

Chapter 2

Non-equilibrium Temperature and Entropy in Flowing Ideal Gases: Maximum-Entropy Approach

The aim of this chapter and of the three subsequent ones is to provide a microscopic basis for the macroscopic thermodynamic description of flowing systems that has been presented in Chap. 1. Indeed, a close interaction between macroscopic and microscopic approaches is necessary and convenient. On the one hand, it gives explicit expressions for the quantities appearing in the macroscopic description and allows understanding the peculiar characteristics of the several different systems. On the other hand, the macroscopic approach outlines some common features which should be shared by very different physical systems. Usually, the microscopic analysis of non-equilibrium systems is focused on the calculation of transport coefficients; here, we pay particular attention to the non-equilibrium contributions to the entropy and the free energy.

The systems we have chosen for this analysis are ideal gases, phonons, real gases, and polymer solutions. Although from the microscopic point of view their study is rather different, we will underline their common aspects concerning the non-equilibrium contributions to the entropy and to the evolution equation for the viscous pressure tensor.

We explore the thermodynamics of ideal gases in shear flows from two different microscopic points of view: information theory and kinetic theory. It will be seen that the entropy exhibits an influence on the viscous pressure tensor or on the velocity gradient, thus leading to a modification with respect to the local equilibrium entropy, as postulated from a macroscopic point of view in Chap. 1. The expressions in this chapter allow us to go beyond the second order in contributions of the viscous pressure tensor to the non-equilibrium entropy, temperature and chemical potential.

Some of the expressions studied here are useful to discuss in detail several definitions of temperature out of equilibrium, and their respective relations as well as their connection with different physical variables. This is a fundamental topic in non-equilibrium statistical physics beyond the local-equilibrium approximation, and therefore we pay to it a detailed attention.

2.1 Review of Some Basic Concepts

The basic quantity in the microscopic description of ideal monatomic gases is the velocity distribution function $f(\mathbf{r}, \mathbf{c}, t)$, which accounts for the number of particles between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ with velocity between \mathbf{c} and $\mathbf{c} + d\mathbf{c}$ at time t . The classical hydrodynamic description is based on the first five moments of the velocity distribution function, namely, the mass density ρ , the mean velocity \mathbf{v} , and the internal energy u per unit mass, which are, respectively, defined in terms of the distribution function as

$$\rho(\mathbf{r}, t) = \int m f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c}, \quad (2.1)$$

$$\rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) = \int m \mathbf{c} f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c}, \quad (2.2)$$

$$\rho(\mathbf{r}, t) u(\mathbf{r}, t) = \int \frac{1}{2} m \mathbf{C} \cdot \mathbf{C} f(\mathbf{r}, \mathbf{c}, t) d\mathbf{c}, \quad (2.3)$$

where $\mathbf{C} = \mathbf{c} - \mathbf{v}$ is the relative velocity of the molecules with respect to the mean motion of the gas and m the mass of the particles. As is well known, these quantities are related to general conservation laws of mass, momentum and energy. Their respective evolution equations are

$$\rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{P}, \quad (2.4)$$

$$\rho \dot{\mathbf{v}} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (2.5)$$

$$\rho \dot{u} = -\nabla \cdot \mathbf{q} - \mathbf{P} : \nabla \mathbf{v}. \quad (2.6)$$

Here, \mathbf{v} is the reciprocal of the mass density ρ , i.e. the specific volume, \mathbf{P} the pressure tensor and \mathbf{q} the heat flux, which are given in microscopic terms by

$$\mathbf{P} = \int m \mathbf{C} \mathbf{C} f d\mathbf{c}, \quad (2.7)$$

$$\mathbf{q} = \int \frac{1}{2} m \mathbf{C}^2 \mathbf{C} f d\mathbf{c}. \quad (2.8)$$

Since, at equilibrium, f is an isotropic function of \mathbf{C} , the pressure tensor reduces in equilibrium to $\mathbf{P} = p \mathbf{U}$, with \mathbf{U} the identity tensor and p the equilibrium pressure, given by

$$p = \frac{1}{3} \int m \mathbf{C}^2 f d\mathbf{c}. \quad (2.9)$$

Thus, for ideal gases $\text{Tr}\mathbf{P}^v = \text{Tr}\mathbf{P} - 3p = 0$. It is found from the definition (2.3) of the internal energy that $p = \frac{2}{3}\rho u$. The macroscopic thermal equation of state for ideal gases, $p = nk_B T$, leads to define the absolute equilibrium temperature as:

$$p = \frac{2}{3}\rho u = nk_B T, \quad (2.10)$$

with n the number of particles per unit volume and k_B the Boltzmann constant. Note that (2.10) is a mathematical definition which is very appealing and useful from a microscopic perspective and in computer simulations, because kinetic energy has a clear physical meaning and it is easy to evaluate in molecular dynamics calculations. However, this definition does not bear direct relation to the measurement of temperature in non-equilibrium situations. Thus, the simplicity of the definition (2.10) should not mask the fact that the understanding of temperature in non-equilibrium situations is still a conceptual challenge, as we will underline in Sect. 2.4.

The main challenge in the microscopic description of non-equilibrium situations is to find the non-equilibrium distribution function f . Here, we will obtain it from information theory to explore in a simple way entropy and temperature in non-equilibrium situations.

2.2 Information Theory: General Formalism

The success of the Gibbsian ensemble method in equilibrium statistical mechanics has fostered the search for an extension for it in non-equilibrium situations. Of course, the latter situations are much more complicated than the equilibrium situations; indeed, it is required to determine not only the equations of state (which are often taken to be those of local-equilibrium) but also the temporal and spatial dependence of measurable properties, to calculate transport coefficients and to describe dissipation.

Several methods have been devised with this aim. One of the most appealing is a non-equilibrium statistical operator method based on the maximum entropy approach (Grandy 1987; Levine and Tribus 1979; Zubarev et al. 1997; Luzzi and Vasconcellos 1990; Luzzi et al. 2001, 2002). Another is more inspired by a canonical extension of the moment method in the kinetic theory of gases (Eu 1998, 2002). We will begin this analysis by using the first method.

The maximum entropy method consists in the maximization, in the context of information theory, of Gibbs statistical entropy, subjected to constraints on the average values of a given set of variables. This principle states that the probability distribution function should be taken to maximize the average missing information of the system, subjected to the constraints corresponding to the available information. In this way, the amount of spurious information attributed to the system is minimized. On several occasions, this method has been criticized as being unduly subjective. In our view, this is not a justified criticism. Indeed, the method will give sound physical results only when the choice of variables on which we focus our attention

coincides with the truly relevant variables in the context of the experiments we want to describe, but not when we arbitrarily fix the choice of the variables. Thus, one of the open problems in this field is the choice of which variables are needed to describe the system. In equilibrium these are the conserved variables, which are microscopic constants of motion, but in non-equilibrium the problem is much more complicated, because it involves, in principle, a host of non-conserved variables.

Here, we will focus our attention on non-equilibrium steady states, which are the most natural and simplest non-equilibrium generalization of equilibrium states. The essential difference between them is the presence of non-vanishing fluxes of energy, mass, momentum and charge in non-equilibrium systems. Note, also, that the assumption of maximum entropy in steady states is not in contradiction with the principle that entropy is maximum at equilibrium, since both statements refer to different sets of constraints. The maximum 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. Indeed, the latter one is submitted to a wider set of constraints than the equilibrium state, because the fluxes, or other relevant non-equilibrium variables, must be also specified. Each restriction reduces the number of accessible microstates and, therefore, it lowers also the value of entropy.

