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Influence of Non-Boltzmann Distributions on the Thermodynamics Properties of Gaseous Species

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A simple method of statistical thermodynamics is proposed that permits the quantitative estimation of the influence that non-Boltzmann distributions can have on the thermodynamic properties of gaseous species. After a brief recall of basic statistical definitions relative to entropy, energy, and population distributions, the method is described and successively applied to theoretical and experimental vibrational distributions of O_2, N_2, and CO selected from the literature. The results of the analysis are discussed and recommendations are proposed concerning possible approaches to deal with the situations in which the thermodynamic models based on the Boltzmann distribution are not applicable.

Introduction

THE applicability to nonequilibrium flows of thermodynamic models constructed on the assumption that the quantum state populations follow a Boltzmann distribution has been long debated and the argument has not been settled yet. The correct description of the population distributions is an important and critical issue that has far-reaching consequences. It affects the thermodynamic and transport properties of a gas mixture and the rates of the thermal and chemical relaxation processes. The assumption of a Boltzmann distribution is very convenient because the thermodynamics of the gas mixture can be described by algebraic functions and the evolution of nonequilibrium flows can be treated as a progression of constrained-equilibrium states[1,2] characterized by a condition of maximum entropy (thermodynamic approach). Moreover, relatively simple formulations for predicting transport coefficients and thermal, chemical relaxation rates become possible. However, experimental evidence[3–14] shows that circumstances do occur in which the populations differ from a Boltzmann distribution. Some researchers propose to deal with such flow situations via the rigorous approach of solving simultaneously the traditional gasdynamics equations and the master equations that govern the kinetics of the particle exchanges among the quantum states (kinetic approach). Other researchers hesitate to follow this approach because, for realistic applications, it implies the necessity of numerically integrating a prohibitively great number of differential equations. As a result, thermodynamic models based on the assumption of a Boltzmann distribution are still widely used in flow situations for which it is known that such an assumption is not tenable. The critical aspect of this practice is that the adoption of these models is often made in the majority of the engineering applications without an estimate of (even the order of magnitude of) the errors involved. There are, however, efforts[15–20] aiming to a better understanding of the problem, and a considerable amount of work has been devoted in molecular physics to investigate the interdependence between the existence of non-Boltzman distributions and the thermal (rotational, vibrational) and chemical (dissociation) relaxation rates. On the other hand, efforts concerned with understanding the influence of non-Boltzmann distributions on the transport[21–23] and thermodynamic[24] properties appear rather scarce.

This paper concentrates on the thermodynamic properties. Its main purpose is to present a statistical thermodynamics method that permits a quantitative assessment of the influence that non-Boltzmann distributions can have on the thermodynamic properties of gaseous species. The method is applied to theoretical and experimental vibrational distributions of O_2, N_2, and CO selected from the literature and representative of nonequilibrium situations that can settle in after a shock wave, in high-enthalpy wind tunnels and in propulsive nozzles. The purpose of the application is to reaffirm from a thermodynamic point of view, to which researchers performing routine calculations of nonequilibrium flows for engineering applications are more sensitive, the findings of the kinetic approach,[24] i.e., that departure from the Boltzmann distribution may produce errors in the state (and flow) parameters that are negligible for nonequilibrium compressed flows and appreciably great for nonequilibrium expanding flows.

Statistical Thermodynamics

From a statistical thermodynamics viewpoint, a gas mixture in disequilibrium with respect to mass and energy exchanges can be considered as an ensemble[1,25] of distinguishable systems represented by the molecular degrees of freedom of each chemical constituent. The δth degree of freedom of the ϵth component embraces statistically all of the N_ϵ particles of that component: the particles assume, therefore, the role of indistinguishable subsystems for that given degree of freedom. One can, thus, introduce the entropy $s_{\epsilon\delta}$ and the energy $u_{\epsilon\delta}$ per particle of the ϵth component according to the standard definitions of the Gibbs statistics, which, rephrased in the quantum formalism, read

$$s_{\epsilon\delta} = -k \sum_n p_{\epsilon\delta,n}\, \ell n\, p_{\epsilon\delta,n} \tag{1}$$

$$u_{\epsilon\delta} = \sum_n p_{\epsilon\delta,n} \varepsilon_{\epsilon\delta,n} \tag{2}$$

In Eqs. (1) and (2), k is the Boltzmann constant, n is a quantum number that enumerates the quantum states associated with the δth degree of freedom of the particle statistically representative of the ϵth component, and $p_{\epsilon\delta,n}$ and $\varepsilon_{\epsilon\delta,n}$ are, respectively, the probabilities and the energies of the quantum states. The probabilities $p_{\epsilon\delta,n}$ are subjected to the normalization condition

$$\sum_n p_{\epsilon\delta,n} = 1 \tag{3}$$

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and correspond to the normalized populations of the Boltzmann statistics, i.e., the ratios of the particles $N_{\epsilon\delta,n}$ occupying the nth quantum state to the total number N_ϵ of particles. In principle, they can be either obtained experimentally or calculated from master equations. When the probabilities, or normalized populations, are available, one can find the entropy and the energy of the distribution by direct substitution into Eqs. (1) and (2).

