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A Simple Model For Dissociation of Diatomic Molecules

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A simple model for dissociation of diatomic molecules was implemented in the equation of state which is currently in use in the "FAST" code at NRL. Hugoniot curve, obtained with this equation of state is compared with experimental results.

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A SIMPLE MODEL FOR DISSOCIATION OF DIATOMIC MOLECULES

1 Equation of state

The equation of state (EOS) which is currently used in the NRL hydro code is an improved version of the EOS described in reference [1]. In this section We shall briefly review the parts of this EOS which are relevant to dissociation.

1.0.1 The basic approach

The fundamental assumption in the formulation of this EOS is that the free energy of the system (and therefore all the thermodynamic quantities) may be written as a superposition of three terms representing the free energy associated with;

1. atomic and electronic interactions at zero temperature-$F_c(\rho)$
2. Thermal motion of atoms and ions-$F_n(\rho, T)$
3. Thermal motion, excitation and ionization of electrons.-$F_e(\rho, T)$
   (T is the temperature and ρ is the mass density.)

1.0.2 Nuclear contribution to the EOS

In order to describe the motion of atoms and ions in solid, liquid and gaseous states in a single analytical formula, the authors of [1] use an interpolation method. Equations (4.18),(4.19),(4.20) of reference [1] present an interpolation between the free energy of solid according to the Debye-Grüneisen model and the free energy for ideal gas. Explicitly these equations read;

$$F_n = N_0 k_B T \left\{ 3 \ln(1 - e^{-\frac{\theta}{T}}) - 1 + \frac{3}{2} \ln(1 + \Psi) \right\} \tag{1}$$

where

$$\Psi = \frac{N_0^{\frac{5}{3}} h^2 \rho^{\frac{2}{3}}}{2\pi k_B} \frac{T}{\theta^2} e^{\left\{ \frac{2}{3} \sum_l \frac{N_l}{N_0} \ln \left(\frac{N_l}{N_0^{\frac{5}{2}} m_l^{\frac{3}{2}}} \right) \right\}} \tag{2}$$

In these equations, h is the Plank constant, k_B is the Boltzman constant, N_l is the number of atoms per unit mass with atomic number Z_l and atomic mass m_l, N_0 is the number of atoms per unit mass; $N_0 = \sum_l N_l$. θ is the Debye temperature which in this model has the following functional dependence on the mass density: (equation (4.12) in reference [1]):

$$\theta(\rho) = \theta_0 * \left(\frac{\rho_0}{\rho} \right)^{-\frac{3}{2}} e^{\Gamma_0 (1 - (\frac{\rho_0}{\rho})) - \frac{3}{4} (3 - 4 (\frac{\rho_0}{\rho}) + (\frac{\rho_0}{\rho})^2)} \tag{3}$$

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In the above formula, θ_0 and Γ_0 are reference values of the Debye temperature and the Grüneizen coefficient at a reference mass density ρ_0 .The pressure and energy associated with this free energy (by $P_n = \rho^2 \frac{\partial F_n}{\partial \rho}$ and $E_n = -T^2 \frac{\partial \left(\frac{F}{T}\right)}{\partial T}$) are:

$$P_n = \rho N_0 k_B T \, \frac{3\Gamma + \Psi}{1 + \Psi} \tag{4}$$

and

$$E_n = \frac{3}{2} N_0 k_B T \, \frac{2 + \Psi}{1 + \Psi} \tag{5}$$

where Γ is the Grüneisen coefficient:

$$\Gamma \equiv \frac{\rho}{\theta} \frac{d\theta}{d\rho}$$

2 The partition function

In the present section We will derive the effective "single particle partition function" from which the free energy of equation 1 ,and therefore also the nuclear parts of the equation of state used at NRL are derivable. In section 3 We will use this partition function in the derivation of the equation for the degree of dissociation.

