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THE EQUATION OF STATE FOR STELLAR ENVELOPES: COMPARISON OF THEORETICAL RESULTS

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RESUMEN. Una comparación anterior de los parámetros termodinámicos calculados respectivamente en los cuadros químico y físico resultó en un renombrado acuerdo en las zonas de ionización del H y del He en el Sol, a pesar del tratamiento radicalmente diferente de los estados ligados en los dos formalismos. Este acuerdo se debió a un dominio inesperado del término (clásico) de la presión de Coulomb. En comparaciones recientes, a temperaturas y densidades más altas y para una mezcla solar representativa (H, He y O), se han encontrado grandes diferencias en las fracciones de ionización del O. Los parámetros termodinámicos también reflejan estas diferencias, a tal grado de estar al alcance de la heliosismología.

ABSTRACT. A previous comparison of thermodynamical quantities, computed in the chemical and physical pictures, revealed a remarkable agreement in the H and He ionization zones of the Sun, despite the radically different treatment of bound states in the two formalisms. This agreement was due to an unexpectedly dominating (classical) Coulomb pressure term. New comparisons, for higher temperatures and densities, and for a representative solar mixture (H, He and O), have demonstrated substantial differences in the O-ionization fractions. Also, the thermodynamic quantities reflect these differences to a degree that is within reach of helioseismology.

Key words: EQUATION OF STATE – STARS: INTERIOR

1. INTRODUCTION

There are two basic approaches to the equation of state for stellar envelopes and interiors. Both want to realize the same goal, equilibrium statistical mechanics of reacting plasmas, but their methods differ. The traditional method chooses the so-called "chemical picture", in which the notion of atoms is maintained despite the plasma environment. A mixture of atoms, molecules, ions, electrons and nuclei is considered, and the occurring ionization and dissociation reactions (thus the name chemical picture) are treated according to the entropy-maximum (or free-energy-minimum) principle, which is, in the language of the astrophysicists, the Saha equation. Interactions of the plasma with atoms and ions are introduced separately in a heuristic way. The more recent, alternative method is based on the so-called "physical picture" where only fundamental particles (electrons, nuclei) explicitly enter. Furthermore, through the means of activity expansions, the problems of plasma physics and statistical mechanics are treated simultaneously and on the same footing.

The international "Opacity Project" (OP, see Seaton, 1987) uses the Mihalas, Hummer and Däppen equation of state (Hummer and Mihalas, 1988; Mihalas, Däppen and Hummer, 1988; Däppen *et al.*, 1988; hereinafter MHD) realized in the chemical picture. The opacity effort pursued at Livermore (OPAL) uses an equation of state realized in the physical picture (Rogers, 1986; hereinafter Livermore equation of state). It is clear that the equation of state plays an important role in any opacity calculation because it predicts both level populations and ionization degrees. Therefore, equation-of-state comparisons are an important part of opacity comparisons. Only such a parallel comparison will allow us to disentangle discrepancies that arise from different treatments of atomic physics and statistical mechanics. Equation-of-state comparisons are also needed because, to the desired level of accuracy, there are so far no laboratory experiments that can discriminate between one or the other formalism. There is hope that solar oscillations could be used to put constraints on thermodynamical quantities and thus on the equation of state (Christensen-Dalsgaard and Däppen, 1992), but, at the moment, comparisons of theoretical formalisms are the only means to estimate the part of the opacity uncertainty that is due to the equation of state.

In the following, I discuss what has so far emerged from such comparisons. While earlier comparisons showed a striking agreement between the MHD and Livermore equation of state for conditions as found in the hydrogen-helium ionization zones of the Sun (Däppen, Lebreton and Rogers, 1990; Däppen, 1990), it turned out later that this agreement was nearly accidental. Of course, solar physicists were happy that two completely different formalisms delivered the same equation of state, but, by the same token, a first attempt to use the Sun as a test was also thwarted. Nevertheless, from these first comparisons a practically useful simple equation of state has resulted, which mimics several features of the more complete formalism (see section 3.1). Recently, Forrest Rogers and I have extended these comparisons to higher densities and also beyond the simple hydrogen-helium mixtures by including a representative heavy element. I will show and discuss the results of these new comparisons which establish the heavy elements, despite their small abundance, as first candidates for an astrophysical test of the chemical and physical picture.

