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An Introduction to
Two-Temperature Equations of State

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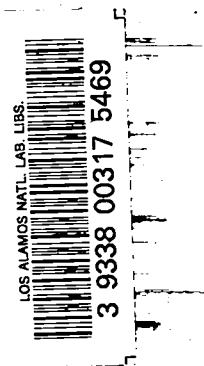This report was not edited by the Technical Information staff.

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by

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ABSTRACT

In this report we present a brief introduction
to two-temperature equations of state. We also dis-
cuss current capabilities of T-4 in this area as
well as plans for future development. In addition,
we point out various conceptual and practical dif-
ficulties in implementing a two-temperature approxi-
mation.

I. INTRODUCTION

Within LASL and elsewhere two-temperature equations of state (EOS) are used
for modeling systems which are not in local thermodynamic equilibrium (non-LTE).
The purpose of this report is: (i) to briefly define what is meant by a two-
temperature EOS, (ii) to discuss current capabilities of T-4 in this area as well
as plans for future development, and (iii) to point out that a two-temperature
EOS is not always a good approximation. In addition we present the results of a
study which demonstrate some technical problems that a user must surmount in the
current method of implementing a two-temperature EOS.

To motivate our discussion we will now briefly mention one possible applica-
tion for using a two-temperature scheme. The discussion of this application,
which is highly oversimplified and leaves out many important considerations, is
used for didactic purposes only and we hope that the reader will not be distract-
ed by side issues.

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Consider shining a high intensity laser (in the visible region of the frequency spectrum) at some target. In elementary quantum mechanics one learns to expect such radiation to deposit energy in the material of the target by means of electronic excitations (e.g., dipole transitions in atoms) and that such processes occur on a very fast time scale ($\sim 10^{-8}$ sec). Assume that this happens and then turn off the laser.

Most of the deposited energy is now concentrated in what we will call the "electron system". We know, however, that there are many other degrees of freedom besides electronic excitations. Since these are usually associated with ion motion, we will call them the "ion system". Typical examples of the latter type of excitations include translational degrees of freedom of the ions (we may normally think of ions as the positively charged nuclei plus the bound electrons which adiabatically follow the nuclei), the rotations and vibrations of molecules, and the phonons in crystalline phases.

If the electronic excitations are more strongly coupled to themselves than to ionic excitations, we may reasonably attempt to model the nonequilibrium state of the target as a quasi-independent system of electrons at some temperature T_e which is different from (and in our application higher than) a temperature T_i of a second quasi-independent system, the ions. This is the two-temperature approximation. Within this scheme the approach to equilibrium of the target, after the laser is turned off, is described by the relaxation of the two subsystems to a common temperature $T_e = T_i = T$.

From the above application we generalize our observations to conclude that there are two conditions which must be met for a two-temperature approximation to be useful. First, we must be able to divide our general system into two weakly coupled quasi-independent systems. Second, we must establish the initial nonequilibrium state of the general system by selectively adding energy to only one of the two subsystems while leaving the other for the most part undisturbed.

In Sec. IV we will further discuss the concepts involved in a two-temperature EOS. In Sec. II we explain the current approximation used for a two-temperature EOS. In Sec. III we present the results of a study which has revealed some technical problems that face the user who attempts to use the method described in Sec. II.

We hope that this brief report may be of some help to those users who have only vaguely heard of two-temperature equations of state, and wonder what they are, and whether they might be useful for their purposes.

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II. A SIMPLE APPROXIMATION FOR A TWO-TEMPERATURE EOS

A standard one-temperature equation of state is usually composed of three parts.[1,2] The pressure, for example, as a function of mass density ρ and temperature T, is divided into contributions from a cold curve, a thermal electronic part, and a thermal ion part:

$$P(\rho,T) = P_{cold}(\rho) + P_e^{TH}(\rho,T) + P_i^{TH}(\rho,T) \; . \tag{1}$$

By definition the two thermal contributions are zero at T = 0 K. The thermal electronic contribution is assumed to arise from the thermal occupation of excited electronic states (e.g., excited bound and continuum electronic states of atoms and molecules or partial filling of the higher electronic energy bands in crystals). The ionic thermal contribution arises from the thermally excited translational, rotational, and vibrational degrees of freedom (e.g., ideal gas pressures and energies at very low densities and thermally excited phonons in crystalline phases).

Whatever remains at zero temperature is called the cold curve contribution. In the crystalline phase (neglecting zero point motion of the ions) the cold curve is what an electronic-band structure calculation should give and in this sense is usually considered to be electronic in origin.

The above separation has long been successfully used for a wide variety of applications. In some cases, for example, for rotations and vibrations of molecules[3] and for phonons in solids,[4] it can be rigorously justified on the basis of the adiabatic approximation.