The Boltzmann distribution

$$p^*_{\epsilon\delta,n} = e^{-\beta_{\epsilon\delta}\varepsilon_{\epsilon\delta,n}}/q_{\epsilon\delta} \tag{4}$$

is the distribution that maximizes the entropy [Eq. (1)] for a prescribed energy [Eq. (2)] compatibly with the normalization condition [Eq. (3)]. The partition function $q_{\epsilon\delta}$ is given by the sum-over-states

$$q_{\epsilon\delta} = \sum_n e^{-\beta_{\epsilon\delta}\varepsilon_{\epsilon\delta,n}}$$

The equality between the average energy

$$u^*_{\epsilon\delta} = \sum_n p^*_{\epsilon\delta,n}\varepsilon_{\epsilon\delta,n} = \sum_n \varepsilon_{\epsilon\delta,n}e^{-\beta_{\epsilon\delta}\varepsilon_{\epsilon\delta,n}} \Big/ \sum_n e^{-\beta_{\epsilon\delta}\varepsilon_{\epsilon\delta,n}} \tag{5}$$

of the Boltzmann distribution [Eq. (4)] and the prescribed energy [Eq. (2)] yields the statistical parameter $\beta_{\epsilon\delta} = \beta_{\epsilon\delta}(u^*_{\epsilon\delta}, \varepsilon_{\epsilon\delta,1}, \varepsilon_{\epsilon\delta,2}, \ldots)$. When account is taken of Eq. (5), the substitution of the Boltzmann distribution [Eq. (4)] into the entropy general definition [Eq. (1)] leads to the algebraic function

$$s^*_{\epsilon\delta} = k\beta_{\epsilon\delta}u^*_{\epsilon\delta} + \ell n\ q_{\epsilon\delta} \tag{6}$$

The thermodynamic properties associated with the δth degree of freedom derive basically from the existence of such a function [Eq. (6)]. For example, the temperature $T_{\epsilon\delta}$ and the contribution $P_{\epsilon\delta}$ to the total pressure are obtained from the formulas

$$T_{\epsilon\delta} = \frac{1}{k\beta_{\epsilon\delta}} \qquad P_{\epsilon\delta} = kN_\epsilon T_{\epsilon\delta}\left(\frac{\partial\ \ell n\ q_{\epsilon\delta}}{\partial V}\right)_{T_{\epsilon\delta}} \tag{7}$$

In the partial derivative of Eq. (7), V represents the volume occupied by the gas mixture. All of the algebraic models in use today to describe the thermodynamic behavior of nonequilibrium flows are embedded in Eq. (6). For an assigned non-Boltzmann distribution, therefore, the difference between its entropy [Eq. (1)] and the (maximum) entropy [Eq. (6)] of the Boltzmann distribution [Eq. (4)] that carries the same energy [Eq. (2)] constitutes a quantitative measure of the capability of the Boltzmann distribution to approximate the non-Boltzmann one, and of the applicability of the thermodynamic model generated from Eq. (6).

Other approximating Boltzmann distributions rather than the one of same energy can be considered. They have come in use to compromise the necessity of predicting thermodynamic properties with the limitation that sometimes only the first few energy levels are accessible to experimental investigation. Thus, one can adopt the Boltzmann distribution that can be accommodated on the ground state ($n = 1$) population of the assigned distribution; in this case, the statistical parameter $\beta_{\epsilon\delta}$ is calculated from

$$p_{\epsilon\delta,1} = e^{-\beta_{\epsilon\delta}\varepsilon_{\epsilon\delta,1}} \Big/ \sum_n e^{-\beta_{\epsilon\delta}\varepsilon_{\epsilon\delta,n}} \tag{8}$$

A similar Boltzmann distribution is obtained if the statistical parameter $\beta_{\epsilon\delta}$ is calculated from the definition

$$p_{\epsilon\delta,2} = p_{\epsilon\delta,1}e^{-\beta_{\epsilon\delta}(\varepsilon_{\epsilon\delta,2}-\varepsilon_{\epsilon\delta,1})} \tag{9}$$

which makes use also of the population of the first level ($n = 2$) above the ground state. In both cases, the temperature obtained as $1/k\beta_{\epsilon\delta}$ should be interpreted as a first-level temperature. The energies carried by these first-level Boltzmann distributions can be calculated directly from Eq. (5) and, of course, they differ from the energy [Eq. (2)] of the assigned distribution. The entropies follow again from Eq. (6).

Analysis of Test Cases

The method described in the previous section has been applied to vibrational population distributions (see Table 1) that are representative of nonequilibrium flows subjected to either compression or expansion. In the following sections, therefore, entropy and energy must be understood as vibrational contributions and the subscripts ϵ, δ will be omitted from the notation because they are unnecessary.

