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THE OPACITY PROJECT – EQUATION OF STATE

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RESUMEN. Se describe brevemente la ecuación de estado que se utiliza en los cálculos de opacidades del Proyecto de la Opacidad.

ABSTRACT. The equation of state used in the opacity calculations of the Opacity Project is described briefly.

Key words: EQUATION OF STATE – OPACITIES

I. THE EQUATION OF STATE IN ASTROPHYSICS

The need for an equation of state (EOS) occurs in many areas of astrophysics. If we restrict attention primarily to stellar astrophysics then we encounter the EOS heavily in two applications: (1) stellar evolution and hydrodynamics codes and (2) calculation of opacities.

In stellar evolution codes we always require a *mechanical EOS* of the form $p = p(\rho,T)$ and a *caloric EOS* of the form $e = e(\rho,T)$. Here p is pressure, e is material energy density, ρ is density, and T is temperature. Depending on the physical conditions addressed, the underlying physics may be simple (essentially ideal gas) or complex (relativistic, degenerate, phase transitions, ...). Most evolution codes use some form of a Henyey method so we also need quantitites like $(\partial p/\partial T)_\rho$, $(\partial p/\partial \rho)_T$, $(\partial e/\partial T)_\rho$, and $(\partial e/\partial \rho)_T$. At a practical level, the tables for p and e and their derivatives must be *smooth* so that reasonable derivatives can be estimated for the Henyey procedure; otherwise the evolution code will just crash. For stellar stability analyses we require quantities like the specific heats c_v and c_p, and the generalized adiabatic gradients Γ_1, Γ_2, Γ_3. These depend upon the next higher level of derivatives of p, e, and the derivatives given above, and are therefore even more demanding on the smoothness (differentiability) of the calculated EOS.

For stellar opacities we require the *occupation numbers* N_{ijk} of the excitation states i of the ion stages j of each chemical element k in the mix so that we can add up the absorption from all atoms, ions, and molecules present. In the EOS calculation itself it is much more convenient and economical to work with total *ion densities* N_{jk}, from which the occupation numbers can be reconstructed at a later time.

II. THE FREE ENERGY METHOD

(a) Basic Physical Picture

For the thermodynamic equilibrium of an ideal gas we can in principle use the Boltzmann-Saha equations. (Even then we face the problem of divergent partition functions). But to work at higher densities we need to account for nonideal effects resulting from various types of interactions amongst the particles in the plasma.

Two basic formalisms have been developed, one using the *physical picture* (see the paper by F. Rogers in this volume). The other involves the *chemical picture* in which one makes two key assumptions: (1) that one can identify *clusters* of fundamental particles as entities such as "molecules," "atoms," or "ions," and (2) that the partition function of the canonical ensemble is factorizeable, i.e.

$$Z = Z_{\mathrm{trans}} \cdot Z_{\mathrm{internal}} \cdot Z_{\mathrm{config}} \quad . \tag{1}$$

Clearly both of these assumptions must break down at sufficiently high densities, at sufficiently low temperatures. For example, at high density and low temperature, material is found in a crystal lattice, in which electrons are not bound to individual nuclei but are free to roam in conduction bands formed from the coalescence of many isolated-atom eigenstates. Thus, the distinction between "bound" and "free" electrons becomes blurred. Likewise equation (1) must fail at sufficiently high densities because the atomic/molecular eigenvalues can become functions of ρ and T, or put another way, the same physical effects that determine Z_{config} may influence Z_{internal} significantly.

(b) Methodology

The free energy method is usually implemented along the lines pioneered by Gilda Harris (1-5) and has been elaborated by many other authors (6-9). One notes that for given T, V, and chemical composition, thermodynamic equilibrium is achieved when the Helmholtz free energy F achieves an absolute minimum with respect to allowed variations of the complete set of ion densities $\{N_{jk}\}$. The interactions are in general strongly nonlinear, so one resorts to a numerical iteration scheme, preferably a second-order scheme like Newton-Raphson, to determine the appropriate ion densities. A detailed description of the methods we have used is given in (10-12), so we will make only a few brief comments here.

The free energy of a mixture of gases is

$$F \equiv - kT \sum_{s} N_s \,\ell n\, Z_s \tag{2}$$

where "s" denotes "species" (i.e. a specific ion of a specific element) and the sum extends overall physically allowable species. If we assume that Z is factorizeable, then F is *modular*

$$F = F_1 + F_2 + F_3 + F_4 \tag{3}$$

which is convenient because then different physical pieces can be put into separate subroutines. We used (thus far) four contributions to F:

F_1: translational motions of classical point particles (nuclei),

F_2: internal energy of all molecules, atoms, ions, summed over all rotation, vibration, and electronic excitation states

F_3: translational motions of partially degenerate electrons

F_4: coulomb interactions among free charged particles.