The simplest and most naive form of a two-temperature EOS, which is the only one we know of in use, is to carry this separation one step further and to define

$$P_e(\rho,T_e) \equiv P_{COLD}(\rho) + P_e^{TH}(\rho,T_e) \tag{2}$$

and

$$P_i(\rho,T_i) \equiv P_i^{TH}(\rho,T_i) \tag{3}$$

for the electrons at temperature T_e and for the ions at temperature T_i; note that we no longer assume T_e and T_i are necessarily equal and that the electron

contribution is independent of the ion temperature and vice versa. In this approximation we have therefore, decoupled the ions from the electrons by assuming that we can <u>independently</u> calculate their contributions. As we discuss in Sec. IV this assumption is in general wrong. Nevertheless, since it is difficult to develop a tractable calculational scheme without it, we may regard the above scheme as a zeroth order approximation to a two-temperature EOS and hope that further investigation will show that corrections to the decoupling approximations are small for applications of interest.

In the current mode of usage, a simple analytic model is used for the ion contribution which is then subtracted from the standard EOS Sesame tables to define the electronic contribution. For example, if $P_i^{ANALYTIC}(\rho,T)$ is the pressure from an analytic ion model, then

$$P_e(\rho,T) \equiv P^{TABLE}(\rho,T) - P_i^{ANALYTIC}(\rho,T) \qquad (4)$$

is defined to be the electronic pressure. This prescription has the advantage that at $T_i=T_e$, the sum of the electronic and ion contributions give the correct total equation of state.

A commonly used analytic ion model is that developed by R. D. Cowan of T-4 (see Ref. 5 for a subroutine listing and brief discussion of this model), which basically interpolates between a Debye model at low temperatures and solid densities and an ideal gas model at high temperatures and low densities. Ideally, instead of the Cowan model, one would like to use the same ion contributions that were used to generate the Sesame library EOS tables. However, most of these tables were generated by a variety of methods before an interest in two-temperature equations of state developed, and hence it is impractical now to recalculate their ion contributions.

In the future, whenever T-4 calculates a new EOS, or old materials are redone, an attempt will be made to save the ion contribution and store it as an additional table on the Sesame library in order to alleviate this problem. This will not always be possible, however, since some EOS models do not distinguish between separate electronic and ion components.

III. TECHNICAL PROBLEMS

We have performed a study in order to ascertain any obvious practical difficulties entailed in subtracting the Cowan ion model from the total EOS to

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generate an electronic model. At the end of this report we have included some plots of such electronic tables for beryllium in order to show typical behavior (Figs. 1-4). Similar plots for a wide variety of Sesame materials may be obtained from T-4.

Several of the features that are shown in these plots may cause some users difficulty if they are unaware of them:

(1) $(\partial P_e/\partial\rho)_T$ is negative in some regions of the density-temperature plane (see, e.g., Fig. 2 at densities between 0.1 and 1 MG/M^3; note that 1MG/M^3 = 1 gm/cc). If the plotted tables were total rather than electronic equations of state this would imply imaginary sound speeds (neglecting the difference between adiabatic and isothermal derivatives).

The negative electronic pressure derivatives arise from two sources. First, some Sesame equations of state include a negative pressure region at low temperatures so that they may be used with spall models in hydro codes and hence the density derivatives of the total pressure are negative in this region. Second, a Maxwell construction[6] is often used under the vapor dome in a total EOS. In this region $(\partial P/\partial\rho)_T = 0$. Since the pressure derivative of the Cowan ion model is always positive, the electronic pressure derivative must be negative so that the derivative of the total pressure is zero.

(2) Isotherms of the subtracted tables often cross at temperatures below 10 eV for both pressures and energies (see, e.g., Figs. 2 and 4 at densities near 1 MG/M^3). For the energy tables this implies negative electronic specific heats in certain regions of the density-temperature plane.

With the older Sesame tables these problems often arise since in the region below 1 eV in temperature the total EOS was calculated in a way which has little resemblance to the Cowan nuclear model and is therefore, not surprisingly, in-consistent with it. With many of the more recent Sesame tables the difficulties result from (i) the use of more complicated ion models (e.g., the liquid Cris model[7]), (ii) the inclusion of molecular dissociation and chemical equilibrium (e.g., as occurs in deuterium[8]), and (iii) the inclusion of phase transitions (e.g., as occurs in Lithia-Boria glass[9]).

(3) A variety of "glitches"or "wiggles" occur in many of the isotherms, usually when the original EOS has a phase transition (see, e.g., the glitch near a density of 0.5 MG/M^3 in Fig. 5 for deuterium, which is the result of a mole-cular solid to metallic solid phase transition).

At high temperatures many of the complications discussed above tend to play a lesser role and most ion models approach an ideal gas limit. This explains why almost all the subtracted electronic tables are so well behaved at the higher temperatures.