The population distributions representative of compressed flows have been taken from the study of Gonzales and Varghese[26,27] relative to the vibrational relaxation and dissociation of shock-heated O_2 and CO (cases 1–2 and 3, respectively), highly diluted in Ar ($\rho_{Ar} = 1.28 \times 10^{17}$ molecules/cm^3 for all cases). These distributions have been calculated via master equations. The population distributions representative of expanding flows are relative to the experimental investigations made by Brechignac et al.[14] in a CO-laser plasma (case 4), and to the nonequilibrium dissociation and ionization of N_2 in an electric discharge (case 5) studied by Cacciatore et al.[28] via master equations. Readers interested in the details are referred to the original papers.

In the following sections, the characteristics of the various population, entropy, and energy distributions relative to the considered test cases are discussed. Comparative data for en-

Table 1 Selected vibrational population distributions

Case	Reference source	Gas	T, K	P, N/m^2	Remarks
1	26	O_2	6000	1.1×10^7	Master equations
2	26	O_2	12,000	2.1×10^7	Master equations
3	27	CO	15,000	2.7×10^7	Master equations
4	14	CO	230	2.7×10^3	Experimental
5	28	N_2	500	4.0×10^2	Master equations

Table 2 Entropy, energy (eV), and percentual errors for the considered test cases

			Boltzmann distributions									
Assigned distribution			Same energy		First-level, Eq. (8)				First-level, Eq. (9)			
Case	s/k	u	s^*/k	Δ_s	s^*/k	u^*	Δ_s	Δ_u	s^*/k	u^*	Δ_s	Δ_u
1	1.989	0.511	1.992	0.1	2.031	0.531	2.1	3.8	2.054	0.542	3.3	6.1
2	2.482	0.820	2.498	0.6	2.647	0.939	6.6	14.6	2.779	1.058	11.9	29.0
3	2.545	1.195	2.550	0.2	2.630	1.286	3.3	7.6	2.688	1.357	5.6	13.5
4	1.821	0.529	1.927	5.8	1.449	0.287	−20.4	−45.8	1.148	0.183	−37.0	−65.4
5	1.664	0.504	1.818	9.3	1.394	0.288	−16.2	−42.7	1.239	0.230	−25.5	−54.4

tropy, energy, and percentual error are listed in Table 2. The percentual errors are defined as

$$\Delta_s = 100[(s^* - s)/s] \qquad \Delta_u = 100[(u^* - u)/u]$$

Distributions Representative of Compressed Flows

Figures 1a–1c and 2a–2c are relative to cases 1 and 2. The open circles in Fig. 1a represent a steady-state vibrational population distribution of dissociating O_2 after relaxation to a final translational temperature of 6000 K (see Fig. 14a of Ref. 26, p. 7621). Given the high dilution, the total pressure of the mixture coincides practically with the Ar partial pressure $P_{Ar} = 1.1 \times 10^7$ N/m^2. Deviations from the typical Boltzmann trend begin to settle in on the levels above 1 eV and become severe on the levels from 2.6 eV up to the dissociation limit. The approximating Boltzmann distributions appear almost

