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Temperature in ideal gas mixtures in Couette flow: A maximum-entropy approach

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Abstract

A binary mixture of ideal gases in Couette flow is studied in the framework of information theory. It is shown that if the total shear viscous pressure is imposed as a constraint, there is equipartition of energy between the different chemical species but not amongst the different spatial directions. In contrast, if a same shear rate is imposed on both species, there is no equipartition between species neither amongst spatial directions. In both situations, the thermodynamic temperature, defined from the Lagrange multiplier conjugated to the internal energy, is the same for both species, independently of the equality or not of their local-equilibrium temperature.
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Temperature is one of the most basic thermodynamic concepts, whose clarification is necessary to propose consistent formulations of non-equilibrium thermodynamics. In classical irreversible thermodynamics, temperature retains its usual meaning, but this is not so beyond the local-equilibrium hypothesis, where a number of open problems arise [1,2]. Thus, a diversity of aspects of temperature in non-equilibrium steady states is being the subject of recent analyses in a variety of systems, as glasses, granular systems, colloidal fluids, electromagnetic radiation, ideal gases or abstract models [1–8].

In previous publications [9–13] we have studied ideal gases under Couette flow by using the maximum entropy method by including non-equilibrium constraints on the viscous pressure, besides the usual constraints on the internal energy and the number of particles. This provides a model system which may be useful to clarify some aspects of the mentioned diversity. For instance, in [13] we showed that energy equipar-

tition in the three spatial directions is broken for a single ideal gas in Couette flow, and we plotted the kinetic temperatures in the three spatial directions, the non-equilibrium thermodynamic temperature defined from the reciprocal of the Lagrange multiplier conjugated to the internal energy, and the fluctuation-dissipation temperature in terms of the local-equilibrium temperature and the shear viscous pressure. It was seen that some of these temperatures increase with the shear viscous pressure whereas other temperatures decrease. Thus, this model system is useful to illustrate the diversity of non-equilibrium temperatures, the dramatic differences in their behaviour, and makes us aware of open problems in this field.

It is logical to assume that energy equipartition will be also broken in mixtures of gases. In fact, kinetic theory of mixtures clearly shows that this is so (for a very detailed and extensive introduction to the kinetic theory of flowing gases see reference [14]). 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 for ideal gases [14]. Thus, it is worthwhile to extend our previous analyses of one-

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component gases to binary mixtures of gases, as we are not aware of the application of maximum-entropy arguments to such mixtures, which may contribute to clarify some aspects which are not sufficiently explicit in usual development of kinetic theory [15–19]. We use the maximum-entropy formalism on phenomenological grounds as a method especially simple and direct, because for an explicit illustration of the theoretical topic analyzed here it is sufficient to aim for a conceptual qualitative clarification rather than for precise quantitative results. We will compare the results under two different situations: fixed total viscous pressure, and fixed velocity gradient. In each case, we will compare the breaking of equipartition between different species and different spatial directions.

The velocity distribution function for each species of gases maximizing the entropy under a fixed energy, number of particles, and shear viscous pressure is [10]

$$f_i = z_i^{-1} \exp\left[-\frac{1}{2}\beta_i m_i c_i^2 - \lambda_{xy,i} c_{x,i} c_{y,i}\right], \tag{1}$$

where β_i and $\lambda_{xy,i}$ are the Lagrange multipliers conjugate to the internal energy and to the shear viscous pressure, and indices x and y refer to the spatial Cartesian coordinates: the flow is along direction x and the velocity gradient along direction y. Index i refers to the chemical species, which will be denoted by a and b. Thus, m_i stands for the mass of particles of species i and c_i for the relative velocity of the particles with respect to the local-barycentric velocity, and z_i stands for the partition function, taking into account the normalization. The introduction of shear viscous pressure as an additional constraint is logical, because on experimental grounds the shear pressure may be controlled. One could alternatively use the velocity gradient as the non-equilibrium constraint, which could correspond to a slightly different physical situation. Since in ideal gases the viscous pressure is related to the second moments of the peculiar velocity, this gives a specially symmetrical and self-contained form to the exponent in (1). The use of the shear viscous pressure as a constraint implies that it will become an independent variable of the corresponding thermodynamic formalism. Indeed, in Extended Irreversible Thermodynamics [9,10], the viscous pressure tensor is taken as independent variable. In these conditions, the dissipation depends not only on the viscous pressure but also on its time derivative.