IV. CONCEPTUAL DISCUSSION

Any two-temperature model assumes a division of a general system into two subsystems, which in our case are called the electrons and the ions. Except for very unusual situations any such division is approximate and there is an interaction between the two subsystems. In addition there are also interactions which tend to establish internal equilibrium within each subsystem. These effects are schematically sketched in Fig. 6. We define the effective relaxation times τ_{ee} and τ_{ii} for the electron and ion systems to establish equilibrium within themselves and τ_{ei} for the time it takes the two subsystems to come into mutual equilibrium. Clearly τ_{ei} must depend on the temperatures T_e and T_i.

The validity of a two-temperature EOS depends upon meeting the conditions:

$$\tau_{ee} \ll \tau_{ei} \tag{5}$$

and

$$\tau_{ii} \ll \tau_{ei} , \tag{6}$$

i.e., internal equilibrium is first established within each subsystem, which then relax towards each other over a much longer time scale.

Similar types of effects are well known in magnetic systems[10,11] as well as for transport properties[12] in some simple metals at very low temperatures. Nevertheless, to the best of our knowledge conditions (5) and (6) have not been demonstrated for all ρ and τ in all materials. In fact, metals provide a counter example at room temperature and below since electron-ion (electron-phonon) collisions usually dominate over electron-electron collisions.[13]

Indeed, we can turn the question around and ask if there is any region of the ρ-T plane where we can expect a two-temperature EOS to be valid. Unfortunately, little theoretical work has been done in this area and we cannot in general answer this question.

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At low densities, however, a two-temperature model is used in a variety of contexts.[15,17] There it is argued that conditions (5) and (6) are satisfied since collisions between particles of greatly unequal mass are much less efficient for transferring energy than collisions between particles of equal mass.[16,17]

This argument contains two points which are probably essential if one is to justify a two-temperature EOS. First, the large mass difference between the electrons and ions must be the dominant reason why a separation of the total system into those two subsystems can be a useful approximation. Second, in any collisions or other coupling between ions and electrons, the efficiency of energy transfer is very important. For example, even if the rate at which electrons scattered off of ions were many times higher than between electrons alone, nevertheless, if the electron-ion collisions were completely elastic, then τ_{ei} would be infinite because energy could not be passed from one system to the other to establish the required equilibrium partition of energy between the two subsystems. Hence, any microscopic investigation which attempts to justify a two-temperature EOS through an examination of the relaxation times must not only study all the possible different interaction mechanisms, but also their efficiency in transferring energy from one subsystem to the other.

Let us now assume that a two-temperature EOS is a good approximation and consider the form it should take. If we again use pressure as a typical equation of state variable, we expect that

$$P_e = P_e(\rho, T_e; T_i) \tag{7}$$

and

$$P_i = P_i(\rho, T_i; T_e) . \tag{8}$$

That is, the electron pressure will depend not only on the electron temperature but will also depend on the ion temperature as well and vice versa.

To make this distinction more concrete, consider the calculation of an effective ion-ion potential in the adiabatic approximation. In the simplest approach, neglecting any core-core, Van der Waals, or 3-body interactions, etc., we expect the effective ion-ion potential to be something like a screened Coulomb interaction. In the Thomas Fermi approximation this interaction would be

$[(Ze)^2/r]\exp(-k_s r)$. Our point is that the inverse screening length k_s will depend upon the temperature of the electrons[18] (e.g., in the Thomas-Fermi approximation at low temperatures $k_s^2 \sim 4\pi e^2 n/\varepsilon_F$, where ε_F is the Fermi energy and n the electron number density, and at high temperatures $k_s^2 \sim 4\pi e^2 n/k_B T_e$). This change in the effective ion-ion interaction will naturally be reflected in the thermodynamic pressures, energies, and other properties of the ion subsystem.

More generally we can say that the electron-ion interaction V_{ei} has two effects. First, it provides a mechanism for the energy transfer between the two subsystems which is necessary to establish complete thermodynamic equilibrium. Second, it modifies the average properties of each subsystem. For example, in metals a knowledge of V_{ei} is needed both to determine the electron excitation (the band structure) and also the ion excitations (the phonon frequencies). Indeed, when ion and electron temperatures are different one could argue about how to divide the average effects of V_{ei} between the two subsystems, especially at higher densities where these effects are probably most pronounced.

Finally, we mention four areas where a two-temperature model may get into difficulty.

First, users who attempt to resolve nonequilibrium processes over very short time scales or at very high temperatures may need to consider more than two subsystems. For example, if time steps are less than the relaxation times for rotations and vibrations of molecules to equilibrate with translational degrees of freedom,[19] one might want to treat rotations and vibrations as independent subsystems. At high temperatures the equilibrium radiant energy density and pressure increases rapidly with $E_{rad} = 137\, T_{ev}^4$ ergs/cm^3 and $P_{rad} = 1/3\, E_{rad}$ for T_{ev} the temperature in electron volts. At a temperature of 1 keV, for example, $E_{rad} \sim 10^{14}$ ergs/cc and $P_{rad} \sim 45$ Mbars. Whenever there is a significant amount of radiation present, the electron system and radiation must probably be treated together as one coupled system since they interact so strongly.