To be specific, let us present the essential ideas of the method for a system of N particles characterized by their positions and momenta, $\mu' = \{\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N\}$. Assume that we know the local mean values $\langle A_i \rangle$ of a set of extensive observables $A_i(\mu')$. The aim is to obtain the probability density $f_N(\mu')$ which maximizes the information in the system compatible with the measured quantities. In other words, one calculates the probability density which maximizes the global entropy S defined by

$$S = -k_B(h^{3N}N!)^{-1} \int f_N(\mu') \ln f_N(\mu') d\Gamma_N, \quad (2.11)$$

and subject to the constraints expressing the known values of the controlled variables, namely

$$(h^{3N}N!)^{-1} \int f_N(\mu') A_i(\mu') d\Gamma_N = \langle A_i \rangle. \quad (2.12)$$

Here, $d\Gamma_N = d\mathbf{r}_1 d\mathbf{p}_1 \dots d\mathbf{r}_N d\mathbf{p}_N$ is the volume element in the phase space, and h and k_B are, respectively, the Planck and Boltzmann constants.

To achieve the maximization of S subject to constraints (2.12), one has to maximize the quantity

$$-k_B \int \left[f_N \ln f_N + f_N \lambda_0 + f_N \sum_i \lambda_i(\mathbf{r}) \cdot A_i(\mu') \right] d\Gamma_N, \quad (2.13)$$

where the $\lambda_i(\mathbf{r})$ are the Lagrange multipliers corresponding to the quantities $A_i(\mathbf{r})$. The dot between λ_i and A_i indicates a scalar product. In equilibrium these quantities are the internal energy and the particle density. Out of equilibrium, additional

restrictions must be imposed. In extended irreversible thermodynamics, these further restrictions are the fluxes across the system. For instance, a simple non-equilibrium situation would consist of a closed system with internal energy U subjected to a viscous pressure tensor \mathbf{P}^v ; in this case, the constraints are U and \mathbf{P}^v . Finally, λ_0 is the Lagrange multiplier accounting for normalization. In what follows, subscript i starts with $i = 1$.

Expression (2.13) is an extremum under the condition that f_N satisfies

$$\frac{\partial}{\partial f_N} \left[f_N \ln f_N + f_N \lambda_0 + f_N \sum_i \lambda_i(\mathbf{r}) \cdot \mathbf{A}_i(\mu') \right] = 0. \quad (2.14)$$

This yields a generalised canonical distribution of the form

$$f_N = Z^{-1} \exp \left[- \sum_i \lambda_i(\mathbf{r}) \cdot \mathbf{A}_i(\mu') \right], \quad (2.15)$$

where Z , related to λ_0 by $\ln Z = 1 + \lambda_0$, is a generalised partition function that follows from the normalization condition for f_N , namely

$$Z = (h^{3N} N!)^{-1} \int \exp \left[- \sum_i \lambda_i(\mathbf{r}) \cdot \mathbf{A}_i(\mu') \right] d\Gamma_N. \quad (2.16)$$

The explicit expressions of the Lagrange multipliers in terms of the average values of the basic variables are derived from constraints (2.12). In view of the form (2.16) of the partition function, the constraints may be written in the compact form

$$-\frac{\partial \ln Z}{\partial \lambda_i} = \langle \mathbf{A}_i \rangle, \quad (2.17)$$

as follows from definition (2.16) of Z and relations (2.12). These are the equations of state corresponding to this description.

Introduction of the distribution density (2.13) in the definition (2.11) for the entropy yields

$$S(\mathbf{r}) = k_B \left[\ln Z + \sum_i \lambda_i \cdot \langle \mathbf{A}_i \rangle \right]. \quad (2.18)$$

The differential of S obtained from (2.18) is

$$dS = k_B \left[d \ln Z + \sum_i \langle \mathbf{A}_i \rangle \cdot d\lambda_i + \sum_i \lambda_i \cdot d\langle \mathbf{A}_i \rangle \right] = k_B \sum_i \lambda_i \cdot d\langle \mathbf{A}_i \rangle. \quad (2.19)$$

The second equality in (2.19) follows from relation (2.17), which cancels the contributions from $d \ln Z$ with those coming from $\sum_i \langle \mathbf{A}_i \rangle \cdot d\lambda_i$.

Comparison of (2.19) with the macroscopic Gibbs equation yields a general interpretation for the Lagrange multipliers in physical terms. For instance, in an

equilibrium system with a given average value of the internal energy, (2.15) reduces to

$$f = Z^{-1} \exp \left[- \sum_i \lambda_1 \mathcal{H} \right], \quad (2.20)$$

with \mathcal{H} the Hamiltonian of the system. The corresponding differential form (2.19) is then

$$dS = k_B \lambda_1 dU, \quad (2.21)$$

which, when compared with the macroscopic Gibbs equation $dS = T^{-1}dU$ yields $\lambda_1 = (k_B T)^{-1}$, with T the absolute temperature, and (2.20) is simply the well known canonical distribution function. If one imposes as a further restriction the average value of the particle number, (2.15) takes the form

$$f = Z^{-1} \exp[-\lambda_1 \mathcal{H} - \lambda_2 \mathcal{N}], \quad (2.22)$$

with \mathcal{N} the particle-number operator. Equating the differential of the entropy in terms of the Lagrange multipliers with the macroscopic Gibbs equation one obtains

$$dS = k_B \lambda_1 dU + k_B \lambda_2 dN = T^{-1}dU - \mu T^{-1}dN, \quad (2.23)$$

which corroborates the previous result for λ_1 and yields $\lambda_2 = -\mu(k_B T)^{-1}$ with μ the chemical potential. With these identifications, (2.22) is the macrocanonical probability distribution function.

Out of equilibrium, when new non-equilibrium variables are included in the description, the physical meaning of the Lagrange multipliers is, in general, unknown, because of the lack of a Gibbs equation in such situations. Extended irreversible thermodynamics gives a generalised Gibbs equation which allows such a physical interpretation of the Lagrange multipliers conjugated to the fluxes, as will be emphasized below.

In some cases it is important to have information on the fluctuations of the basic variables with respect to their average values. The expression for the second moments of the fluctuations of the observables $A_i(\mu')$ around their average values is straightforwardly derived in terms of Z by differentiation of (2.16) and is given by

$$\left\langle (A_i(\mu') - \langle A_i \rangle) (A_j(\mu') - \langle A_j \rangle) \right\rangle = \frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j}. \quad (2.24)$$

It must be emphasized that the generalised canonical distribution function (2.11) is not the exact distribution function which would be obtained from first principles (for instance, starting from the Liouville equation). Indeed, it does not satisfy the Liouville equation, it only gives the correct averages and the fluctuations of the basic variables considered in the description, but not for the other variables, and it does not describe the dissipation in the steady state. However, it is the basis of

the thermodynamics in the space of the chosen variables, in the approach known as informational statistical thermodynamics, which also deals with the transport equations, for whose analysis more information than that given in (2.16) is needed (Luzzi and Vasconcellos 1990; Luzzi et al. 2001, 2002).

2.3 Information Analysis of an Ideal Gas Under Viscous Pressure

Now, we apply these general ideas to a flowing ideal gas of N particles in a volume V under the restrictions on the internal energy U and the viscous pressure tensor \mathbf{P}^v (Bidar et al. 1996; Jou and Criado-Sancho 2001). Of course, the quality of the results in the description of actual experiments will depend on how the choice of these variables faithfully grasps the essential physical features of the system. It has been shown in Chap. 1 that this choice is satisfactory for viscoelastic fluids, which cover a wide and rich phenomenology on which we focus our attention.