The Lagrange multipliers are given by [9,11]

$$\frac{U_i}{N_i} = \frac{3\beta_i^2 - \lambda_{xy,i}^2}{2\beta_i(\beta_i^2 - \lambda_{xy,i}^2)}, \tag{2}$$

$$\frac{V}{N_i} P_{xy,i}^v = -\frac{\lambda_{xy,i}}{\beta_i^2 - \lambda_{xy,i}^2}. \tag{3}$$

It is seen from (3) that in equilibrium, i.e. for vanishing shear viscous pressure, the Lagrange multiplier λ_{xy} vanishes, and (1) reduces to the usual canonical distribution function. The Lagrange multiplier β may be considered as the reciprocal of a non-equilibrium thermodynamic temperature T_{neq} as $\beta = (k_B T_{neq})^{-1}$, which for vanishing viscous pressure becomes equal to the local-equilibrium absolute temperature T.

The values of the Lagrange multipliers are determined in terms of U/N and VP_{xy}^v/N by solving Eqs. (2) and (3). The entropy of each species is obtained by combining the well-known relation $S_i = -k_B \int f_i \ln f_i \, dc_i$ and the distribution function (1). Its differential form is

$$dS_i = \beta_i \, dU_i + \lambda_{xy,i} \, d(V P_{xy,i}^v). \tag{4}$$

Thus, the identification of the Lagrangian multiplier β_i as the reciprocal of a thermodynamic temperature is consistent with the generalized Gibbs equation (4) for a non-equilibrium entropy depending on the internal energy, the viscous pressure, and the composition (which is not made explicit here because the composition of the system does not change). Furthermore, it is known from EIT [9,10] that the Lagrange multiplier $\lambda_{xy,i}$ may be identified as

$$\lambda_{xy,i} = -\frac{\tau_i}{\eta_i} \beta_i P_{xy,i}^v, \tag{5}$$

where η_i is the contribution of species i to the shear viscosity and τ_i the corresponding relaxation time, namely, the inverse of the collision frequency.

From the distribution function (1) the following results may be obtained for the average of the kinetic energy in the different directions

$$\left\langle \frac{1}{2} m_i c_{x,i}^2 \right\rangle = \left\langle \frac{1}{2} m_i c_{y,i}^2 \right\rangle = \frac{1}{2} \frac{\beta_i}{\beta_i^2 - \lambda_{xy,i}^2}, \tag{6}$$

$$\left\langle \frac{1}{2} m_i c_{z,i}^2 \right\rangle = \frac{1}{2} \beta_i^{-1} = \frac{1}{2} k_B T_{neq}. \tag{7}$$

It is seen that equipartition of kinetic energy amongst the different spatial directions is not satisfied; an explicit analysis for different values of the viscous pressure was carried out in [13] for a one-component gas.

Now we will consider that the total internal energy $U = U_a + U_b$ is fixed. Concerning the non-equilibrium constraint on the viscous pressure we will consider two especially relevant situations: (a) the total shear viscous pressure, $P_{xy}^v = P_{xy,a}^v + P_{xy,b}^v$, is fixed; (b) the shear rate $\dot{\gamma} \equiv \partial v_x / \partial y$ is fixed; this will imply, up to the first order in $\dot{\gamma}$, that $P_{xy,i}^v = -\eta_i \dot{\gamma} = -n_i k_B T v_i^{-1} \dot{\gamma}$.

(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 will be $\beta_a = \beta_b$, $\lambda_{xy,a} = \lambda_{xy,b}$. This may be obtained by differentiating the total entropy, in such a way that

$$dS = (\beta_a - \beta_b) \, dU_a + (\lambda_{xy,a} - \lambda_{xy,b}) \, d(V P_{xy,a}^v) \tag{8}$$

and the condition of extremum is the equality of both Lagrange multipliers in both species. According to (2) and (3) this implies that the energy per particle is the same for both species, i.e. $(U_a/N_a) = (U_b/N_b)$. 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 have the same kinetic temperature, and also the same "thermodynamic temperature" defined from the reciprocal of β. This does not imply that equipartition is not broken; as seen in (6)