2. CHEMICAL AND PHYSICAL PICTURE

2.1. The MHD equation of state

In the chemical picture, perturbed atoms must be introduced on a more-or-less *ad-hoc* basis to avoid the familiar divergence of internal partition functions (see, for example Ebeling *et al.*, 1976). In other words, the approximation of unperturbed atoms precludes the application of standard statistical mechanics, i.e. the attribution of a Boltzmann factor to each atomic state. The conventional remedy of the chemical picture against this is a modification of the atomic states, e.g. by cutting off the highly excited states in function of density and temperature of the plasma. Such cut-offs, however, have in general dire consequences due to the discrete nature of the atomic spectrum, i.e. jumps in the number of excited states (and thus in the partition functions and in the free energy) despite smoothly varying external parameters (temperature and density).

The MHD equation of state avoids these discontinuities (in the free energy) by introducing 'soft' cut-offs in the form of occupational probabilities. These occupation probabilities have the same function as the 'hard' cut-offs, that is *they indicate how we imagine that atomic states in a plasma are modified.* Once this description of states is adopted, one applies statistical mechanics as usual using Boltzmann factors.

The MHD equation of state is further characterized by detailed internal partition functions of a large number of atomic, ionic and molecular species. Full *thermodynamic* consistency is assured by analytical expressions of the free energy and its first- and second-order derivatives. This not only allows an efficient Newton-Raphson minimization, but, in addition, the ensuing thermodynamic quantities are of analytical precision and can therefore be differentiated once more, this time numerically. Reliable third-order thermodynamic quantities are thus calculated.

In the occupation probabilities, perturbations by charged and neutral particles are taken into account. Correlations between the two effects are neglected (for lack of knowing how to describe them); thus the occupation probabilities due to charged and neutral perturbers are simply multiplied. The resulting weighted internal partition functions Z_s^{internal} of species s are (with is labelling the state i of species s)

$$Z_s^{\text{internal}} = \sum_i w_{is} g_{is} \exp\left[-\frac{E_{is} - E_{1s}}{kT}\right] \tag{1}$$

The coefficients w_{is} take into account charged and neutral surrounding particles. In physical terms, w_{is} gives the fraction of all particles of species s that can exist in state i with an electron bound to the atom or ion, and

$1 - w_{is}$ gives the fraction of those that are so heavily perturbed by nearby neighbours that the state is effectively destroyed and its electrons dissolved into the continuum. Perturbations by neutral particles are based on an excluded volume treatment, and perturbations by charges are calculated from a fit to a quantum-mechanical Stark-ionization theory. The choice of Hummer and Mihalas (1988) has been

$$\ln w_{is} = -\left(\frac{4\pi}{3V}\right)\left\{\sum_{\nu} N_\nu (r_{is} + r_{1\nu})^3 + 16\left[\frac{(Z_s+1)e^2}{\chi_{is} k_{is}^{1/2}}\right]^3 \sum_{\alpha \neq e} N_\alpha Z_\alpha^{3/2}\right\} . \tag{2}$$

Here, the index ν runs over neutral particles, the index α runs over charged ions (except electrons), r_{is} is the radius assigned to a particle in state i of species s, χ_{is} is the (positive) binding energy of such a particle, k_{is} is a quantum-mechanical correction of order unity and Z_s is the net charge of a particle of species s. Note that $\ln w_{is} \propto -n^6$ for large principal quantum numbers n (of state i), and hence provides a (density-dependent) cutoff for Z_s^{internal}. Finally, the MHD equation of state also includes a Debye-Hückel term for the Coulomb-pressure correction, partially degenerate electrons and radiation pressure.

2.2. The Livermore equation of state

It is clear from the preceding subsection that the advantage of the chemical picture lies in the possibility to model complicated plasmas and to obtain numerically smooth and consistent thermodynamical quantities. Nevertheless, the heuristic method of the separation of the atomic-physics problem from that of statistical mechanics is not satisfactory, and attempts have been made to avoid the concept of a perturbed atom in a plasma altogether. This has suggested an alternative description, the physical picture, in which only fundamental particles (electrons and nuclei) explicitly appear. Since no chemical and ionization reactions have to be controlled, there is nothing that prevents the use of the otherwise practical grand-canonical partition function. (The fact that the grand-canonical partition function is expressed in terms of the chemical potential would be in the way of an easy description of reactions.) Based on this idea, a theory of partially ionized plasmas, similar to the well-known cluster expansions for real gases, was developed (Rogers, 1981; for an introduction into cluster expansions see Huang, 1963).