Since the particles are independent, we will resort to the one-particle distribution function f . To obtain the generalised canonical distribution function f , we maximize the entropy

$$S = -k_B V \int f \ln f d\mathbf{C} \quad (2.25)$$

under the constraints (2.1), (2.3) and (2.7)

$$\int f d\mathbf{C} = \frac{N}{V} = n, \quad \int m \mathbf{C} \mathbf{C} f d\mathbf{C} = \mathbf{P}, \quad \int \frac{1}{2} m \mathbf{C}^2 f d\mathbf{C} = \frac{U}{V} = \rho u, \quad (2.26)$$

\mathbf{C} being the relative velocity of the particles with respect to the mean (barycentric) velocity of the system and n the particle number density. Note that Eqs. (2.26) yield the result

$$U = \frac{1}{2} \text{Tr} V \mathbf{P}. \quad (2.27)$$

Note that the presence of a viscous pressure implies dissipation, in such a way that to keep constant internal energy the dissipated heat should be removed. This removal may be carried out locally, as in the molecular dynamics algorithms that will be examined in Chap. 4, or –more realistically– by means of a heat flow across the system; we do not include the heat flux in the constraints, for the sake of simplicity.

In order to take into account the restrictions associated with tensor \mathbf{P} we consider two options. The first one imposes Lagrange multipliers related to the internal energy and the component P_{12}^v of \mathbf{P} (Bidar et al. 1996) which is expected to be satisfactory enough when normal viscous pressure is small and P_{12}^v is the dominant viscous term, as in plane Couette or Poiseuille flows. As a second alternative (Jou and Criado-Sancho 2001) it is considered that measurable quantities are the energy

and all the components of \mathbf{P} , especially those from which the so-called shear flow material functions are defined as

$$\begin{aligned} P_{12}^v &= -\eta(\dot{\gamma})\dot{\gamma}, \\ N_1 &= P_{11}^v - P_{22}^v = -\Psi_1(\dot{\gamma})\dot{\gamma}^2, \\ N_2 &= P_{22}^v - P_{33}^v = -\Psi_2(\dot{\gamma})\dot{\gamma}^2, \end{aligned} \quad (2.28)$$

where $\Psi_1(\dot{\gamma})$ and $\Psi_2(\dot{\gamma})$ are the first and second normal stress coefficients, respectively, and $\eta(\dot{\gamma})$ the shear-rate dependent viscosity, and N_1 and N_2 are the viscous normal pressures, introduced in Sect. 1.1.

The distribution function (2.15) under these constraints can be written as

$$f = z^{-1} \exp \left\{ -\frac{1}{2} \left[\sum_i (\beta + 2\lambda_{ii}) m C_i^2 + \sum_i \sum_{j(>i)} 2\lambda_{ij} m C_i C_j \right] \right\}, \quad (2.29)$$

or in the more compact form

$$f = z^{-1} \exp \left[-\frac{1}{2} \mathbf{M} : m \mathbf{C} \mathbf{C} \right], \quad (2.30)$$

with \mathbf{M} the symmetric tensor given by

$$\mathbf{M} = \begin{pmatrix} \beta + 2\lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \beta + 2\lambda_{22} & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \beta + 2\lambda_{33} \end{pmatrix}. \quad (2.31)$$

When U and P_{12}^v are taken as the unique independent variables, the only non-vanishing Lagrange coefficients will be β and λ_{12} .

In the case that the average values of U , P_{12}^v , $P_{11}^v - P_{22}^v$ and $P_{22}^v - P_{33}^v$ are imposed as constraints, the expression (2.30) remains valid with \mathbf{M} given by

$$\mathbf{M} = \begin{pmatrix} \beta + 2\lambda_1 & \lambda_{12} & 0 \\ \lambda_{12} & \beta - 2\lambda_1 + 2\lambda_2 & 0 \\ 0 & 0 & \beta - 2\lambda_2 \end{pmatrix}, \quad (2.32)$$

where the parameters β , λ_{12} , λ_1 and λ_2 are the Lagrange multipliers conjugated to the internal energy, the shear viscous pressure P_{12}^v , and the first and second normal pressures N_1 and N_2 respectively.

The matrix \mathbf{M} (2.31) can be expressed in the form

$$\mathbf{M} = \beta \mathbf{U} + \boldsymbol{\lambda} \quad (2.33)$$

with \mathbf{U} the unity matrix. Note that (2.32) could also be written as $\mathbf{M} = (k_B T)^{-1} \mathbf{U} + \boldsymbol{\lambda}'$, with the component of $\boldsymbol{\lambda}'$ defined accordingly.

The partition function related to the normalization of f is given by

$$z = V \int \exp \left[-\frac{1}{2} m \mathbf{M} : \mathbf{C} \mathbf{C} \right] d\mathbf{C}, \quad (2.34)$$

which after integration turns out to be

$$z = \frac{(2\pi)^{3/2} V}{m^{3/2} N |\mathbf{M}|^{1/2}}, \quad (2.35)$$

with $|\mathbf{M}|$ the determinant of the matrix \mathbf{M} . A similar result has been obtained by Farhat and Eu (1998), who also included normal-pressure effects in a non-equilibrium ensemble method proposed by Eu (1998). However, our aims are different from those of these authors, because we are interested in obtaining explicit expressions for the entropy, temperature and chemical potential, and in identifying explicitly the Lagrange multipliers conjugated to the non-equilibrium variables N_1 , N_2 and P_{12}^v .

The first aim is the interpretation of the tensor λ in terms of \mathbf{P}^v . To achieve this goal, note that from the Gaussian character of (2.30), which implies $\langle \mathbf{C} \mathbf{C} \rangle = m^{-1} \mathbf{M}^{-1}$, one has

$$\mathbf{P} = n \langle m \mathbf{C} \mathbf{C} \rangle = n \mathbf{M}^{-1}. \quad (2.36)$$

We will write the tensor \mathbf{P} as

$$\mathbf{P} = n \beta^{-1} \mathbf{U} + \mathbf{P}^v, \quad (2.37)$$

with \mathbf{P}^v the viscous pressure tensor. In fact, it is usually assumed that $\mathbf{P} = n k_B T \mathbf{U} + \mathbf{P}^v$ rather than (2.37) because $\beta \neq (k_B T)^{-1}$ is usually ignored in literature. However, the splitting (2.37) is mathematically more convenient and natural in the present context (Camacho and Jou 1995; Criado-Sancho et al. 1994, 1998). Using (2.36) and (2.37) it immediately follows that

$$\mathbf{M} = \beta \left[\mathbf{U} + \sum_{i=1}^{\infty} (-\beta n^{-1} \mathbf{P}^v)^i \right], \quad (2.38)$$

where the series expansion for $(1+x)^{-1}$ has been used.

From the latter result, the Lagrange multipliers λ_{12} , λ_1 and λ_2 may be written in terms of β , n and \mathbf{P}^v . Comparing (2.38) and (2.33) it follows that

$$\lambda = \beta \sum_{i=1}^{\infty} (-\beta n^{-1} \mathbf{P}^v)^i. \quad (2.39)$$

This expression gives the Lagrange multipliers in terms of the viscous pressure in any order in \mathbf{P}^v .

A physical interpretation of the Lagrange multipliers can be given from the comparison between expression (2.19), rewritten as

$$dS = k_B \beta dU + k_B \sum_i \lambda_i \cdot \langle d\mathbf{A}_i \rangle, \quad (2.40)$$

and the non-equilibrium entropy (1.29) in the presence of a shear viscous pressure. If we are only dealing with the Lagrange multipliers β and λ_{12} the Gibbs Eq. (1.29) takes the form

$$dS = \theta^{-1} dU - \frac{\tau P_{12}^v}{\eta T} d(V P_{12}^v), \quad (2.41)$$

with θ a generalised non-equilibrium temperature, τ the relaxation time associated to P_{12}^v and η the coefficient of shear viscosity. Comparison of (2.40) and (2.41) leads to

$$\beta = \frac{1}{k_B \theta}, \quad \lambda_{12} = -\frac{\tau P_{12}^v}{\eta k_B T} = \frac{\tau \dot{\gamma}}{k_B T}, \quad (2.42)$$

with $\dot{\gamma}$ the shear rate. Note that (2.41) is valid for small values of P_{12}^v , i.e. the identification proposed here is strictly valid only in this limit. In Sect. 2.3 we will discuss in detail the differences between T and θ or other possible definitions of temperature.