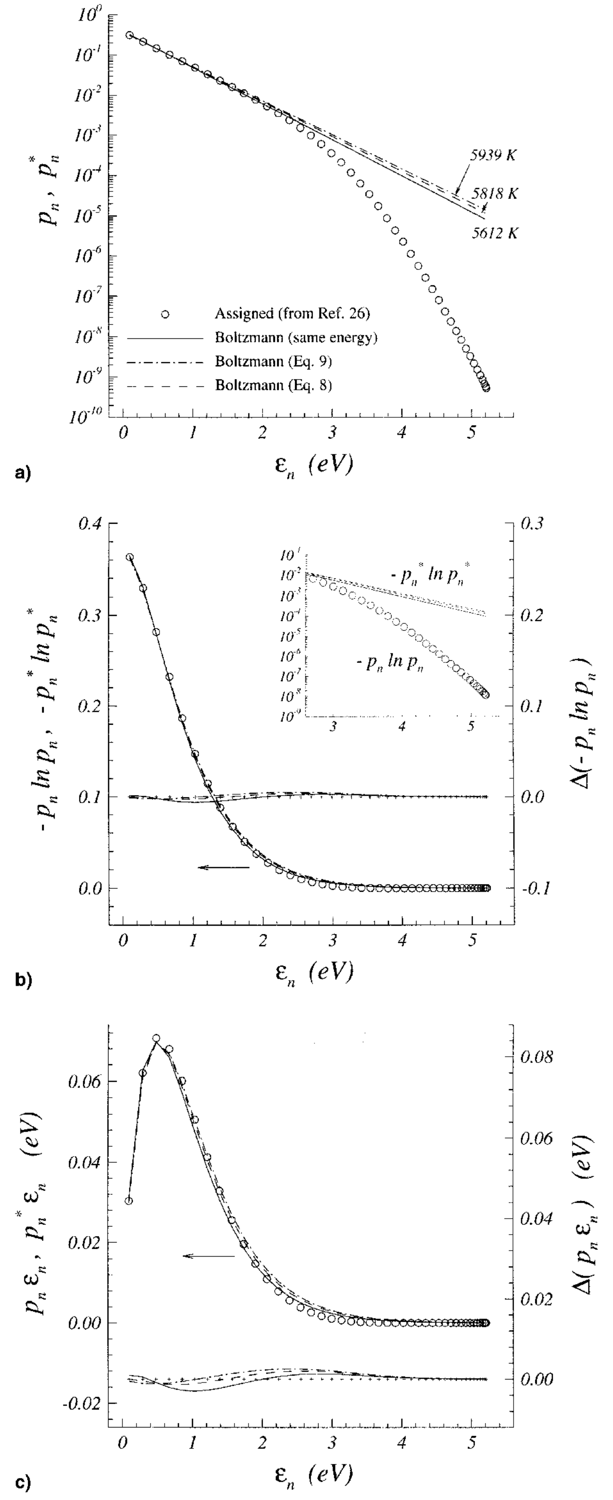

Fig. 1 **Steady state of vibrationally relaxing and dissociating O_2 in Ar at a translational temperature of 6000 K: a) assigned and approximating population distributions, b) entropy and entropy deviation distributions, and c) energy and energy deviation distributions.**

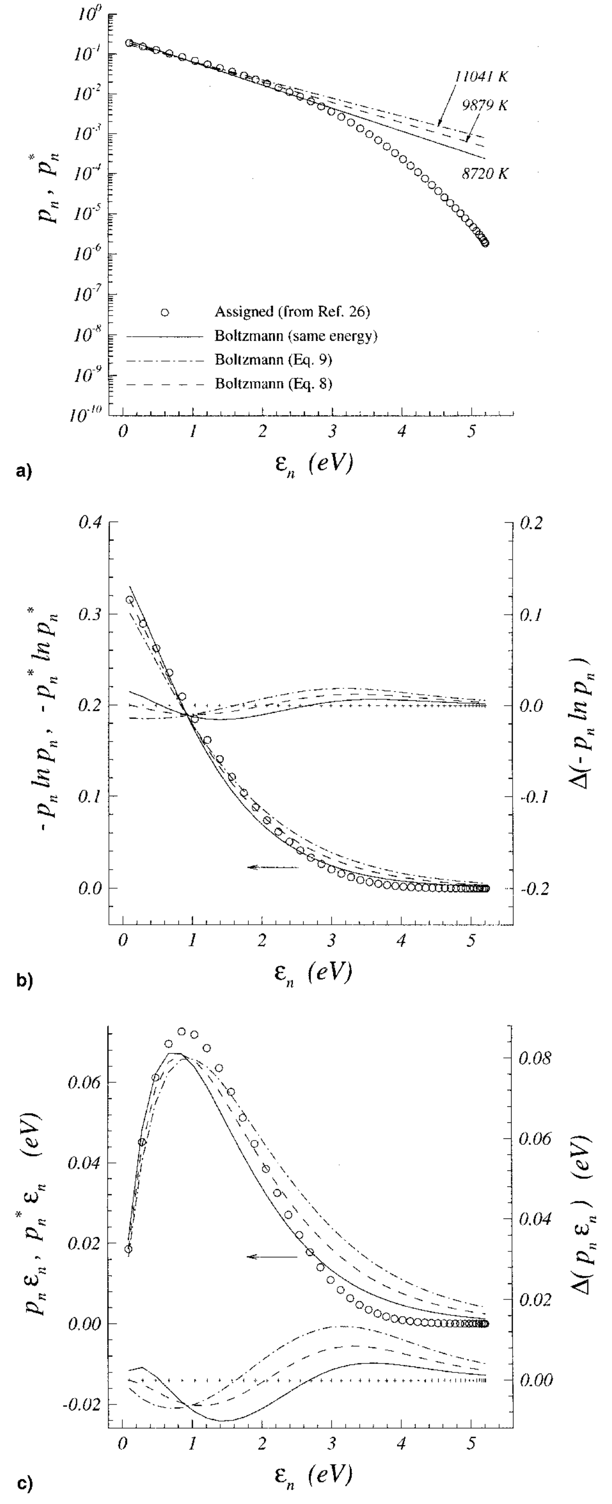

Fig. 2 **Steady state of vibrationally relaxing and dissociating O_2 in Ar at a translational temperature of 12,000 K: a) assigned and approximating population distributions, b) entropy and entropy deviation distributions, and c) energy and energy deviation distributions.**

equivalent, although there are minor differences among the vibrational temperature (5612 K) of the Boltzmann distribution with same energy (BDSE) and the first-level temperatures (5818 and 5939 K) relative to the Boltzmann distributions defined from Eqs. (8) and (9) (BD8 and BD9, respectively). The entropy distributions $(-p_n\, \ell n\, p_n, -p_n^*\, \ell n\, p_n^*)$ are shown in Fig. 1b. The shape of the curves indicate that, regardless of which population distribution one considers, the vibrational levels in the strongly non-Boltzmann region give contributions that, although different (see the particular in logarithmic scale in Fig. 1b), are negligible when compared to those of the ground state. The same figure shows also the entropy deviations