To explain the advantages of this approach for partially ionized plasmas, it is instructive to discuss the activity expansion for gaseous hydrogen. The interactions in this case are all short ranged and the pressure is determined from a self-consistent solution of the equations (Hill, 1960)

$$\frac{p}{kT} = z + z^2 b_2 + z^3 b_3 + \ldots \tag{3}$$

$$\rho = \frac{z}{kT}\left(\frac{\partial p}{\partial z}\right) \tag{4}$$

where $z = \lambda^{-3}\exp(\mu/kT)$ is the activity, $\lambda \equiv h/\sqrt{2\pi m_e kT}$ is the thermal (de Broglie) wavelength of electrons, μ is the chemical potential and T is the temperature. The b_n are cluster coefficients such that b_2 includes all two particle states, b_3 includes all three particle states, etc. The second cluster coefficient for hydrogen includes the formation of H_2 molecules as well as scattering states in the $^1\Sigma_g$ potential. It also includes scattering states in the $^3\Sigma_u$ potential and all excited electronic-state potentials. The third cluster coefficient includes H_3 bound states, $H - H_2$ and $H - H - H$ scattering states. Equation (3) demonstrates that the equation of state for associating gases can be obtained without an explicit knowledge of the occupation numbers of associate pairs. Further details can be found in Rogers (1981, 1986) and also in the review by Däppen, Keady and Rogers (1990).

To illustrate how the physical picture allows avoiding the divergences that plague the chemical picture, I note that b_2 is convergent because the bound state part of b_2 is divergent, but the scattering state part, which is normally omitted in the chemical approach (e.g. in MHD), has a compensating divergence. Consequently the total b_2 does not contain a divergence of this type (Ebeling, Kraeft, and Kremp, 1976; Rogers, 1977). A major advantage of the physical picture is that it incorporates this compensation at the outset. As a result, the Boltzmann sum appearing in the atomic (ionic) free energy is replaced with the so-called Planck-Larkin partition function (PLPF), given by (Ebeling, Kraeft, and Kremp, 1976)

$$\text{PLPF} = \sum_{nl}(2l+1)\left[\exp\left(-\frac{E_{nl}}{kT}\right) - 1 + \frac{E_{nl}}{kT}\right] . \tag{5}$$

The PLPF is convergent without additional cut-off criteria as are required in the chemical picture. I stress, however, that despite its name the PLPF is not a partition function but merely an auxiliary term in a virial coefficient (see Däppen, Anderson and Mihalas, 1987).

3. RESULTS FROM COMPARISONS

3.1. Reference equations of state

Let me first present the two different reference equations of state that appear in this section. The first is the Eggleton, Faulkner and Flannery (1973) equation of state (EFF), which is realized in the chemical picture. It describes a mixture of ideal gases (including partially degenerate electrons), and determines the ionization equilibrium by the simple Saha equation with ground-state partition functions of the bound systems. In addition to the simple Saha equation of state, it incorporates an artificial pressure ionization term but no Coulomb-pressure correction. It starts out from a model of a free-energy, and therefore all resulting thermodynamic quantities are consistent.

As mentioned in the introduction and shown below in section 3.2, the result of the first low-density comparisons was that in the hydrogen-helium ionization zones the Coulomb-pressure correction is the dominant non-ideal contribution. Thus guided, Jørgen Christensen-Dalsgaard and I have upgraded the EFF equation of state by adding a Coulomb-pressure term (in its standard Debye-Hückel form, as in MHD). We have called this improved equation of state CEFF, to symbolize the Coulomb term. As expected, the CEFF equation of state performs well in solar models (Christensen-Dalsgaard, 1991; Christensen-Dalsgaard and Däppen, 1992), yet it is simple enough to be used as a convenient reference equation of state.