When we use (2.42) and only the first term of the expansion (2.39) is taken into account one has

$$\boldsymbol{\lambda} \approx -\beta^2 n^{-1} \mathbf{P}^v = -\frac{1}{n k_B^2 \theta^2} \mathbf{P}^v, \quad (2.43)$$

Note that near equilibrium it is known from kinetic theory that the viscosity coefficient $\eta = n k_B T \tau$, with τ the collision time and therefore (2.43) may be extrapolated from equilibrium yielding

$$\boldsymbol{\lambda} \approx -\frac{\tau}{k_B \theta \eta} \mathbf{P}^v. \quad (2.44)$$

in agreement with the second equality in (2.42). This is the expression for $\boldsymbol{\lambda}$ in the usual formulation of EIT, when only quadratic terms in \mathbf{P}^v are included in the non-equilibrium entropy. The present analysis shows how to incorporate terms at any order in \mathbf{P}^v in a more general non-equilibrium entropy.

2.3.1 *Non-equilibrium Entropy and Chemical Potential: General Formalism*

The fundamental assumption underlying information theory establishes that in a physical situation described in terms of a complete set of macroscopic restrictions, the entropy takes its maximum value consistent with such restrictions. This does

not imply any subjectivity or arbitrariness in the choice of the restrictions: the description of the system will lead to satisfactory results only when the choice of the restrictions corresponds to the suitable information required to describe the actual physical state of the system. From the Eqs. (2.25), (2.30) and (2.36), the entropy may be written explicitly as

$$\frac{S}{Vk_B} = n \ln z + \frac{1}{2} \mathbf{M} : \mathbf{P}. \quad (2.45)$$

In order to stress the role played by the viscous pressure tensor on the non-equilibrium entropy, an alternative expression to (2.45) in terms of \mathbf{P}^v can be derived using the Eqs. (2.35–2.37) and the relation

$$\frac{1}{2} \mathbf{M} : \mathbf{P} = \beta \frac{U}{V} + \frac{n}{2} \text{Tr}[\mathbf{U} - \beta n^{-1} \mathbf{P}]. \quad (2.46)$$

From (2.45) and (2.46) we obtain for the entropy (2.42) the explicit form

$$\begin{aligned} \frac{S}{Nk_B} = & \frac{3}{2} \left[\ln \left(\frac{2\pi}{m} \right) - 1 \right] + \ln \left(\frac{V}{N} \right) + \beta \frac{U}{N} - \frac{3}{2} \ln \beta \\ & + \frac{1}{2} [\ln |\mathbf{U} + \beta n^{-1} \mathbf{P}^v| - \text{Tr}(\beta n^{-1} \mathbf{P}^v)]. \end{aligned} \quad (2.47)$$

One equivalent but more compact expression for the entropy can be written by using (2.35) and (2.36) together with (2.45)

$$\frac{S}{Nk_B} = \frac{3}{2} \left[\ln \left(\frac{2\pi}{m} \right) + 1 \right] + \ln \left(\frac{V}{N} \right) - \frac{1}{2} \ln |\mathbf{M}|. \quad (2.48)$$

When a N -particle distribution function f_N is introduced instead of the one-particle distribution f previously considered, and when we deal with a general system whose energy and extensive observables are given by $\{U, \mathbf{A}_i\}$ and their conjugated Lagrange multipliers are $\{\beta, \boldsymbol{\lambda}_i\}$, the distribution function that fulfils the requirements of maximum entropy has the form

$$f_N = Z_N^{-1} \exp \left[-\beta U - \sum_i \boldsymbol{\lambda}_i \cdot \mathbf{A}_i \right], \quad (2.49)$$

where Z_N is the N -particles partition function.

According to (2.18), the expression for the total entropy is given by

$$S = k_B \beta U + k_B \sum_i \boldsymbol{\lambda}_i \cdot \mathbf{A}_i + k_B \ln Z_N. \quad (2.50)$$

where \mathbf{A}_i refer to observables different from U .

Expression (2.50) may be compared with the macroscopic Gibbs equation

$$S = \frac{1}{\theta} U + \frac{\pi}{\theta} V - \frac{1}{\theta} \mu N - \frac{1}{\theta} \sum_i \mathbf{X}_i \cdot \mathbf{A}_i, \quad (2.51)$$

with π the generalized pressure defined by $\pi/\theta = (\partial S/\partial V)_{U,V\mathbf{P}^v}$, whose physical meaning has been examined in (Domínguez and Jou 1995), μ the chemical potential and $\mathbf{X}_i \equiv -k_B \theta \lambda_i$.

By comparing (2.50) and (2.51) it follows that

$$\frac{\mu}{\theta} - \frac{\pi}{\theta} \frac{V}{N} = -\frac{k_B}{N} \ln Z_N, \quad (2.52)$$

which generalizes the equilibrium relation

$$\frac{\mu_{\text{eq}}}{T} - \frac{p}{T} \frac{V}{N} = -\frac{k_B}{N} \ln (Z_N)_{\text{eq}}. \quad (2.53)$$

It turns out from (2.47) or (2.48) that

$$\frac{\pi}{\theta} = \left(\frac{\partial S}{\partial V} \right)_{U,V\mathbf{P}^v} = nk_B = \frac{p}{T}. \quad (2.54)$$

Thus, in spite of the fact that T and p are changed, respectively, to θ and π , the relation between T and p , namely $p/T = nk_B$ is the same as that between θ and π , since $\pi/\theta = nk_B$. This result was also found independently (Farhat and Eu 1998). Combining (2.54) with (2.52) one has for the chemical potential

$$\frac{\mu}{\theta} - \frac{\mu_{\text{eq}}}{T} = -\frac{k_B}{N} \ln \frac{Z_N}{(Z_N)_{\text{eq}}}. \quad (2.55)$$

Taking into account that $Z_N = z^N/N!$ together with the explicit expression (2.35) for z , (2.55) is rewritten as

$$\frac{\mu}{\theta} - \frac{\mu_{\text{eq}}}{T} = \frac{1}{2} k_B \ln \frac{|\mathbf{M}|}{|\mathbf{M}|_{\text{eq}}}. \quad (2.56)$$

Since $|\mathbf{M}|$ depends on the whole pressure tensor [cf. Eq. (2.36)], the chemical potential depends also on all the components of the pressure tensor. The chemical potential (2.56) may be useful to describe some shear-induced effects (for instance, modification of the chemical composition of a mixture of gases under shear, or shift of the spinodal consolution line), which will be analysed in Chaps. 6–10.

2.3.2 Analysis of Plane Couette Flow: Pure Shear Effects

In this section we will obtain explicit expressions for the non-equilibrium entropy (2.48) in terms of U , P_{12} , $P_{11} - P_{22} \equiv N_1$ and $P_{22} - P_{33} \equiv N_2$. First of all we note that expression (2.48) may be written as

$$\frac{S - S_{\text{eq}}}{N k_B} = -\frac{1}{2} \ln \frac{|\mathbf{M}|}{|\mathbf{M}|_{\text{eq}}} = -\frac{1}{2} \ln [|\mathbf{M}| (k_B T)^3] \quad (2.57)$$

where we have used $\mathbf{M}_{\text{eq}} = (k_B T)^{-1} \mathbf{U}$ so that $|\mathbf{M}|_{\text{eq}} = (k_B T)^{-3}$.

