, we have proposed a limited but explicit version of a possible non-equilibrium entropy including second-order corrections in some unspecified non-equilibrium variable (fluxes, gradients, moments of the distribution function, microstructural variables, etc), which is helpful in obtaining expressions for several definitions of absolute temperature in non-equilibrium steady states. This tentative proposal aims to illustrate some possible connections between different definitions of temperature, and to critically assess the mutual consistency of these approaches. It turns out, in fact, that many of the proposals are only approximations and cannot be considered as rigorous definitions of non-equilibrium temperature, in spite of their possible relevance in their respective fields. We have pointed out that the derivative of such generalized non-equilibrium entropy, $(\partial S/\partial U)_{V,N}$ is not equal to the reciprocal of the local-equilibrium temperature. We have emphasized that, whereas the local-equilibrium temperature T retains its meaning as the measure of the average translational kinetic energy in non-equilibrium states of ideal gases, it is the non-equilibrium temperature θ rather than the local equilibrium T, the temperature which is related to the disordered part of the internal energy, and which acts as a potential for heat transfer in non-equilibrium situations. Furthermore, we have obtained the relation between several different effective temperatures and the temperature obtained from the entropy. For instance, in this setting one could have a non-equilibrium temperature (4.2) obtained from entropy considerations which would be different from temperature (5.66) defined from the second moments of fluctuations or from temperature (5.71) based on the extrapolation of Einstein's relation. Since in several situations the relation between effective temperatures and the absolute temperature is monotonous, it is also logical that they may be used as an indication of the direction in which heat will flow. Also we have examined some specific examples, which could be amenable to dynamic computer simulations and helpful in deciding which of the several temperatures is measured by a given thermometer.

Some points to be emphasized are the following.

(1) Physical interpretations of the several temperatures and their relation to experimental probes and to their mutual relation in non-equilibrium steady states are needed. Assigning a temperature to each degree of freedom would be equivalent to a fully microscopic description of the system. From a thermodynamic point of view, one would expect that this distribution of temperatures depends on a few macroscopic parameters (related both to classical

variables and to some parameters specifying the fluxes or some other relevant non-equilibrium parameters).

(2) Non-equilibrium effective temperatures are usually expressed as a local-equilibrium temperature plus some non-equilibrium corrections. It is necessary to characterize the equilibrium state to which the local-equilibrium temperature is referred. Indeed, in the non-linear regime it is important to specify which kind of projection from the non-equilibrium state to the equilibrium space is carried out. For instance, projections at constant energy, at constant entropy, constant temperature and so on, may relate a given non-equilibrium state to different equilibrium states. Of course, if the system is near equilibrium, the difference between these different states will be negligible, but not if the system is far enough from equilibrium. This may be important, for example, in microscopic approaches based on projection operator techniques.

(3) More attention should be paid to the analysis of non-linear relations (e.g. fluctuation–dissipation theorem, Einstein relation, equations of state, etc) in order to discriminate those non-equilibrium non-linear contributions coming from a non-equilibrium temperature, from those of other origins (for example, dynamical origin).

(4) There is much interest in studying, from a computational point of view, heat transport in lattices and gases. In such works the usual kinetic definition for the temperature is always assumed. It could be of interest to carry out more detailed studies by taking into account the analysis of configurational temperatures, as defined in other fields, in order to understand how kinetic temperature and configurational temperatures (which are usually different in non-equilibrium situations) contribute to heat transport. Another situation that we have not examined, but that may be of much interest for the microscopic understanding of temperature, is the thermodynamics of chaotic dynamical systems (Beck and Schlögl 1993, Gaspard and Dorfman 1995, Berdichevsky 1997, Gaspard 1998, Hoover 1999, Cohen and Rondoni 2002).

In summary, there is at present a burst of activity in situations where the meaning of temperature is not yet well established, as is the case in glasses, granular media, nuclear collisions, mesoscopic systems, systems under high electric fields or temperature gradients. Also, there are new algorithms for the calculation of temperature, and much activity on molecular dynamics simulations of non-equilibrium systems. Thus, the seemingly familiar concept of temperature turns out to be in the centre of lively practical and theoretical discussions, both from applied and fundamental perspectives.

Acknowledgments

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