3.2. Previous low-density H-He comparisons

For convenience, a representative result from Däppen, Lebreton and Rogers (1990) is shown in Figure 1, which compares MHD and Livermore with the simple EFF equation of state.

The absolute curves of part *a* are merely able to show the difference between MHD (or Livermore) and EFF results. The difference between the MHD and Livermore results is alone visible in the magnified part *b*, which shows the *relative* differences between MHD and EFF, and between Livermore and EFF values. This relative plot not only now allows us to see the difference between MHD and Livermore results clearly, but also to realize their striking similarity.

By varying the parameters of the MHD equation of state (see Däppen, 1990), the ***physical reason*** of this agreement was found to be that, on the chosen isochore, all thermodynamical quantities are mainly dominated by the Coulomb pressure correction. This correction overshadows the effect of the excited states (which are of course treated differently in the MHD and Livermore approach). However, the Coulomb term acts principally indirectly, because it is not mainly the free-energy of the Debye-Hückel term itself (it would be 1-2 orders of magnitude too weak) but rather the Coulomb-term induced shift in the ionization equilibrium, which is responsible for the deviation from the unperturbed EFF result. Why the excited states in MHD have so little influence has not yet been satisfactorily demonstrated. Indeed, an elementary estimation of the shift of the ionization equilibrium due to all the excited states contained in the MHD partition functions shows that this shift, taken alone, should be at least comparable to that due to the Coulomb term. That this is not the case when the two contributions are brought together could indicate an accidental cancellation within the MHD formalism (at the chosen temperature and density).

3.3. Present comparisons

While the rather striking agreement shown above is important for solar physics, it also follows that the hydrogen-helium ionization zones of the Sun cannot be used as an observational test that could discriminate between the MHD and Livermore equations of state. (In contrast, solar oscillations clearly distinguish between the MHD