For a system submitted to a fixed shear viscous pressure P_{12}^v , where normal effects are negligible, corresponding to a plane Couette flow with only β and λ_{12} as non-vanishing Lagrange multipliers, and taking into account (2.32) with $\lambda_1 = \lambda_2 = 0$, the determinant $|\mathbf{M}|$ adopts the form

$$|\mathbf{M}| = \beta^3 - \beta\lambda_{12}^2. \quad (2.58)$$

On the other hand, from Eqs. (2.17) and (2.35) it immediately follows that

$$\langle A_i \rangle = \frac{1}{2} \frac{\partial \ln |\mathbf{M}|}{\partial \lambda_i}, \quad (2.59)$$

and Eqs. (2.40), (2.41), (2.58) and (2.59) let us write

$$\frac{U}{V} = \frac{1}{2} \frac{\partial \ln |\mathbf{M}|}{\partial \beta} = \frac{3\beta^2 - \lambda_{12}^2}{2(\beta^3 - \beta\lambda_{12}^2)}, \quad P_{12}^v = \frac{1}{2} \frac{\partial \ln |\mathbf{M}|}{\partial \lambda_{12}} = -\frac{\lambda_{12}}{\beta^2 - \lambda_{12}^2}. \quad (2.60)$$

Note that near equilibrium, i.e. when $\lambda_{12} \rightarrow 0$, Eqs. (2.60) tend to $U/V = 3/(2\beta)$ and $\lambda_{12} = -\beta^2 P_{12}^v$, respectively. Thus, when $P_{12}^v = 0$ one recovers from (2.29) the standard Maxwell–Boltzmann distribution function. From (2.60) we obtain β and λ_{12} in terms of u and P_{12}^v as

$$\beta = \frac{1-y}{2[R^2 + (1-y)]} \frac{N}{U}, \quad \lambda_{12} = \frac{3R^2 + 2(1-y)}{2R[R^2 + (1-y)]} \frac{N}{U}, \quad (2.61)$$

where the following auxiliary functions have been introduced

$$R = VP_{12}^v/U, \quad y = (1 + 3R^2)^{1/2}, \quad (2.62)$$

which let us write

$$|\mathbf{M}| = \frac{1}{4} \frac{(y-1)^3}{R^2[R^2 - (y-1)]^2} \left(\frac{N}{U}\right)^3. \quad (2.63)$$

It easy to show that $\lim_{R \rightarrow 0} |\mathbf{M}| = \beta^3 = (k_B T)^{-3}$ as expected.

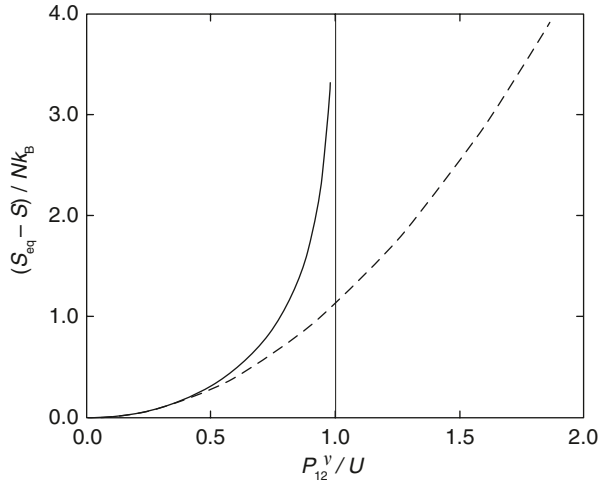
By using (2.57) together with (2.63) and recalling that $k_B T = \frac{2}{3}(U/N)$ the expression for the entropy can be written as

$$\frac{S_{\text{eq}} - S}{Nk_B} = -\frac{1}{2} \ln \frac{27R^2[R^2 - (y-1)]^2}{2(y-1)^3}, \quad (2.64)$$

where S_{eq} stands for the equilibrium value of the entropy.

The latter equation, a main result in this section, gives an explicit expression for a non-equilibrium entropy dependent on the shear stress, and which is not limited to second-order non-equilibrium contributions, thus providing a generalization of

Fig. 2.1 Non-equilibrium contribution to the entropy as a function of the ratio VP_{12}^v/U . The solid line corresponds to (2.64) whereas the dashed line corresponds to its second-order approximation in VP_{12}^v/U . (Bidar et al. (1997))



previous results on thermodynamics of fluids systems under shear viscous stress, restricted to second order in P_{12}^v . In Fig. 2.1, is plotted the entropy (2.64) and its second-order approximation in the viscous pressure.

It has been seen in (2.61) that although the present formalism yields the equation of state for τ/η , it does not give any information on τ . Indeed, we have already mentioned that the generalised canonical distribution function (2.13) only gives the thermodynamic quantities (entropy, equations of state) in the space of the selected variables, but not the dynamics nor the dissipation. Thus, τ must be obtained from a kinetic equation, whose formulation requires the full detail of the non-equilibrium statistical operator method (Zubarev et al. 1997; Luzzi and Vasconcellos 1990; Galvao et al. 1995; Luzzi et al. 2002). This is rather complicated, and we will not deal with it in this monograph, which concentrates on the thermodynamic aspects. Here, we will tentatively assume that τ does not depend on $\dot{\gamma}$ in order to explore the consequences of identification (2.61). When (2.61) is combined with (2.60), it yields for the dependence of the shear viscosity $\eta(\dot{\gamma})$ on the shear rate $\dot{\gamma}$

$$\eta(\dot{\gamma}) \equiv \frac{P_{12}^v}{\dot{\gamma}} = -\frac{3}{2}\eta_0 \frac{R^2[R^2 + (1 - y)]}{R^2 + (2/3)(1 - y)}. \quad (2.65)$$

Equation (2.65) describes a considerable reduction of the shear viscosity with increasing $\dot{\gamma}$, a phenomenon (shear thinning) which is experimentally well known. For low values of R , this expression tends to η_0 (the shear viscosity in the linear regime), whereas it tends to 0 when R tends to 1. Therefore, the viscous pressure varies in the range $0 < P_{12}^v < u$ when $\dot{\gamma}$ changes from 0 to ∞ . This limit may be understood from the kinetic interpretation of the pressure. Indeed, in kinetic theory one has $P_{12}^v = \langle mC_1C_2 \rangle$. Due to the inequality $C_1C_2 < \frac{1}{2}(C_1^2 + C_2^2)$ and $\rho u = \frac{1}{2}m(C_1^2 + C_2^2 + C_3^2)$, it follows that P_{12}^v must be less than or equal to the energy density.

Taking into account that the partition function for the N -particle system is $Z_N = z^N/N!$, the characteristic function $F(\beta, V, N, \lambda_{ij})$ which generalizes the usual free energy to the present non-equilibrium situation is

$$F = -\beta^{-1} \ln Z_N = -3B \left\{ F_{\text{eq}} - Nk_B T \ln \left[\left(\frac{27}{2} \right)^{1/2} B(B+1)^{1/2} \right] \right\}, \quad (2.66)$$

where B is the auxiliary function $B = R^2(y-1)^{-1} - 1$, with R and y given by (2.62).

Finally, we may also use the generalised partition function (2.35) to study the fluctuations around non-equilibrium steady states. The second moments of the fluctuations of u and P_{12}^v in a steady state with $|\mathbf{M}|$ given by (2.58) and (2.61) may be directly obtained from the well known relationships (2.24), which yield in this case

$$\langle \delta u \delta u \rangle = \frac{\partial^2 \ln z}{\partial \beta^2} = \frac{u^2}{2} [3(B+1)^2 + (1-y)^2], \quad (2.67a)$$

$$\langle \delta P_{12}^v \delta P_{12}^v \rangle = \frac{\partial^2 \ln z}{\partial \lambda_{12}^2} = u^2 [R^2 + (B+1)^2], \quad (2.67b)$$

$$\langle \delta u \delta P_{12}^v \rangle = \frac{\partial^2 \ln z}{\partial \beta \partial \lambda_{12}} = u^2 R(3+y+4B). \quad (2.67c)$$

These expressions may be of interest, for instance, in connection with the fluctuation-dissipation theorem in non-equilibrium steady states.