Consider the function Ψ of equation 2

$$\begin{aligned}\Psi &= \frac{N_0^{\frac{5}{3}} h^2 \rho^{\frac{2}{3}}}{2\pi k_B} \frac{T}{\theta^2} e^{\left\{ \frac{2}{3} \sum_l \frac{N_l}{N_0} \ln \left(\frac{N_l}{N_0^{\frac{5}{2}} m_l^{\frac{3}{2}}} \right) \right\}} \\ &= \frac{N_0^{\frac{5}{3}} h^2 \rho^{\frac{2}{3}}}{2\pi k_B} \frac{T}{\theta^2} \prod_l \left[\frac{N_l}{N_0^{\frac{5}{2}} m_l^{\frac{3}{2}}} \right]^{\frac{2}{3}\frac{N_l}{N_0}}\end{aligned} \tag{6}$$

Using the relation $N_0 = \sum_l N_l$ in the last equation, one gets

$$\begin{aligned}\Psi &= \prod_l \left[\left(\frac{N_0^{\frac{5}{3}} h^2 \rho^{\frac{2}{3}}}{2\pi k_B} \frac{T}{\theta^2} \right)^{\frac{3}{2}} \frac{N_l}{N_0^{\frac{5}{2}} m_l^{\frac{3}{2}}} \right]^{\frac{2}{3}\frac{N_l}{N_0}} \\ &= \prod_l \left[\left(\frac{h^2 (N_l \rho)^{\frac{2}{3}}}{2\pi m_l k_B} \frac{T}{\theta^2} \right)^{\frac{3}{2}} \right]^{\frac{2}{3}\frac{N_l}{N_0}} \\ &= \prod_l \left(\frac{h^2 (N_l \rho)^{\frac{2}{3}}}{2\pi m_l k_B} \frac{T}{\theta^2} \right)^{\frac{N_l}{N_0}}\end{aligned} \tag{7}$$

Denote the number of atoms with atomic number Z_l and atomic mass m_l in the volume V by η_l and the total number of atoms by η (i.e. $\eta = \sum \eta_l$ $\rho = \frac{1}{V}\sum \eta_l m_l$,and $N_l = \frac{\eta_l}{\sum \eta_l m_l} = \frac{1}{V}\frac{\eta_l}{\rho}$) . Using this notation and rearranging formula 7 , Ψ may be rewritten as:

$$\Psi = \prod_l \left(\frac{\eta_l}{e} \frac{\left\{ \left(e \left(\frac{T}{\theta}\right)^3 \right) \right\}}{\left\{ V \left(\frac{2\pi m_l k_B T}{h^2}\right)^{\frac{3}{2}} \right\}} \right)^{\frac{2}{3}\frac{\eta_l}{\eta}} \tag{8}$$

The term in the denominator of the right hand side of equation 8 is the well known single particle partition function for noninteracting particles of mass m_l in a volume V (ideal gas)

$$q_l^G = V \left(\frac{2\pi m_l k_B T}{h^2} \right)^{\frac{3}{2}} \tag{9}$$

The term in the numerator is the partition function for solid (Debye Grüneisen model, in the limit $\frac{\theta}{T} << 1$)

$$q^D = e \left(\frac{T}{\theta} \right)^3 \tag{10}$$

i.e.:

$$\Psi = \prod_l \left(\frac{\eta_l}{e} \frac{q_D}{q_G} \right)^{\frac{2}{3}\frac{\eta_l}{\eta}} \tag{11}$$

Return now to equation 1, in the limit $\frac{\theta}{T} << 1$, it may be written as:

$$\begin{aligned}
F_n &= N_0 k_B T \left\{ \ln \left(\frac{1}{e} (\frac{\theta}{T})^3 \right) + \frac{3}{2} \ln(1+\Psi) \right\} \\
&= N_0 k_B T \left\{ \frac{1}{\eta} \sum \eta_l \ln \left(\frac{1}{e} (\frac{\theta}{T})^3 \right) + \frac{3}{2} \ln(1+\Psi) \right\} \\
&= N_0 k_B T \left\{ \ln \left(\prod_l \left(\frac{1}{q^D} \right)^{\frac{\eta_l}{\eta}} \right) + \ln \left[1 + \prod_l \left(\frac{\eta_l}{e} \frac{q^D}{q_l^G} \right)^{\frac{2}{3}\frac{\eta_l}{\eta}} \right]^{\frac{3}{2}} \right\} \\
&= N_0 k_B T \ln \left\{ \left(\prod_l \left(\frac{1}{q^D} \right)^{\frac{\eta_l}{\eta}} \right) \left[1 + \prod_l \left(\frac{\eta_l}{e} \frac{q^D}{q_l^G} \right)^{\frac{2}{3}\frac{\eta_l}{\eta}} \right]^{\frac{3}{2}} \right\} \\
&= N_0 k_B T \ln \left\{ \left\{ \frac{\left[1 + \prod_l \left(\frac{\eta_l}{e} \frac{q_l^D}{q_l^G} \right)^{\frac{2}{3}\frac{\eta_l}{\eta}} \right]}{\prod_l (q^D)^{\frac{2}{3}\frac{\eta_l}{\eta}}} \right\}^{\frac{3}{2}} \right\}
\end{aligned} \tag{12}$$

$$= -N_0 k_B T \ln \left\{ \left\{ \frac{\prod_l \left(q^D\right)^{\frac{2}{3}\frac{\eta_l}{\eta}}}{\left[1 + \prod_l \left(\frac{\eta_l}{e}\frac{q^D}{q_l^G}\right)^{\frac{2}{3}\frac{\eta_l}{\eta}}\right]} \right\}^{\frac{3}{2}} \right\}$$

We therefore conclude that the interpolated free energy of equation 1 is derivable from the partition function:

$$Z_n = \left\{ \frac{\prod_l \left(q^D\right)^{\frac{2}{3}\frac{\eta_l}{\eta}}}{\left[1 + \prod_l \left(\frac{\eta_l}{e}\frac{q^D}{q_l^G}\right)^{\frac{2}{3}\frac{\eta_l}{\eta}}\right]} \right\}^{\frac{3}{2}} \tag{13}$$

In the limit $\Psi >> 1$, the interpolated partition function reduces to the partition function for a mixture of ideal gases;

$$\lim_{\Psi \to \infty} Z_n = \prod_l \left(\frac{e}{\eta_l} q_l^G\right)^{\frac{\eta_l}{\eta}}$$

In the opposite limit.$\Psi \to 0$ the partition function reduces to the Debye formula:

$$\lim_{\rho \to \infty} Z_n = \prod_l \left(q^D\right)^{\frac{\eta_l}{\eta}} = q^D$$

(Since $\sum_l \eta_l = \eta$)

Notice that far from these limits, the partition function 13 does not factor into the partition functions the various species participating in the mixture..

3 Dissociation of diatomic molecules

3.1 Law of mass action

The incorporation of dissociation process into the equation of state is based on the law of mass action[2]. According to this law, the equilibrium constant for dissociation of diatomic molecules X_2 ($X_2 \rightleftarrows 2X$) is related to the single particle partition function for atoms, q_x, and for molecules, q_{x_2}, by:

$$K = \frac{(\eta_x/V)^2}{\eta_{x_2}/V} = \frac{(q_x/V)^2}{q_{x_2}/V} \tag{14}$$

Where η_x is the number of atoms in the volume V, η_{x_2}, is the number of molecules in the volume V. Equation 14 together with the obvious relation

$$\eta_x + 2\eta_{x_2} = \eta \tag{15}$$

(which states that the total number of atoms in the system is constant) allows us to solve for the densities of the atoms and the molecules $n_x = \eta_x/V$ and $n_{x_2} = \eta_{x_2}/V$, in terms of the partition functions, q_x/V and q_{x_2}/V. Strictly speaking, the law of mass action is applicable only to mixtures of reacting *ideal gases*, in the present work We will ignore this restriction (without any justification) and use equation 14 together with the interpolated partition function.