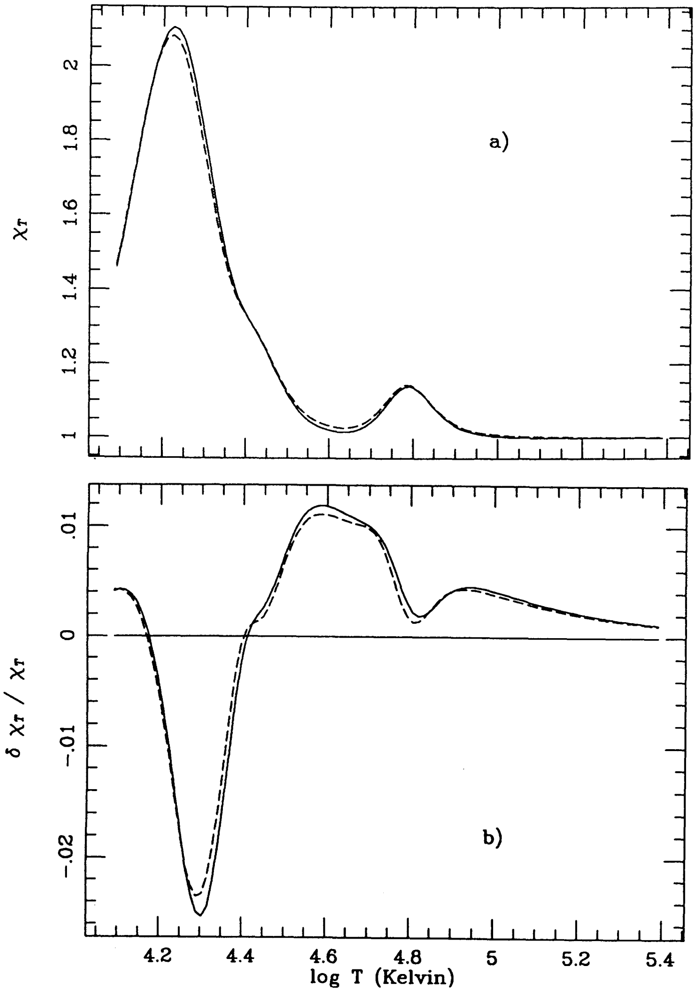

Fig. 1. Comparison of the logarithmic pressure derivative $\chi_T = (\partial \ln p / \partial \ln T)_\rho$ on an isochore with $\rho = 10^{-5.5}$ g cm^{-3}. Part *a* shows absolute values; the solid line representing EFF and the dashed line MHD. The chemical composition is hydrogen and helium only, with number abundances of 90% H and 10% He. The Livermore result would lie indistinguishable on the MHD curve. Part *b* magnifies the effect by showing the relative differences between Livermore and EFF values, i.e. $(\chi_T^{Livermore} - \chi_T^{EFF})/\chi_T^{EFF}$ (solid line) and between MHD and EFF values, i.e. $(\chi_T^{MHD} - \chi_T^{EFF})/\chi_T^{EFF}$ (dashed line). Other thermodynamic quantities essentially show the same behaviour. (From Däppen, Lebreton and Rogers, 1990.)

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and EFF equation of state, see Christensen-Dalsgaard *et al.*, 1988.) Looking for testable manifestations of the influence of internal partition functions, Forrest Rogers and I have extended our comparison to higher densities and, for the first time, beyond H-He mixtures.

3.3.1. Intermediate- and high-density H-He comparison

Figures 2 and 3 show analogous results for an intermediate-density ($\rho = 0.1$ g cm^{-3}) and a higher-density ($\rho = 1.0$ g cm^{-3}) isochore. The display is essentially as in Fig. 1; however, this time Γ_1 is shown, and CEFF (see section 3.1) has replaced EFF. More detailed results, also for other thermodynamic quantities, will be published elsewhere.

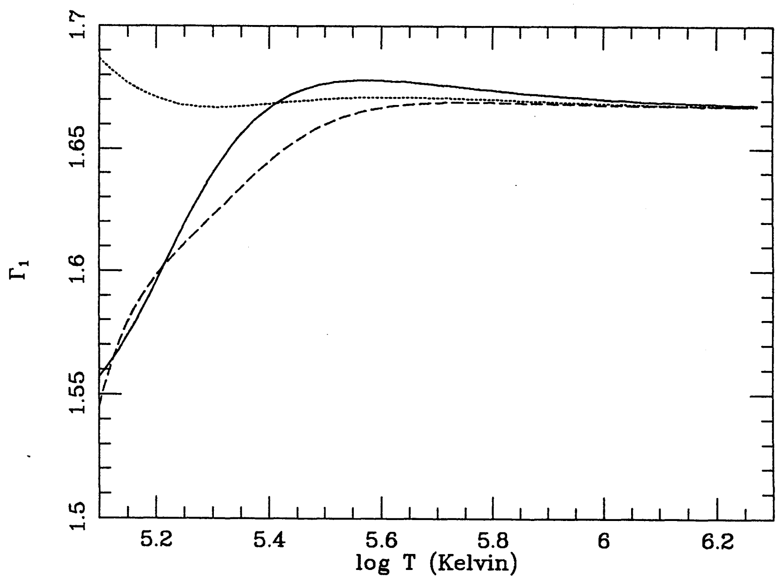

Fig. 2. Γ_1 for $\rho = 0.1$ g cm^{-3} for the mixture of Fig. 1. The solid line denotes the CEFF, the dashed the MHD and the dotted the Livermore equation of state.

3.3.2. A first case involving a heavy element

Forrest Rogers and I have compared results for a H, He and O mixture. Density has been chosen as $\rho = 0.005$ g cm^{-3}, suggested from a study on the solar helium abundance (Christensen-Dalsgaard *et al.*, 1992). Figure 4 shows the result for Γ_1 (more detailed results will be published elsewhere). Here, the large MHD partition functions not only cause shifts in the ionization balance but also a propagation of these shifts into thermodynamic quantities. Despite their small relative number in the mixture, the heavy elements cause a distinct discrepancy, which appears to be within reach of helioseismology (Christensen-Dalsgaard and Däppen, 1992). To examine the MHD ionization fractions, I have run a single case ($T = 2.10 \times 10^5 K$, $\rho = 5.00 \times 10^{-3}$g cm^{-3}), once with the full MHD equation of state, once with a "stripped-down" version of MHD which does not contain any excited states (but is otherwise identical). The resulting ionization fractions of O^{3+}, O^{4+}, O^{5+} were, respectively, 0.314, 0.248, 0.364 for the stripped-down MHD (without excited states) and 0.304, 0.476, 0.182 for the full MHD. (The result for the stripped-down very closely reflects the ground-state weights of the ions.) Not unexpectedly in view of the Planck-Larkin partition function, the Livermore equation of state predicts ionization fractions close to those of the stripped-down MHD equation of state (Rogers, *private communication*).