Second, the two-temperature approximation of Sec. II may work well for some properties but not others. For example, in a given density-temperature region the pressures and energies of the electrons and ions may be effectively decoupled. Nevertheless, the absorption coefficient for photons of a given frequency may depend not only on the electron temperature through the thermal populations of the electronic energy levels, but also on the ion temperatures because of Doppler and collision broadening of absorption lines as well as the intensity of the radiation field.

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Third, phase transitions and critical points may shift to different temperatures and densities when the ions and electrons are at different temperatures. For example, the ion lattice may melt at a lower ion temperature when the electron temperature is high. In general, the decoupling approximation described in Sec. II will probably be poor in these regions since the electrons and ions are probably strongly coupled.

Four, for moderate solid densities and low to moderate temperatures the two-temperature separation of Sec. II is likely to be poor. The electronic models which are typically used are unreliable in these regions and the phenonmenological ion models, whose parameters are determined by forcing the total equation of state to agree with experiment, probably contains some unknown mixture of electronic contributions.

In conclusion, although we have a recipe for calculating two-temperature equations of state for all densities and temperatures, such a scheme is probably unreliable in some density-temperature regions and for some applications. The method of Sec. II should be regarded as a first step towards the resolution of the very complex and difficult set of problems associated with systems which are not in local thermodynamic equilibrium.