2.3.3 Plane Couette Flow: Shear and Normal Effects

In order to obtain explicit results when, instead of only the β and λ_{12} Lagrange multipliers we consider those conjugated to U , P_{12}^v , $P_{11}^v - P_{22}^v \equiv N_1$ and $P_{22}^v - P_{33}^v \equiv N_2$, (Jou and Criado-Sancho 2001) we write $|\mathbf{M}|$ as a function of the four later variables, but restricting our attention to the case $N_2 = 0$, which is a good approximation to the experimental observations.

Using the identity $k_B T = \frac{2}{3}(U/N)$, the expression (2.57) may be written as

$$\frac{S - S_{\text{eq}}}{Nk_B} = -\frac{1}{2} \ln \left\{ \left(\frac{2}{3} \frac{U}{N} \right)^3 \left[\det \left(\frac{V}{N} \mathbf{P} \right) \right]^{-1} \right\}, \quad (2.68)$$

and due to the form of the pressure tensor given by (2.26), one finds immediately

$$\det \left(\frac{V}{N} \mathbf{P} \right) = m^3 \langle C_3^2 \rangle [\langle C_1^2 \rangle \langle C_2^2 \rangle - \langle C_1 C_2 \rangle^2]. \quad (2.69)$$

In equilibrium, $\langle C_1 C_2 \rangle = 0$ and

$$\langle C_1^2 \rangle_{\text{eq}} = \langle C_2^2 \rangle_{\text{eq}} = \langle C_3^2 \rangle_{\text{eq}} = \frac{k_B T}{m} = \frac{2}{3} \frac{U}{N}, \quad (2.70)$$

and therefore the term inside the logarithm in (2.68) reduces to 1 and one has $S = S_{\text{eq}}$, as it should be. Out of equilibrium, $m \langle C_1 C_2 \rangle = P_{12}^v$ and the condition $N_2 = 0$ implies $\langle C_2^2 \rangle = \langle C_3^2 \rangle$.

The entropy (2.68) may be finally written in terms of P_{12}^v and N_1 as

$$\frac{S - S_{\text{eq}}}{N k_B} = \frac{1}{2} \ln \left[\frac{1}{4} \left(2 - \frac{V N_1}{U} \right)^2 \left(1 + \frac{V N_1}{U} \right) - \frac{9}{8} \left(2 - \frac{V N_1}{U} \right) \left(\frac{V P_{12}^v}{U} \right)^2 \right] \quad (2.71)$$

which is the explicit expression we were looking for, and which is plotted in Fig. 2.2 as a function of $V P_{12}^v / U$ for different values of $V N_1 / U$.

As concerning to the non-equilibrium chemical potential (2.56) we have

$$\frac{\mu}{k_B \theta} - \frac{\mu_{\text{eq}}}{k_B T} = -\frac{1}{2} \ln \left[\frac{1}{4} \left(2 - \frac{V N_1}{U} \right)^2 \left(1 + \frac{V N_1}{U} \right) - \frac{9}{8} \left(2 - \frac{V N_1}{U} \right) \left(\frac{V P_{12}^v}{U} \right)^2 \right]. \quad (2.72)$$

Note that (2.71) and (2.72) are mutually consistent. Indeed, recall that by definition

$$\frac{\mu_{\text{eq}}}{T} = - \left(\frac{\partial S_{\text{eq}}}{\partial N} \right)_{U,V}, \quad \frac{\mu}{\theta} = - \left(\frac{\partial S}{\partial N} \right)_{U,V, V P_{12}^v, V N_1, V N_2}. \quad (2.73)$$

Since the right hand side of (2.71) will remain constant during the differentiation with respect to N at the conditions specified by the subscripts attached to the parentheses in (2.73), relation (2.72) follows directly from (2.71) and (2.73). This simple relation between non-equilibrium entropy and chemical potential is a consequence of the fact that in an ideal gas both U and $V \mathbf{P}$ are simply additive, namely

$$U = \frac{1}{2} \sum_{\gamma=1}^N m C_{\gamma}^2, \quad V P_{ij} = \sum_{\gamma=1}^N m (C_i C_j)_{\gamma}. \quad (2.74)$$

The presence of interactions amongst the particles, as in real gases, would make more complicated the relation between both non-equilibrium corrections.

Figure 2.2 shows a divergence of $(S - S_{\text{eq}})/N k_B$ at a value of $V P_{12}^v / U$ which depends on the value of $V N_1 / U$. In Fig. 2.3 the isentropic curves are plotted, corresponding the dashed one to divergence of $(S - S_{\text{eq}})/N k_B$. This divergence indicates in fact a limit of the admissible values for the ratio $V P_{12}^v / U$, which must be lower than 1.

Fig. 2.2 Non-equilibrium contribution of the viscous pressure to the entropy as a function of VP_{12}^v/U for several values of VN_1/U . (Jou and Criado-Sancho 2001)

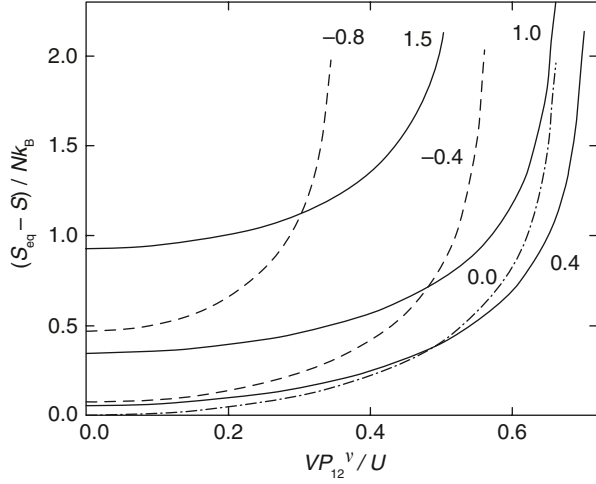
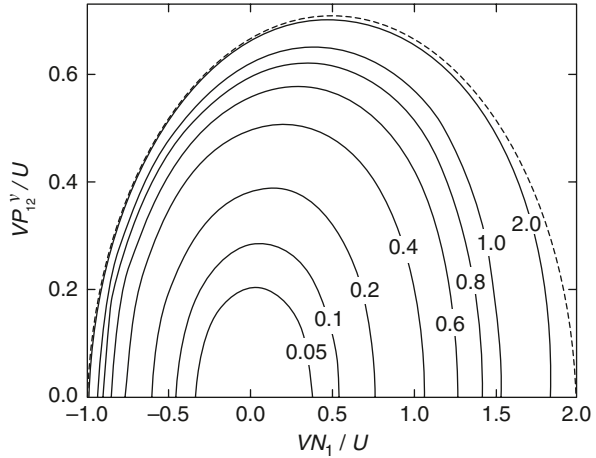


Fig. 2.3 Isentropic curves in the plane VP_{12}^v/U , VN_1/U . The values of $(S - S_{eq})/Nk_B$ are given in the corresponding line. The dashed curve corresponds to the divergence of the entropy. (Jou and Criado-Sancho 2001)



It is not yet clear whether this divergence of the entropy corresponds to an actual instability of the system or to a failure of the classical statistics in the regime where only a few microstates are available; for instance, Boltzmann statistics predicts an infinite entropy (with minus sign) when T tends to zero, but for low T a quantum statistics must be used which yields a vanishing entropy. At this moment, it is still premature to focus the attention on this extreme situation.

In summary, we have explored the influence of non-equilibrium variables (shear viscous pressure, and normal pressures) in the entropy and chemical potential of a dilute gas. In this way, we provide a microscopic basis for these quantities beyond the local equilibrium regime and we generalize extended irreversible thermodynamics beyond the second order in these non-equilibrium parameters.