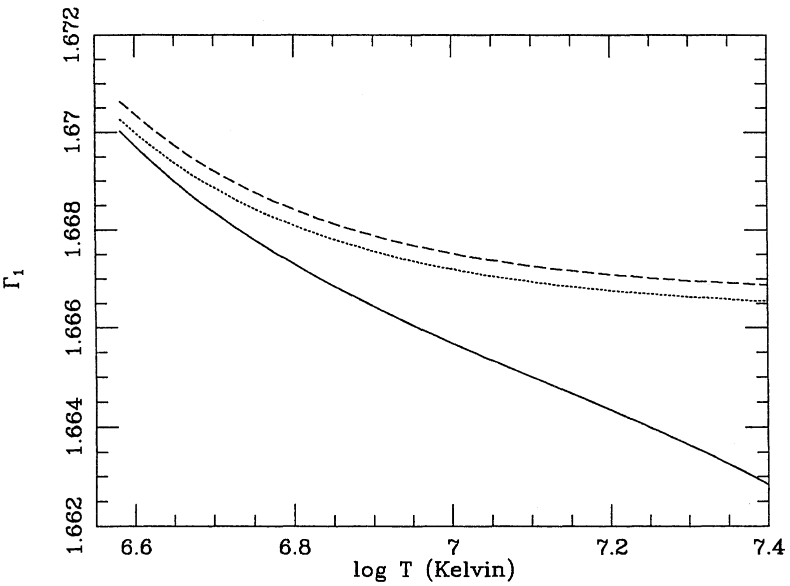

Fig. 3. Same as in Figure 2, but for $\rho = 1.0$ g cm^{-3}.

4. DISCUSSION AND CONCLUSIONS

The first low-density comparisons concentrated on the case of conditions as found in the H-He ionization zones of the Sun. This was motivated by a successful modelling of solar oscillation with the MHD equation of state (Christensen-Dalsgaard *et al.*, 1988). It was seen that the major part of the improvement over simple equations of state came from the different thermodynamic quantities in the H-He ionization zones. The comparison with the Livermore equation of state was therefore, in the first place, intended to confirm this success with an independent, alternative approach. However, as a second goal, a solar test of the equation of state was also envisaged.

The ensuing virtually perfect low-density agreement was by no means expected, and, even when it turned out that it was essentially due to the Coulomb interaction (contained both in the MHD and Livermore equations of state), it is still somewhat mysterious. At the selected temperature and density, the number of excited states in the MHD formalism, when compared to the admittedly large Boltzmann weight of the ground state, would predict a sizeable shift in the ionization balance, at least of the same order of magnitude as that due to the Coulomb pressure. The implicit cancellation of the contribution of the partition functions in the thermodynamic quantities is therefore perhaps accidental.

In the case of higher temperatures and densities ($\rho = 0.01$ to 10 g cm^{-3}), there is good agreement for *solar conditions*, that is for temperatures such as those found in the Sun at these densities. However, the Sun just marginally passes: for slightly less massive stars, the discrepancy soon becomes very important indeed. In the case of heavier elements, for the first time, Forrest Rogers and I succeeded in establishing a clear case of disagreement between the MHD and Livermore results. It follows that for a solar composition and, for example, $T = 2.10 \times 10^5 K, \rho = 5.00 \times 10^{-3}$g cm^{-3} the predicted MHD and Livermore ionization degrees of C, N and O are drastically different, with the Livermore values lying closer to the simple Saha results. Clearly, the origin of the discrepancy in the ionization degrees is due to the treatment of the excited states.

Of course, only some 2 percent of the matter in the Sun consists of elements heavier that H and He, and therefore the signature of the MHD-Livermore discrepancy on thermodynamic quantities (Fig. 4) is small (of the order of 10^{-3}). Since the Livermore equation of state contains higher-order Coulomb terms beyond the Debye-Hückel approximation, we have had to verify that the net difference of the thermodynamic quantities does not originate from these higher terms, which have no analogon in the MHD formalism. A run of the same case with the Livermore equation of state in the Debye-Hückel approximation has essentially given the same results.