F_1 and F_3 are standard; F_4 comes from (6). F_2 is the difficult term because the sum over all eigenstates of an unperturbed atom or ion is infinite, some kind of (physically sensible) "cutoff" procedure is needed. In our work we used special care to get *analytic* (differentiable to all orders) mathematical representations of the F's. This assures smoothness of F and all its derivatives for stellar evolution work, and also allows us to use analytical derivatives in the Newton-Raphson procedure, which enhances convergence.

(c) The Internal Partition Function

The fundamental problem to be overcome in a practical implementation of the free energy method is that the sum

$$Z_s = \sum_{i} g_{is}\, e^{-Eis/kT} \tag{4}$$

diverges for atoms and ions. On the other hand, common sense tells us that this divergence must be only formal, not physical, because for an atom in any real environment, high quantum-number states must be strongly perturbed, and eventually destroyed, by neighboring particles once their radii are of the same order as the interparticle separation. Thus we must introduce some kind of cutoff in the sum in equation (4).

Several cutoff procedures have been proposed over the years.

(1) Fixed n_{max}; stop the sum at some prechosen n_{max}. This idea is clearly unphysical because we know that n_{max} must be $f(\rho)$.

(2) Use a Debye-shielded potential (which has a finite number of eigenstates) as the atomic potential. This approach is unsatisfactory because (a) eigenstates disappear unto the continuum abruptly, which produces discontinuties in F, hence δ-functions in the derivatives of F, and worse behavior in the higher derivatives; and (b) the large density-dependent lineshifts predicted by this model are *not* observed (**10**). Indeed it can easily be shown that a Debye potential is *not* a valid *intra*-atomic potential under any realizable conditions (**10**).

(3) Confined-atom model where the atom resides in a square-well potential whose radius depends on the interatomic spacing. Again this is an unphysical potential leading to a discontinuous F as in (2) above. Further, this model makes no distinction between charged and neutral perturbers, which one knows is unphysical.

Both laboratory and astronomical spectroscopy can provide direct guidance on how to proceed. For example, if one observes the spectra of A-type supergiants, dwarfs, and white dwarfs in the region of the confluence of the upper Balmer-series lines into the continuum, one finds that as the density of the atmosphere increases, we see fewer and fewer lines in the series. For supergiants one sees up to $n' \approx 40$, in a dwarf one sees $n' \approx 16$, and in a white dwarf to $n' \approx 8$. Heuristically one has the picture that the upper states suffer *disruption*, *broadening*, and *dissolution*, and that at and above some critical ρ all states with $n \geq n_{max}(\rho)$ will *merge* and/or *dissolve* into a pseudocontinuum which merges continuously with the "real" continuum.

Thus from the point of view of reproducing the *observable* optical properties of the material, it seems reasonable to assign an *occupation probability* w_{is} to state i of species defined such that w_{is} gives the fraction of atoms/ions in that state which are *not* disrupted by the fluctuating fields from interactions with other particles during the lifetime of the state. We then rewrite the internal partition functions as

$$Z^*_s = \sum_i w_{is}\, g_{is}\, e^{-Eis/kT} \tag{5}$$

(d) Occupation Probabilities

We know qualitatively that the more loosely-bound states are more easily destroyed, which implies that w should be essentially unity for the most deeply bound states, then drop rapidly at some characteristic $n_{max}(\rho)$, and be essentially zero for $n \gtrsim n_{max}$. Clearly such a probability distribution keeps Z^* bounded. We must require w to be: (a) a physically sound function of particle density, electron binding energy, ...; (b) continuous and differentiable.

The two problems we now face are: (a) what physical theory do we use to compute w, and (b) how do we assure that the procedure outlined above is statistical-mechanically consistent? In (**10**) we calculated w as the result (i.e. the product) of the probabilities of two independent physical processes: (a) neutral-neutral interactions using a hard-sphere model; and (b) stark ionization produced by charged perturbers. In the latter we have used a full quantum mechanical theory to calculate level crossings and the resulting escape probability. In our initial work we made the nearest-neighbor approximation for the microfield distribution; at present we can use detailed distribution functions including plasma correlation effects.

If we were simply to choose some w_{is} in Z^*_s out of "thin air," the resulting theory would be inconsistent and *ad hoc*. But a rigorous basis for the occupation probability formalism was provided long ago by Fermi (**13**), Urey (**14**), and Fowler (**15**). Fermi showed the essence of the problem by considering a single-species gas, which Fowler generalized to include multiple ion stages of several chemical species; Urey worked in terms of fugacity and a virial expansion technique.