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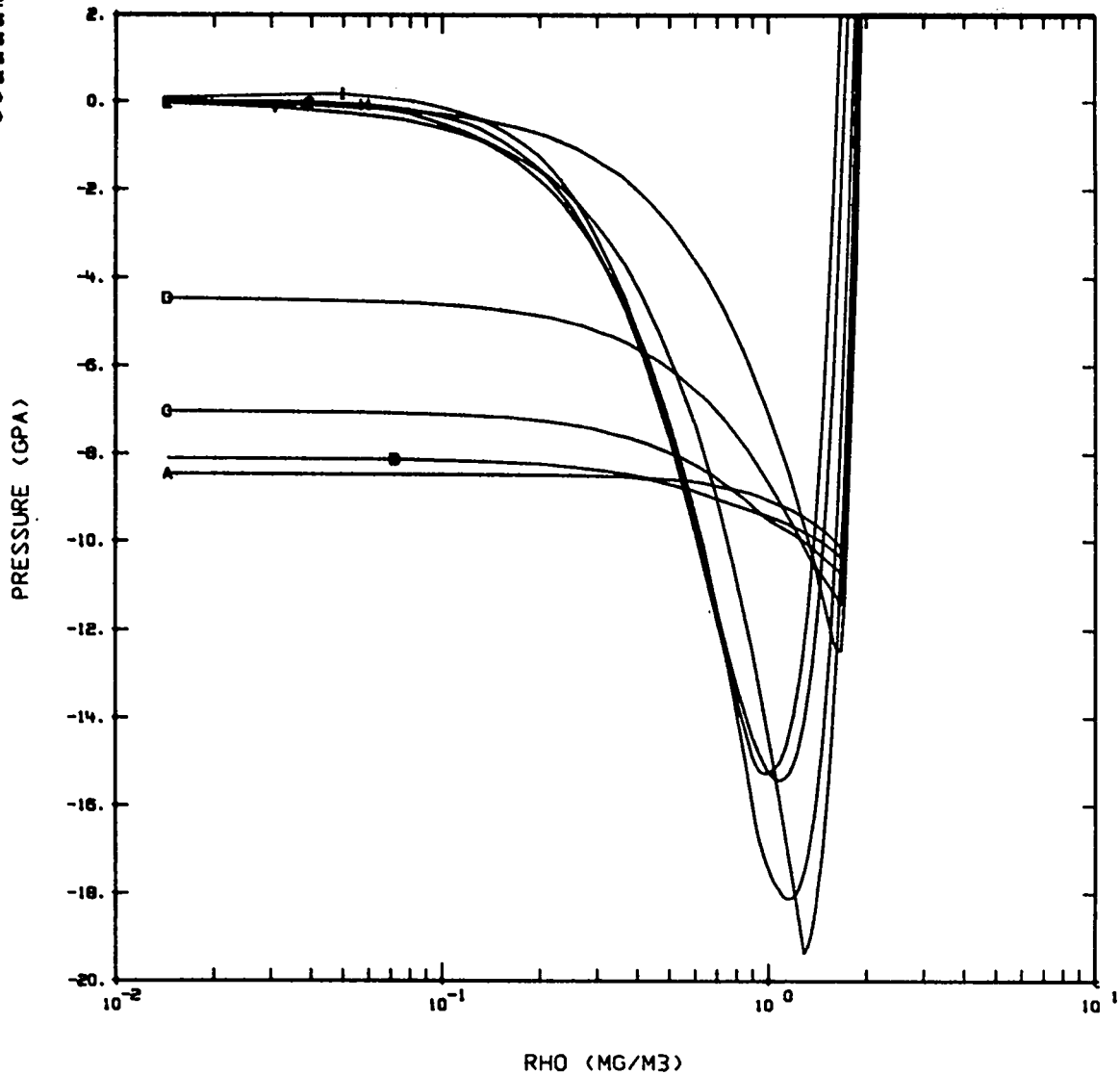
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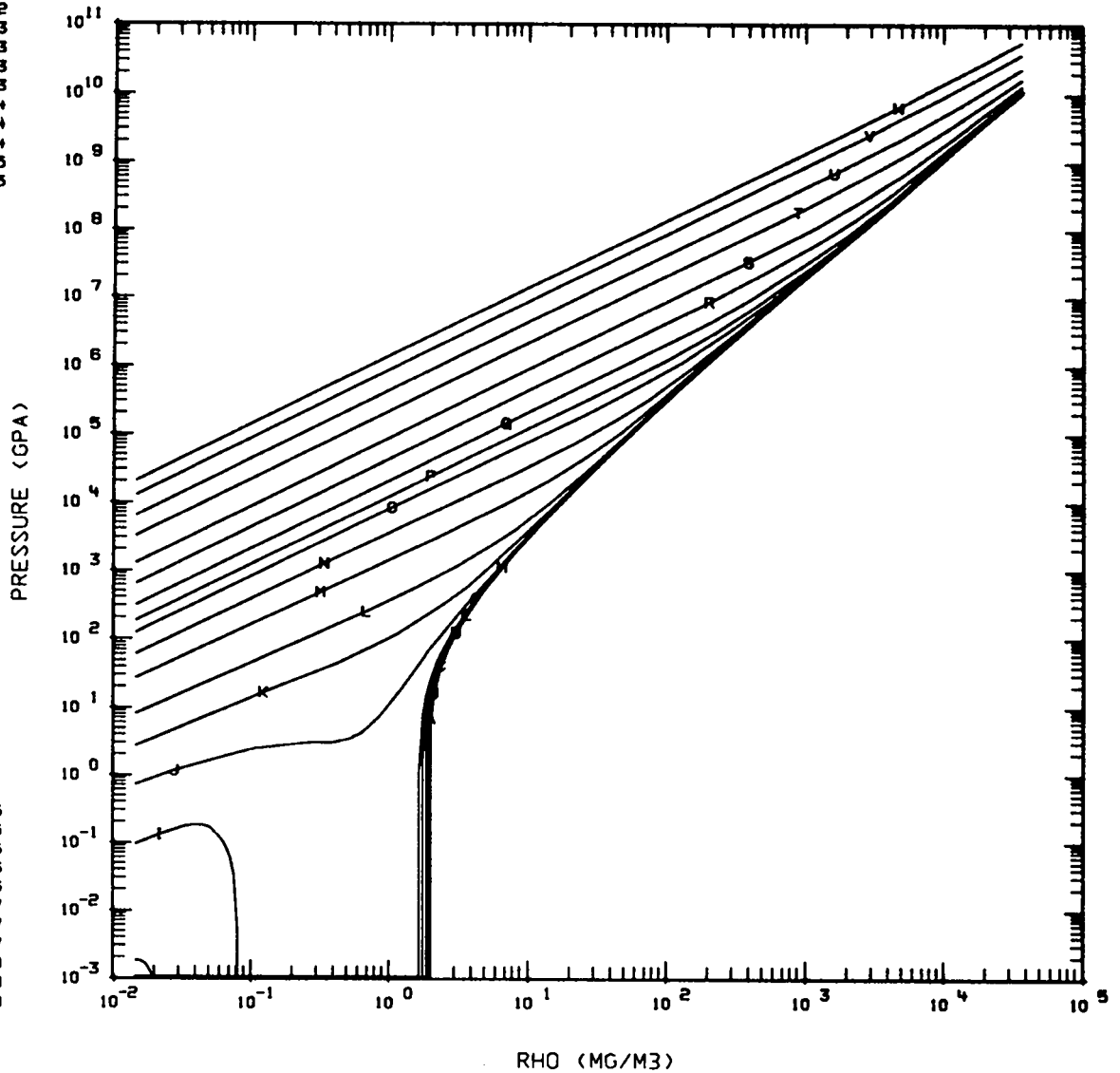
Fig. 1.

Electronic pressure of beryllium. The pressures are given by Eq. (4) for the Cowan analytic ion model (Ref. 5). The total EOS table is that of material No. 2020 on the Sesame Library. The pressure isotherms range from temperatures of 0 K to 3.7 x 10^8 K. The density range shown is from 10^{-2} to 10^5 gm/cc [note: 1 gm/cc = 1 MG/M^3].

Fig. 2.