Thermodynamic quantities can therefore reflect the excited states of the MHD formalism, and the ensuing sound-speed differences seem to be within reach of a helioseismological diagnosis (Christensen-Dalsgaard

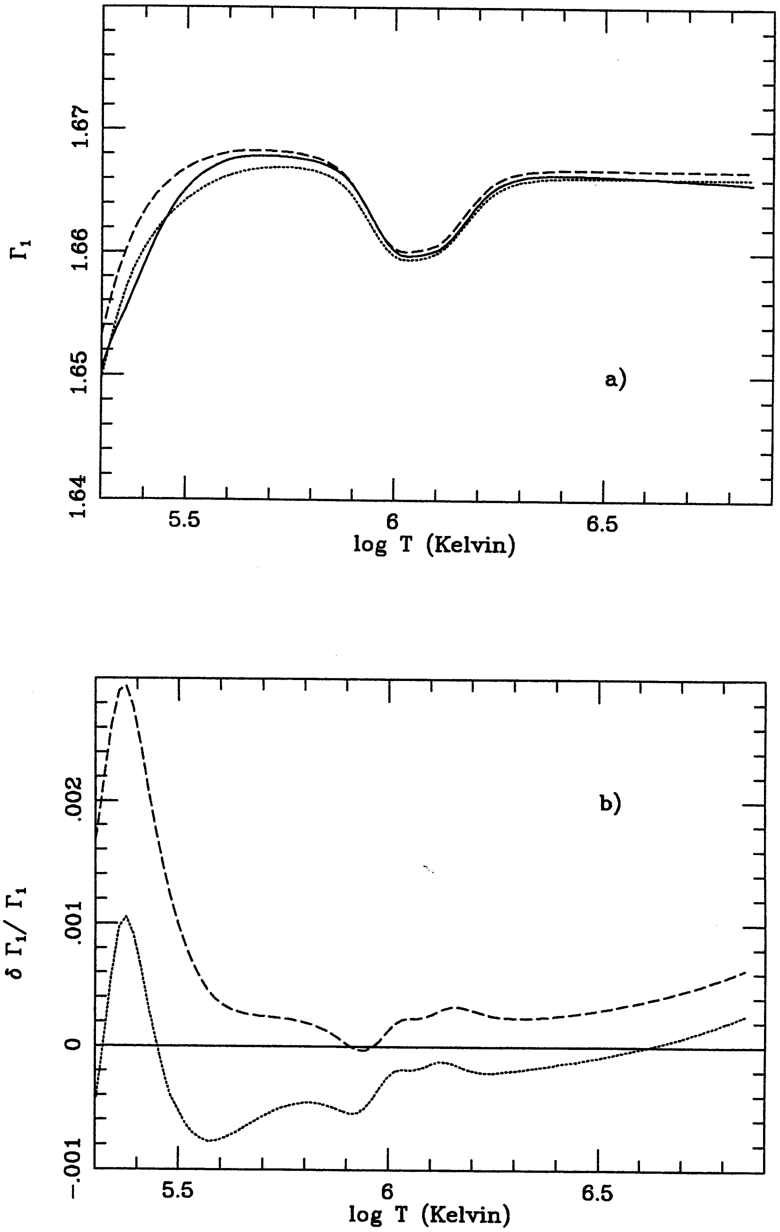

Fig. 4. Same as in Figure 3, but for $\rho = 5.00 \times 10^{-3}$g cm^{-3} and a different chemical composition (a representative solar mixture of H, He and O, with mass abundances of 0.7429, 0.2371, 0.0200, respectively). Part a) shows absolute values, part b) relative differences with respect to the CEFF equation of state similar as in Fig.1b (dashed: MHD, dotted: Livermore).

and Däppen, 1992). Furthermore, in the (quite localized) zones where the full MHD treatment yields distinctly different ionization fractions, opacity will undoubtedly also be influenced by this equation of state issue. Stellar cases might then be found that could test the equation of state via opacity.

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