$$\Delta(-p_n\, \ell n\, p_n) = (-p_n^*\, \ell n\, p_n^*) - (-p_n\, \ell n\, p_n)$$

produced by the approximating Boltzmann distributions. They are really minor because of the low translational temperature of the steady state and become absolutely negligible in the upper part of the non-Boltzmann region. It is, however, important to notice the trend of the curves: the entropy underestimation on the low levels is compensated by an overestimation on the midlevels. For these reasons, the entropy percentual error of the BDSE is completely negligible (Δ_s = 0.1%) and those of the BD8 and BD9 attain only few percents (Δ_s = 2.1 and 3.3%, respectively). Figure 1c shows an analogous situation for the energy distributions $(p_n\varepsilon_n, p_n^*\varepsilon_n)$. However, the energy deviations

$$\Delta(p_n\varepsilon_n) = p_n^*\varepsilon_n - p_n\varepsilon_n$$

are somewhat more emphasized because the level energies increase with the vibrational quantum number. Nonetheless, the curve corresponding to the BDSE averages to zero by definition; instead, the curves corresponding to the BD8 and BD9 indicate that the energy underestimated on the low levels is overcompensated on the midlevels. The energy percentual error relative to the BD8 can be considered moderate (Δ_u = 3.8%), but the one associated with the BD9 becomes appreciable (Δ_u = 6.1%).

An increased translational temperature of the steady state produces an increase of the energy [Eq. (2)] of the assigned distribution. Correspondingly, the low levels depopulate in favor of the high levels and the situation changes significantly. The open circles in Fig. 2a represent another steady-state vibrational population distribution of dissociating O_2, but corresponding to relaxation with a final translational temperature of 12,000 K and Ar partial pressure of 2.1 × 10^7 N/m^2 (see Fig. 14b of Ref. 26, p. 7021). At such a high translational temperature, the approximating Boltzmann distributions differ appreciably. The BDSE, with a vibrational temperature of 8720 K, still performs well. The zero averaging of the BDSE energy deviation (see Fig. 2c) drives the BDSE entropy deviation (see Fig. 2b) to follow a similar trend; the compensation effect is such that the BDSE entropy distribution reproduces that of the assigned non-Boltzmann distribution within a satisfactory Δ_s = 0.6%. On the contrary, the BD8 and BD9 fail in providing the required accuracy. The corresponding deviation curves in Figs. 2b and 2c show how the deficit on the low levels is overcompensated on the mid- and high levels; consequently, their entropy and energy distributions overestimate with ample margins (see Table 2) those relative to the assigned non-Boltzmann distribution. The reason for the BDSE success when the high levels become populated is because its statistical parameter $\boldsymbol{\beta}$, being calculated from the equality of the energies [Eqs. (2) and (5)], takes into account the population variations on the high levels. This information is missing in the statistical parameters of the BD8 and BD9; the only information they take into account is relative to the ground state or, at most, the first level [see Eqs. (8) and (9)]. This limitation explains the failure of the BD8 and BD9 in approximating the properties of the assigned population distribution. However, the failure onset depends on the gas species. This is indicated in Figs. 3a–3c, relative to case 3. The figures illustrate the steady-state situation of CO after relaxation to a final translational temperature of 15,000 K and Ar partial pressure of 2.7 × 10^7 N/m^2 (see Fig. 9 of Ref. 27, p. 242). Notwithstanding the higher translational temperature, the BD8 and BD9 of Fig. 3a produce