Electronic pressure of beryllium at low temperatures. We have expanded the low temperature region in order to show the negative pressures and crossing isotherms. The isotherms range in temperature from 0 K to 2.3 x 10^4 K (1 eV $\cong$ 1.16 x 10^4 K).
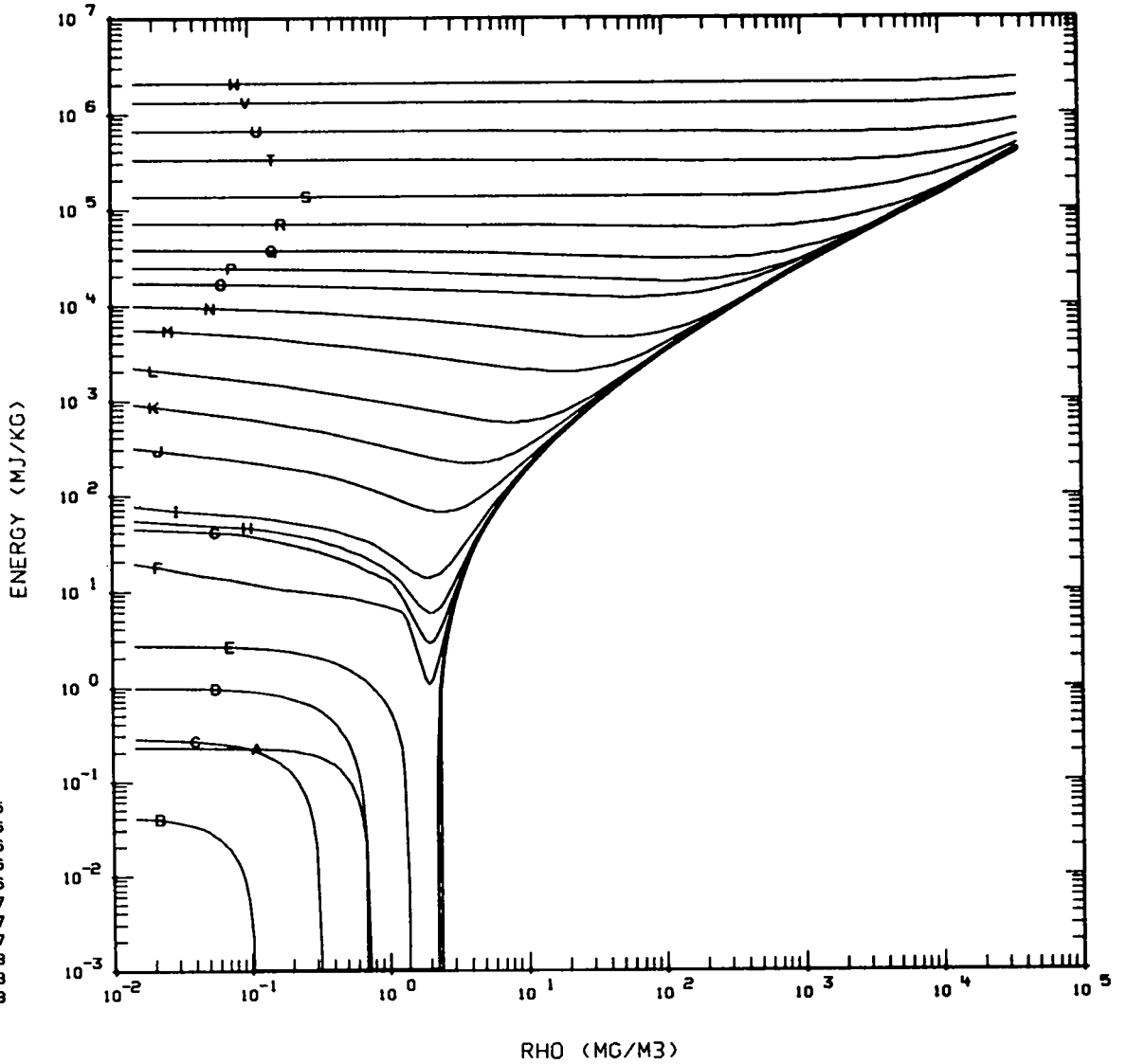
Fig. 3.