These results could be used, for instance, to explore the influence of a flow on the composition of a gas mixture in chemical equilibrium but under a velocity gradient

or a viscous pressure, i.e. in a system whose chemical composition is equilibrated but which, nevertheless, is out of hydrodynamical equilibrium as will be done in Chap. 9.

2.4 Non-equilibrium Temperatures in Flowing Gases and Mixtures

The exploration of temperature out of equilibrium is a relevant topic in statistical physics and thermodynamics beyond the local equilibrium approximation (Casas-Vázquez and Jou 2003). In principle, there are several ways to define effective temperatures out of equilibrium by extrapolating several equilibrium relations to non-equilibrium steady states. Since there is not energy equipartition, the temperatures corresponding to different degrees of freedom will be in principle different from each other, and different definitions will lead to different values of temperature out of equilibrium. In the equilibrium limit, all these values tend to the same value, characterizing the equilibrium temperature.

We may take advantage of the results of Sect. 2.2 to illustrate explicitly that different definitions of temperature lead to different values for it, but that these values may be related to each other if a sufficiently detailed knowledge of the system is available. First, we compute from (2.30) and (2.32) the kinetic temperatures associated to the three spatial directions (namely, direction 1, along the flow, direction 2, corresponding to the velocity gradient, and direction 3, perpendicular to the two previous directions) of a flowing ideal gas in a plane Couette flow. The results are

$$\left\langle \frac{1}{2} m c_1^2 \right\rangle = \left\langle \frac{1}{2} m c_2^2 \right\rangle = \frac{1}{2} \frac{\beta}{\beta^2 - \lambda_{12}^2} \equiv \frac{1}{2} k_B T_1 > \frac{1}{2} k_B T \quad (2.75)$$

and

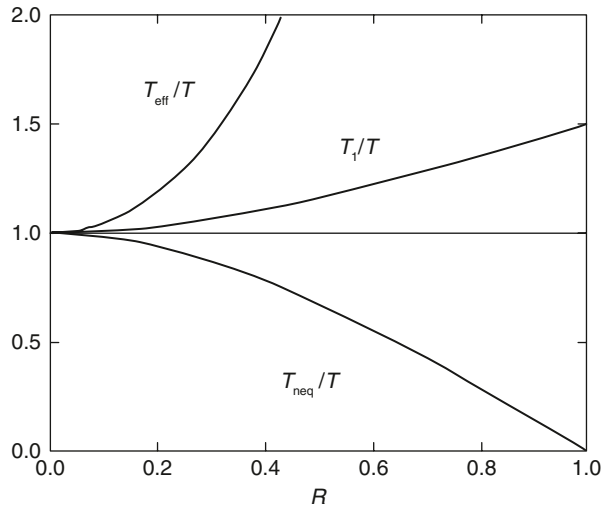
$$\left\langle \frac{1}{2} m c_3^2 \right\rangle = \frac{1}{2\beta} = \frac{1}{2} k_B \theta < \frac{1}{2} k_B T, \quad (2.76)$$

where $\theta \equiv (k_B \beta)^{-1}$. The local-equilibrium temperature T has been defined in terms of the total kinetic energy, as in (2.10). Then

$$\left\langle \frac{1}{2} m (c_1^2 + c_2^2 + c_3^2) \right\rangle = \frac{3}{2} k_B T. \quad (2.77)$$

Notice that, as it may be checked from (2.75) and (2.76), equipartition of energy in the three spatial directions is broken. The average kinetic energy in the direction perpendicular to the velocity and to the velocity gradient is less than in the other two directions; this is also found in non-equilibrium molecular dynamics for simple fluids with interacting molecules, although in that case the temperature along the

Fig. 2.4 Several temperatures are shown at a given value of U as a function of $R = VP_{12}^v/U$. The temperatures shown are: local equilibrium temperature T , thermodynamic non-equilibrium temperature T_{neq} (equal to the kinetic temperature along the z axis), the kinetic temperature in the 1 and 2 directions, $T_1(=T_2)$ and the fluctuation-dissipation effective temperature T_{eff} (Criado-Sancho et al. 2006)



first and the second axes are not exactly equal (Baranyai 2000a, b). Furthermore, it is seen that the kinetic temperature corresponding to direction perpendicular to velocity and to velocity gradient coincides with the non-equilibrium thermodynamic temperature θ , analogously to the situation when a heat flux is present in the system (Camacho and Jou 1995). A third temperature is the thermodynamic one, defined from the non-equilibrium Gibbs Eq. (2.41). It has been evaluated explicitly in terms of U/V and P_{12}^v in (2.61).

In Fig. 2.4, it is seen that θ , denoted as T_{neq} (and therefore the kinetic temperature in the z direction) is reduced for increasing values of viscous pressure, whereas the kinetic temperatures (2.75) in the other two directions increase with viscous pressure (Criado-Sancho et al. 2006).

Still another effective non-equilibrium temperature T_{eff} may be defined from the fluctuation-dissipation theorem (Barrat and Berthier 2000; Berthier and Barrat 2002; Crisanti and Ritort 2003) relating response function and correlation function, as for instance the viscosity and the correlation function of the fluctuations of the shear viscous pressure. Under the assumption of an exponential relaxation for the viscous pressure fluctuations, this effective temperature T_{eff} is defined as

$$\frac{\eta}{\tau} \equiv \frac{1}{k_B T_{\text{eff}}} \langle \delta P_{12}^v(0) \delta P_{12}^v(0) \rangle. \quad (2.78)$$

In equilibrium, $T_{\text{eff}} = T$ and (2.78) is the well-known Green–Kubo relation between shear viscosity and viscous pressure fluctuations when the decay of the latter is exponential with relaxation time τ . In fact, in the general definition of temperature from the fluctuation-dissipation theorem the whole time-dependent response function and correlation function are used, whereas in (2.78) the time integral of both functions are used instead. This may be safely done when the dynamics of the

observable is purely exponential. In the situation we are considering, we find from (2.61) and (2.67b)

$$T_{\text{eff}} = \frac{3 \{ [R^2/(y-1)]^2 \} [R^2 + \frac{2}{3}(1-y)]}{2R^2(y-1-R^2)} T. \quad (2.79)$$

It is seen that $T_{\text{eff}} \geq T \geq \theta$ and that both T_{eff} and θ tend to the local-equilibrium temperature T when the viscous pressure tends to zero. However, their asymptotic limit far from equilibrium is very different, as $\theta \rightarrow 0$ and $T_{\text{eff}} \rightarrow \infty$.

It may be noted that $\theta = 1/k_B\beta < T$, and that it does not coincide with the local-equilibrium temperature except at equilibrium (Casas-Vázquez and Jou 1994; Camacho and Jou 1995; Jou et al. 1988, 1999a, b, 2010). In fact, the meaning of temperature in presence of a flow is being a subject of recent interest in molecular dynamical simulations (Evans and Morriss 1990; Baranyai and Evans 1991; Todd and Evans 1995, 1997).

It is expected that energy equipartition will be also broken in mixtures. In fact, kinetic theory of mixtures clearly shows that this is so (Garzó and Santos 2003). However, the extent and the conditions of the breaking depend on the model system: for instance, using the full Boltzmann equation or the linearized relaxation-time collision operator yields slightly different results. We have extended our previous analysis of one-component gas to binary mixtures (Criado-Sancho et al. 2008), using the velocity distribution function (2.29) with different values of mass, velocity, and Lagrange multipliers for each species of gases (namely a and b). A breaking of equipartition between different chemical species and different spatial directions is obtained when the entropy is maximized under a fixed energy, number of particles, and shear viscous pressure.

One would may alternatively use the velocity gradient as the non-equilibrium constraint, which would correspond to a slightly different physical situation. The Lagrange multipliers for each species are given by (2.60) and can be determined in terms of U/N and VP_{12}^v/N , from which follows similar equations as (2.75) and (2.76) particularized for the respective species a and b .