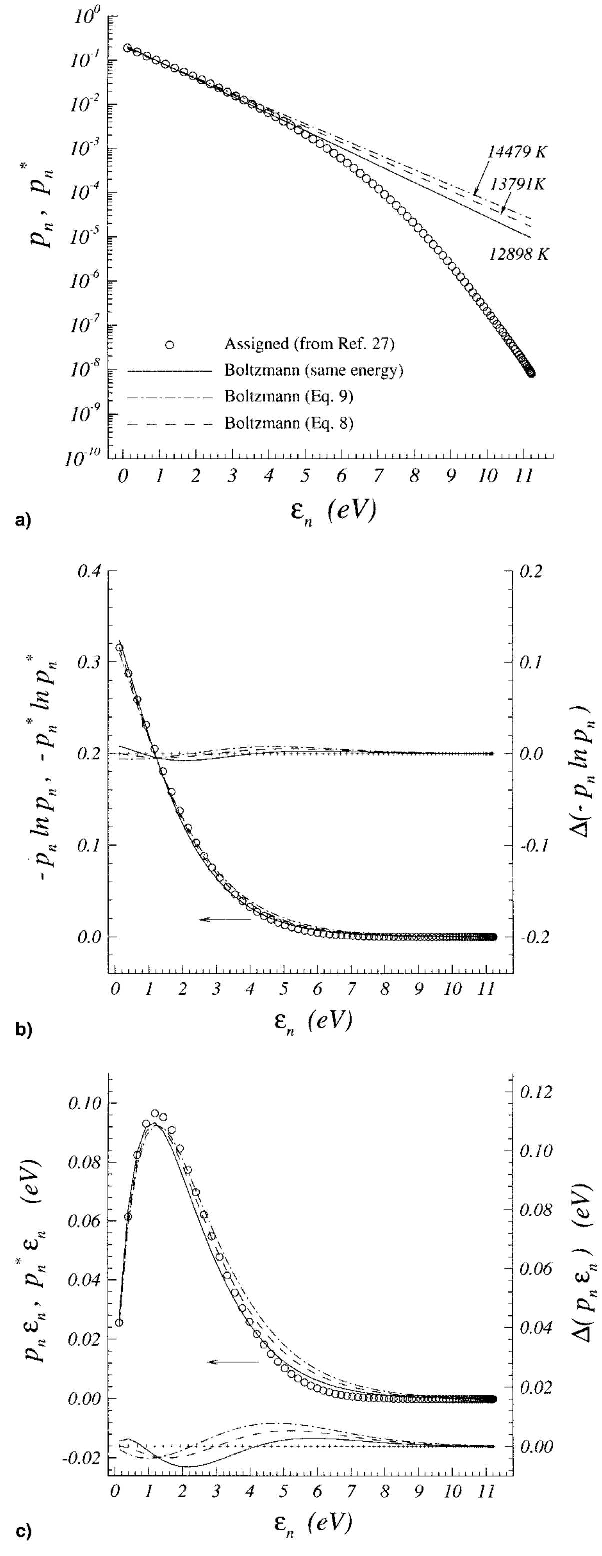

Fig. 3 Steady state of vibrationally relaxing and dissociating CO in Ar at a translational temperature of 15,000 K: a) assigned and approximating population distributions, b) entropy and entropy deviation distributions, and c) energy and energy deviation distributions.

entropy and energy percentual errors more reduced than those produced by the BD8 and BD9 of Fig. 2a (see Table 2). This effect arises because the level energies ε_n of CO are greater than those of O_2. For a given energy [Eq. (2)], a more energetic spectrum presents a major occupancy of the lower levels and that hinders the BD8 and BD9 failure.

Distributions Representative of Expanding Flows

Figures 4a–4c are relative to case 4. The open symbols in Fig. 4a represent a vibrational population distribution of CO in a mixture with partners He and O_2 at a total pressure of 20 torr ($\simeq 2.7 \times 10^3$ N/m^2) and a translational temperature of 230 K (see curve 3 in Fig. 2 of Ref. 14, p. 299). The populations