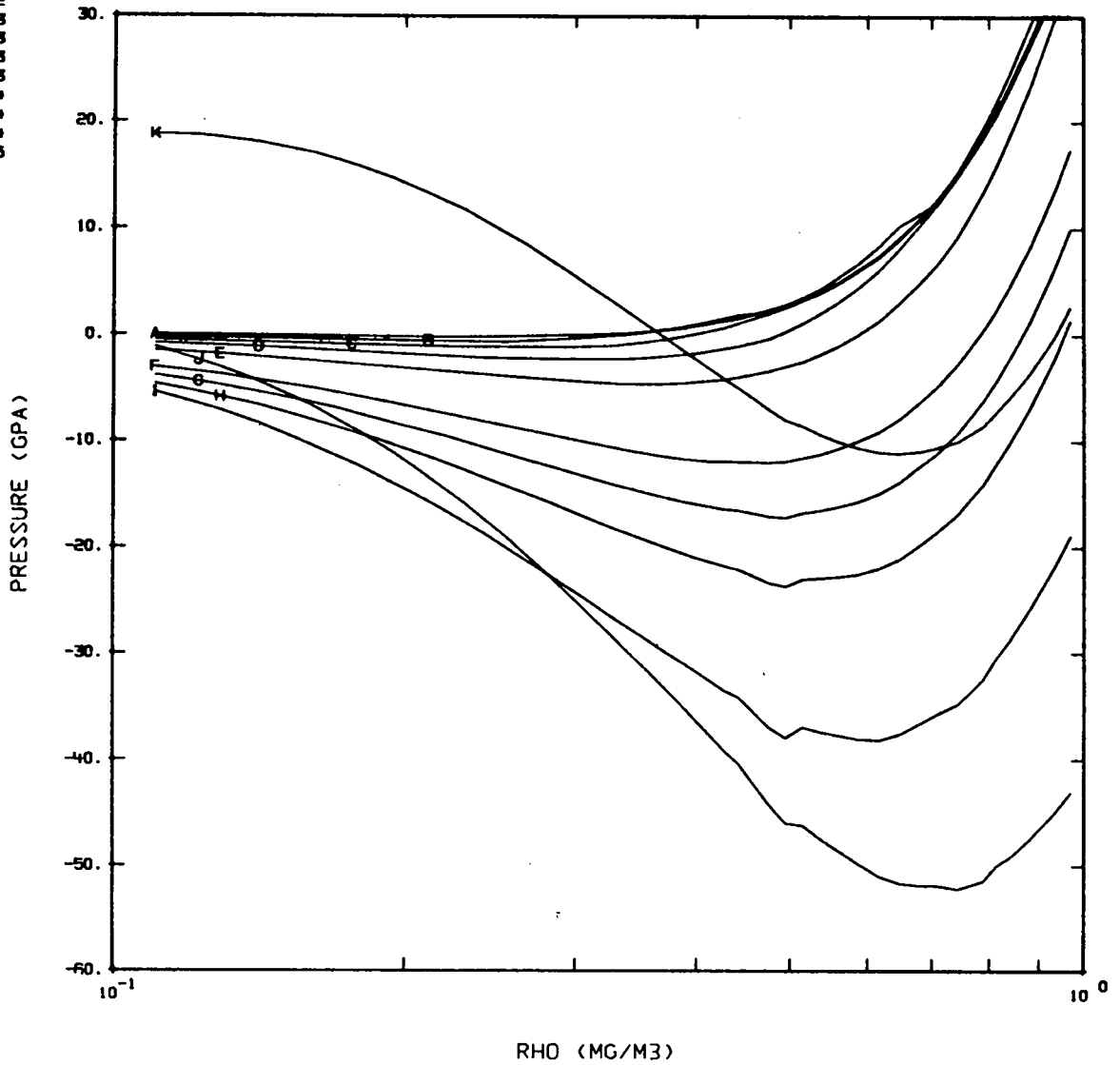Electronic energy density (energy per unit mass) of beryllium.
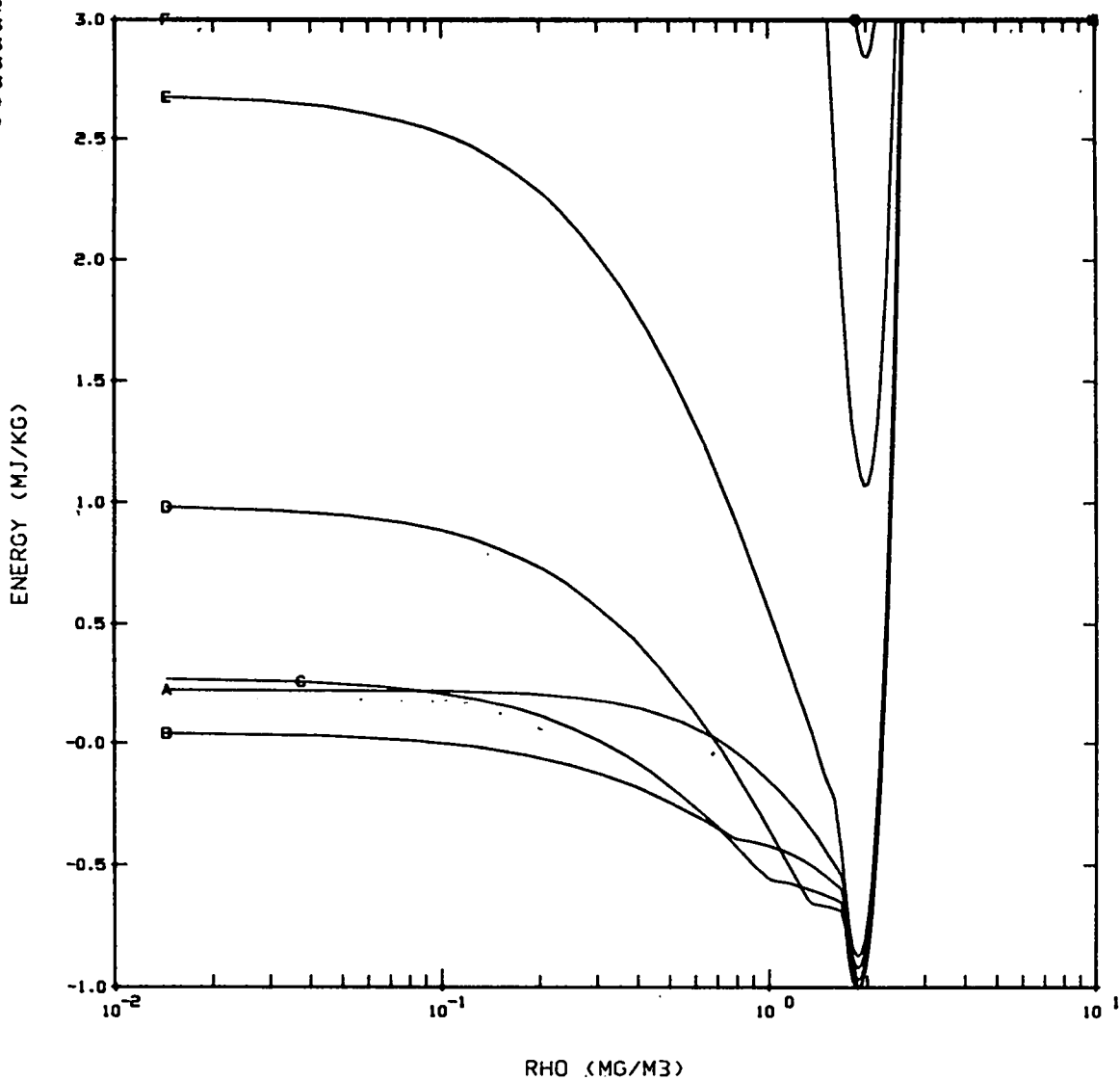
T-4 DISPLAY VER. 1B