Following Fermi, write the free-energy of a single-species gas as

$$F = -nkT\ (3/2\ell n\ T + \ell n\ V + \ell n\ G + 1) + \sum_i n_i \epsilon_i + kT \sum_i n_i\ \ell n\ n_i \tag{6}$$

where $n = \sum_i n_i$. Now add a *nonideal* term $f(T, V, \{n_i\})$ to equation (6). Then one can show

$$\frac{n_i}{n} = \exp[-(\epsilon_i + \frac{\partial f}{\partial n_i})/kT]/\tilde{Z} \tag{7}$$

where

$$\tilde{Z} \equiv \sum_i \exp[-(\epsilon_i + \frac{\partial f}{\partial n_i})/kT]. \tag{8}$$

We see that equation (8) is exactly of the form as equation (5) if we just identify

$$w_i \equiv \exp(-\frac{\partial f}{\partial n_i}/kT). \tag{9}$$

Using (7) and (8) back in (6) we get

$$F = -nkT\ (3/2\ \ell n\ T + \ell n\ V - \ell n\ n + \ell n\ G + 1) - nkT\ \ell n\ Z^* \\ + (f - \sum_i n_i \frac{\partial f}{\partial n_i}) \tag{10}$$

From Fermi's analysis (and Fowler's generalization) we can draw the following conclusions:

(1) if there is a nonideal interaction, then the partition function must contain an occupation probability of the form of equation (9);

(2) if the strength of the perturbation increases with perturber density and the quantum number of the bound state, then $w_i \to 0$ as $n \to \infty$;

(3) if the interaction is linear in the perturber density, then the last term of equation (10) is zero, and the *whole* effect of f is taken care of in Z^*.

The condition of linearity stated above is true for *coulomb* interactions where only the *charge* of a perturber, not its quantum state, matters. It will also be true for neutral-neutral interactions if we can make the *low-excitation approximation*, i.e. assume that the great majority of atoms interacting with an atom in an excited state will be in their ground state; see (**10**).

In short, the occupation probability formalism, through originally motivated by experimental results and heuristic arguments, is actually a necessary *consequence* of the existence of non-ideal interactions. Further, if the interactions are linear (or linearizable) in the perturber densities, it is *statistical-mechanically consistent to modify only* Z^*_s. Thus, to within the accuracy of the basic assumptions stated back in §IIa, this theory is logically consistent.

Our advantage of this theory is that the w's can be used directly in the modeling of plasma spectra (**16, 17**). Detailed comparison with the data in (**18**) shows excellent agreement between theory and experiment for the Balmer-line confluence region of the spectrum. It should also be noted that this theory is not an expansion procedure; there are no subtle subtractions, cancellations, or renormalizations needed. Rather, one can treat directly and consistently the fully nonlinear problem, and then make a direct connection through optical properties with experiment.

III. CRITIQUE

The free energy method clearly must break down at very high densities. As mentioned before, an archetype would be the crystal lattice where the question of an electron being "bound" or "unbound" obviously becomes meaningless. Indeed even at much lower densities in a plasma the split into bound/unbound electrons becomes very ambiguous. The problem is well illustrated in a diagram by Busquet (**19**) showing several different hypothetical electron paths through a plasma. When an electron completes several complete circuits (orbits) about an ion, it may fairly be considered to be "bound" to that ion. If an electron shoots by all ions on a (locally) hyperbolic trajectory, it may fairly be considered to be "unbound." But if the trajectory carries an electron on, say, one or two revolutions around one ion, then, say, it migrates to another, does another loop or two, then, say, migrates past several ions before orbiting briefly around yet another ion, we can say only that it is "quasi-bound," or is wandering about on an equipotential surface reminiscent of a Fermi surface.

Put another way, the occupation probability method gives completely unambiguous answers when $w \approx 1$ or $w << 1$; in between, some ambiguity (and error) is unavoidable. On the other hand, the energy range ΔE, or the corresponding range in quantum number Δn, over which w drops from essentially unity to almost zero is very narrow; in fact we always have $\Delta n < 1$. Thus for calculating ionization equilibria the effect of this transition range is very small. For calculating opacities the error is negligible if we use the w's to fade out "line" opacity into an appropriate "continuum" opacity, because total oscillator strength is conserved. All we are doing is changing the *profile* determining how this oscillator strength is distributed. What happens physically is that as w for some level drops well below unity, any line component from that level will be very strongly broadened, indeed overlapping with adjacent lines, and is effectively smeared out into the continuum.

The very different activity – expansion methods used by the Livermore group in their EOS work are discussed extensively by Rogers elsewhere in this volume. One who examines that theory will find (not surprisingly) that it also has certain difficulties. And it is natural to ask "which theory should we believe?"

My own answer to that question is "neither," along with the remark that *belief* belongs in theology, not science. Rather, our task to develop the logical consequences of these theories as completely as possible, and then *test* them with *experiment* and *observation*. In the first category we need analyses of laboratory spectra, preferably at much higher densities than Wiese, et al. (**18**). In the second category we have modeling of white dwarf spectra (high density), solar oscillations, and stellar pulsation.

At the risk of pointing out the obvious, I predict that the next few years in stellar astrophysics will be very exciting as our new EOS and opacity results are used by the community.

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