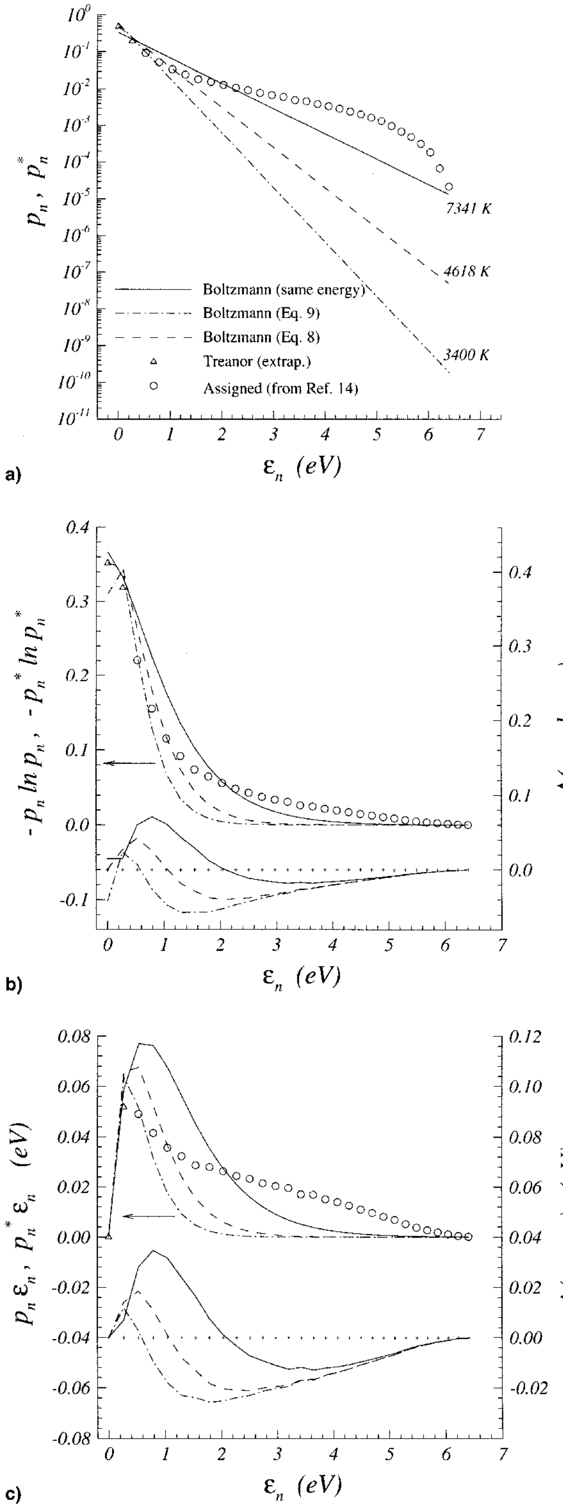

Fig. 4 Vibrational relaxation of CO in a laser plasma at a translational temperature of 230 K and a pressure of 20 torr: a) assigned and approximating population distributions, b) entropy and entropy deviation distributions, and c) energy and energy deviation distributions.

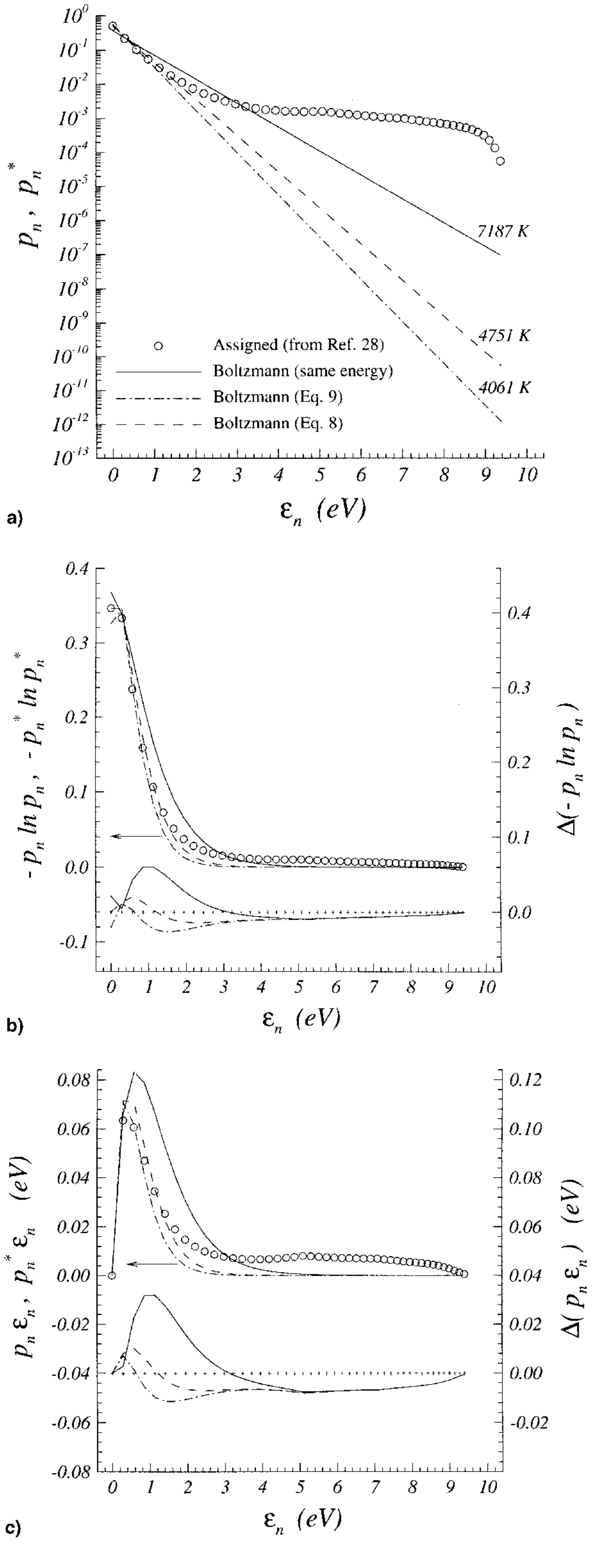

Fig. 5 Vibrational relaxation of dissociating and ionizing N_2 in an electric discharge with a translational temperature of 500 K and a pressure of 3 torr: a) assigned and approximating population distributions, b) entropy and entropy deviation distributions, and c) energy and energy deviation distributions.