Fig. 4.

Electronic energy density of beryllium at low temperatures. Curve A is the cold curve (T = 0 K) and curve E is 2.3 x 10^3 K.

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Fig. 5.

Electronic pressure of deuterium. The total EOS table used is that of material No. 5263 on the Sesame Library. Note the "glitch" at approximately 0.5 MG/M^3 due to the phase transition between the molecular and metallic solid phases of deuterium.
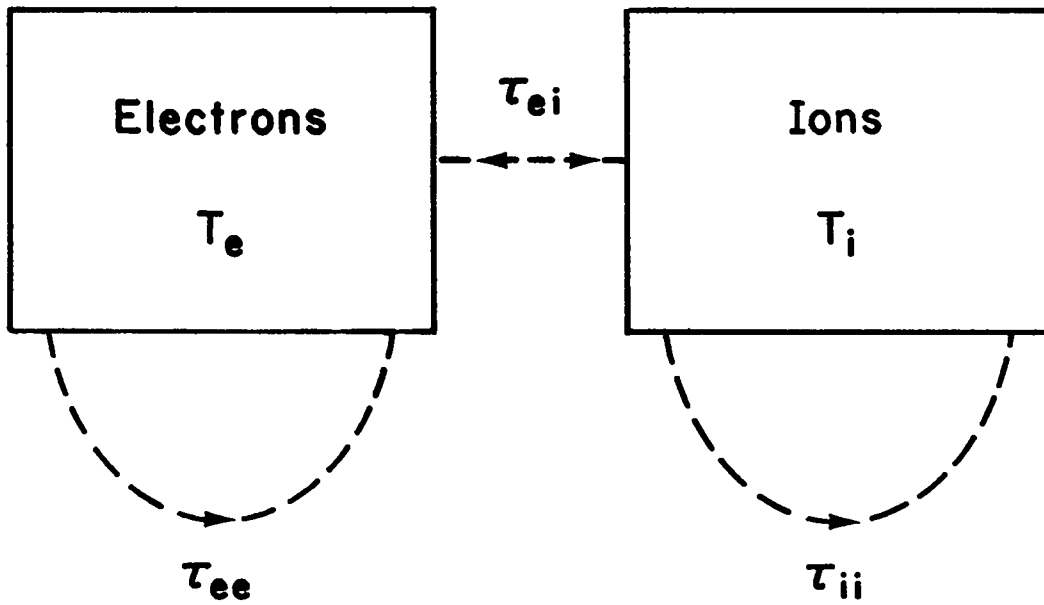
Fig. 6.

Schematic sketch of two-temperature EOS for electrons at temperature T_e and ions at temperature T_i. The various relaxation times τ are discussed in the text.

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