We will consider that the total internal energy of the mixture $U = U_a + U_b$ is fixed, and concerning the non-equilibrium constraint on the viscous pressure, two especially relevant situations will be considered: (a) the total shear viscous pressure is fixed; (b) the shear rate is fixed; this will imply, up to the first order in $\dot{\gamma}$, that $P_{12,i}^v = -n_i k_B T v_i^{-1} \dot{\gamma}$ (where index i refers to species i and v_i the collision frequency of species i).

- a. *Fixed total viscous pressure.* If the total energy and the total shear viscous pressure are fixed, the conditions on the Lagrange multipliers maximizing the total entropy are $\beta_a = \beta_b$, $\lambda_{12,a} = \lambda_{12,b}$ and the energy per particle is the same for both species. By using the definition of the local equilibrium temperature, which in this case is the kinetic temperature, namely $U_i/N_i \equiv \frac{3}{2} k_B T_i$, it follows that both species will share the same kinetic temperature, and also the same “thermodynamic temperature” defined from the reciprocal of β . Equipartition is broken, not at level of the species, but at the level of spatial directions, as in the one-component gas.

b. *Fixed velocity gradient.* This case is called uniform shear flow, and it has been much studied in kinetic theory (Garzó and Santos 2003). The shear rate $\dot{\gamma}$ is imposed to be equal for both species. Assuming, as before, that the total energy is fixed it follows that, $\beta_a = \beta_b$. The $\lambda_{12,i}$ will be different for each gas and they may be expressed in terms of the collision frequencies ν_a and ν_b of the species, which depend on the molar fractions. In this case β , and the corresponding non-equilibrium temperature $T_{\text{neq}} = (k_B \beta)^{-1}$, is equal for both species but their kinetic temperatures are different implying that equipartition is lost at the level of chemical species, and not only at the level of spatial directions.

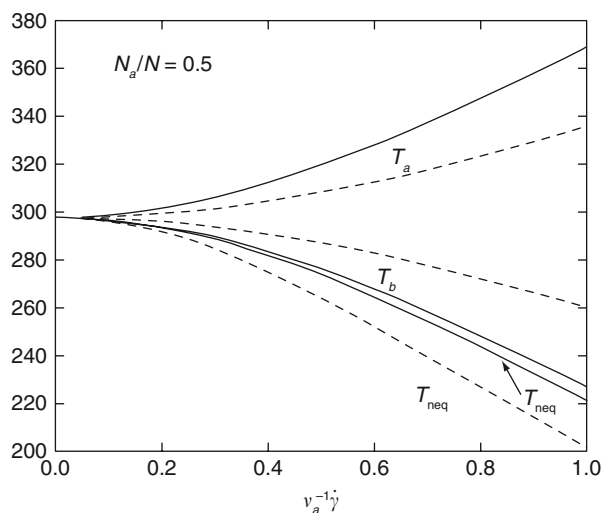
Introducing the variables $w_i \equiv n_i/n$ and $\varepsilon_{ba} \equiv \nu_b^{-1}/\nu_a^{-1}$, the additivity of the energy lets us to write $T = w_a T_a + (1 - w_a) T_b$, and we find from the conditions on $\lambda_{12,i}$ the following connection between T_a and T_b

$$\frac{T_a}{T_b} = 1 + \frac{2}{3}(1 - \varepsilon_{ba}^2)(\nu_a^{-1}\dot{\gamma})^2 = 1 + \frac{4}{3}\nu^{-1}(\nu_a^{-1} - \nu_b^{-1})\dot{\gamma}^2. \quad (2.79)$$

In Fig. 2.5 are plotted T_a , T_b and $T_{\text{neq}} = T_a \left[1 + \frac{2}{3}(\nu_a^{-1}\dot{\gamma})^2\right]^{-1}$. It is seen than the higher the discrepancy in the collision frequencies ν_a and ν_b , i.e. for values of ε_{ba} farther from 1, the differences between the kinetic temperatures of both chemical species are higher and, of course, they increase with increasing $\dot{\gamma}$.

In summary, the results of the present simple analysis are the following ones: (1) Under a non-vanishing viscous pressure, equipartition is broken with respect to the different spatial directions, both for a one-component gas and for each species in the mixture. (2) If the total viscous pressure is imposed on the mixture, both the thermodynamic temperature and the local-equilibrium absolute temperature are the same for both species. In this case, equipartition is broken with respect to different

Fig. 2.5 The kinetic temperatures T_a and T_b of the components a and b and the non-equilibrium temperature $T_{\text{neq}} = T_a \left[1 + \frac{2}{3}(\nu_a^{-1}\dot{\gamma})^2\right]^{-1}$ are plotted in terms of $\nu_a^{-1}\dot{\gamma}$ for $N_a = N_b = 0.5N$ for two different values of ε_{ba} , namely 0.25 (solid lines) and 0.75 (dashed lines) and for $T = 298$ K. (Criado-Sancho et al. 2008)



spatial directions, but not with respect to different chemical species. (3) If homogeneous shear rate is imposed on both kinds of particles, and the total internal energy is fixed, the thermodynamic temperature is the same for both species, but the local-equilibrium absolute temperature is different, and equipartition is broken for the species.

These results show some of the subtleties of temperature in non-equilibrium steady states. For instance, it is surprising that, under some conditions, equipartition may be broken with respect to different spatial directions but not with respect to different chemical species. It is also surprising that the thermodynamic temperature obtained from differentiation of the entropy may be equal, in some circumstances, for both species, although their local-equilibrium absolute temperatures are different.

2.5 Partition Function for a Flowing Relativistic Ideal Gas

In this last section we write for completeness the partition function corresponding to a relativistic ideal gas under a shear viscous pressure P_{12}^v , which complements the information given in Sect. 2.2 concerning the flowing non-relativistic ideal gas. This analysis may be useful for discussions of relativistic nuclear collisions, or of supernovae explosions. The average values of the energy and of the pressure tensor are given, respectively, by

$$\int f(p) p c d\mathbf{p} = u, \quad \int f(p) \frac{1}{2}(\mathbf{p}c + c\mathbf{p}) d\mathbf{p} = \mathbf{P}, \quad (2.80)$$

p being the magnitude of the momentum \mathbf{p} of the particle and c the speed of light. When these conditions, which are analogous to the conditions (2.22) for non-relativistic ideal gases, are considered, we have instead of (2.23), the following momentum distribution function

$$f(p) = z^{-1} \exp \left[-\beta p c - \sum_i \sum_{j>i} \lambda_{ij} \frac{1}{2} (p_i c_j + p_j c_i) \right], \quad (2.81)$$

with z the one-particle partition function.

After integration over p , the partition function in the presence of a shear viscous pressure turns out to be

$$z = \frac{8\pi V}{(c\beta h)^3} \frac{1}{3} \frac{2[1 + 3(\lambda_{12}/\beta)] + [1 - (\lambda_{12}/\beta)^2]^3}{[1 - (\lambda_{12}/\beta)]^3}, \quad (2.82)$$

where h is Planck's constant and λ_{12} the Lagrange multiplier related to P_{12}^v . This partition function reduces to the equilibrium partition function of the relativistic gas in the limit of small λ_{12} and $\beta = (k_B T)^{-1}$, namely

$$z = 8\pi V \left(\frac{k_B T}{ch} \right)^3 \quad (2.83)$$

and it diverges when λ_{12} tends to β . Thus, it shares the same features as (2.32), where these are the two extreme behaviours found. To compute explicitly the Lagrange multipliers, one should use the conditions for the average values of the energy and of the viscous pressure, but taking into account the microscopic expressions for the energy and the pressure of the relativistic gas, by using (2.17) for the average values in terms of the derivatives of the partition function with respect to Lagrange multipliers.

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