of the levels $n = 3$–30 (open circles) were determined experimentally; as indicated in Ref. 14, the ground-state and first-level populations (open triangles) are obtained from the extrapolation of the measured distribution toward a Treanor distribution with $\boldsymbol{\theta}_1^* = 3400$ K. The populations of the levels above $n = 30$ up to the dissociation limit are not available, but this lack of information is irrelevant for the determination of the BDSE because the contributions to the energy [Eq. (2)] appear already negligible from $n = 29$ (see the open-circle curve in Fig. 4c); moreover, the normalization condition [Eq. (3)] relative to a truncation at $n = 30$ is also verified with sufficient accuracy. The assigned population distribution shows on the midlevels the plateau configuration typical of low-pressure situations. The approximating Boltzmann distributions differ noticeably. They produce entropy and energy distributions (see Figs. 4b and 4c) whose trend is opposite to what happens in high-pressure situations (cases 1–3): entropy and energy are overestimated on the low levels and underestimated on the high levels. This fact works against the approximating Boltzmann distributions. The compensation, complete for the BDSE energy distribution (see Fig. 4c), turns out moderately excessive for the BDSE entropy distribution (see Fig. 4b), which, therefore, generates a non-negligible percentual error ($\Delta_s = 5.8\%$). In Fig. 4a, BD8 and BD9 lag below the other two distributions. They carry energies that are lower than the energy of the assigned distribution; consequently, the compensation effect is rather poor and the corresponding entropy and energy percentual errors are enormous (see Table 2). The analysis of case 5 (see Figs. 5a and 5c) shows that, when the pressure decreases, the insufficiency of the compensation effect becomes worse, even for the BDSE entropy distribution. The open circles in Fig. 5a represent a vibrational population of dissociating and ionizing N_2 in an electric discharge at a pressure of 3 torr ($\simeq 4.0 \times 10^2$ N/m^2) and a translational temperature of 500 K. The plateau of the distribution is very flat; correspondingly, the entropy overestimation on the low levels (see Fig. 5b) becomes more pronounced and generates a substantially great percentual error ($\Delta_s = 9.3\%$).

Conclusions

A statistical thermodynamics method to quantitatively estimate the influence of non-Boltzmann distributions on the thermodynamics properties of gaseous species has been proposed. Any kind of population distribution can be processed according to this method. The application to selected vibrational population distributions typical of nonequilibrium flows leads to conclusions consistent with those obtained by other authors[24] via a kinetic approach. Thermodynamic models based on the Boltzmann distribution can still be applied with sufficient accuracy for nonequilibrium flows undergoing compression. In this regard, it is important to keep in mind that, for a given gas species, first-level Boltzmann distributions and their corresponding thermodynamic models tend to fail with increasing translational temperatures. This is of particular concern for diatoms with small quantum-state energies. The situation is more critical for expanding nonequilibrium flows. Under circumstances of decreasing pressure, the first-level Boltzmann distributions are absolutely unrealistic and even the thermodynamic models based on the Boltzmann distribution of same energy can be affected by errors of the order of 10% in the state parameters. This fact is of extreme relevance for the calculation of nonequilibrium flows in high-enthalpy wind tunnels and propulsive nozzles because it may invalidate the applicability of the thermodynamic approach to such flows. It is worth mentioning, however, that the coupling[25,29] between the rotational and vibrational degrees of freedom may have an impact on these conclusions. When rotation and vibration are nonseparable, the gas molecules are characterized by a single rotovibrational spectrum and one should investigate whether or not the population distributions of such a spectrum can be satisfactorily approximated by a Boltzmann distribution. This kind of investigation is very critical but, unfortunately, not much work has been done in this direction. It cannot be stressed enough how convenient it is for the analysis to treat the evolution of nonequilibrium flows according to the thermodynamic approach.

When the thermodynamic models based on the Boltzmann distribution are not applicable, one has to resort to other methods. In this regard, there are other approaches that are worth investigating. A first approach may take advantage of the idea proposed by Park[24] to fit non-Boltzmann distributions like those in Figs. 4a and 5a by suitable polynomial forms that are functions of the relevant energy. One can then attempt to construct thermodynamic models by generating fundamental relations, analogous to Eq. (6), via parametric equations [Eqs. (1) and (2)]. In this way, the evolution of a nonequilibrium flow can still be described as a progression of thermodynamic states, although these are not necessarily characterized by a condition of maximum entropy. A second approach is based on the use of the master equations. This method is very rigorous, but is affected by severe difficulties. The most important is of computational nature: the numerical integration of the great number of differential equations necessary to deal with a multicomponent mixture is extremely time consuming and a real computational burden even for the most powerful computers. A serious drawback is also represented by the necessity to know all of the rate coefficients of the state-to-state exchanges, which is a formidable task to accomplish for a complex gas mixture. Another possible alternative is offered by the direct simulation Monte Carlo (DSMC) methods as used in rarefied gasdynamics. In this approach, the characterization of the state-to-state exchanges is inherent in the collisional models and there is no need to introduce additional equations, as required by the continuum gasdynamics. However, this approach could also prove computationally expensive because the Knudsen number in the expanding regions of nonequilibrium flows may still be too low. At any rate, the advent of more powerful parallel computers makes it worth pursuing these lines of research.

It appears appropriate to emphasize that the previous remarks reflect an investigation focused on the thermodynamic properties and do not take into account other aspects that may arise from arguments relative to transport properties and chemical kinetics. In this regard, preliminary analyses[30] seem to indicate that more severe restrictions on the applicability of the thermodynamic models based on the Boltzmann distribution are raised in the domain of chemical kinetics.

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