3.2 Single particle interpolated partition function for atoms and molecules

By equation 13,the single particle partition function is:

$$q_n = \eta Z_n/e = \frac{\eta}{e}\left\{\frac{\prod_l \left(q^D\right)^{\frac{2}{3}\frac{\eta_l}{\eta}}}{\left[1+\prod_l \left(\frac{\eta_l}{e}\frac{q^D}{q_l^G}\right)^{\frac{2}{3}\frac{\eta_l}{\eta}}\right]}\right\}^{\frac{3}{2}} \tag{16}$$

This partition function takes into account only translation of atoms and molecules. For molecules, rotation , vibration and bonding energy of the molecule also contribute. In the next section We shall use q_n as the single particle partition function for atoms, for molecules We shall multiply by the partition functions for vibration and rotation and dissociation, q^V, q^R, q_{diss} i.e., in equation 14 We shall use:

$$q_x = q_n(m) = \frac{\eta\left(\frac{T}{\theta}\right)^3}{\left[1+\left(\frac{\eta_x\left(\frac{T}{\theta}\right)^3}{V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{\frac{3}{2}}} \tag{17}$$

and;

$$q_{x_2} = q_n(2m)q^V q^R q_{diss} = \frac{\eta\left(\frac{T}{\theta}\right)^3}{\left[1+\left(\frac{\eta_{x_2}\left(\frac{T}{\theta}\right)^3}{V\left(\frac{4\pi m k_B T}{h^2}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{\frac{3}{2}}} q^V q^R q_{diss} \tag{18}$$

Strictly speaking, the right hand side of equation 17 should be multiplied by the partition function for electrons in an atom and the right hand side of equation 18 by the partition function of electrons in a molecule. In the present work a less rigorous approach is used, the effect of electrons is accounted for only trough the dissociation partition function;

$$q_{diss} = e^{\frac{E_{diss}(V)}{k_B T}} \tag{19}$$

which represent the ratio between the partition function of two dissociated atoms and that of a molecule in a phenomenological way with a density dependent dissociation energy. We use the function [3]:

$$E_{diss} = E_{diss0} * \left\{ \begin{matrix} 0 & V > V_d \\ \frac{1}{(2-\frac{V}{V_d})^n} - \frac{n}{(2-\frac{V}{V_d})^{n+1}} & V < V_d \end{matrix} \right\}$$

For q^V We shall take the partition function of harmonic oscillator in the limit where the temperature is higher than the vibrational temperature $\theta_V = \frac{h\nu_V}{k_B} << T$;

$$\begin{aligned} q^V &= \sum_{n=0}^{\infty} e^{-\epsilon_n/k_BT} = \sum_{n=0}^{\infty} e^{-\frac{1}{2k_BT}h\nu_V(2n+1)} \\ &= e^{-\frac{\theta_V}{2T}} \sum_{n=0}^{\infty} e^{-n\frac{\theta_V}{T}} = e^{-\frac{\theta_V}{2T}} \left[\frac{1}{1-e^{-\frac{\theta_V}{T}}} \right] \\ &= \frac{1}{2\sinh(\frac{\theta_V}{2T})} \end{aligned} \tag{20}$$

For q^R we shall take the partition function for rotator with moment of inertia I,:

$$q^R = \sum_{l=0}^{\infty} g_l e^{-\epsilon_l/k_BT} = \sum_{l=0}^{\infty} (2l+1) e^{-\frac{l(l+1)h^2}{8\pi^2 IkT}} \simeq \int_0^{\infty} e^{-x\frac{h^2}{8\pi^2 Ik_BT}} dx = \frac{8\pi^2 Ik_BT}{h^2} = \frac{T}{\theta_R} \tag{21}$$

where:

$$\theta_R = \frac{\hbar^2}{2Ik_B} \tag{22}$$

(For hydrogen molecules the vibrational temperature is $\theta_V = 6320\,K$, the rotational temperature is $\theta_R = 87.5\,K$, and dissociation energy is $E_{diss} = 4.48\,eV$.)

3.3 An equation for the densities of molecules and atoms

Consider a mixture of η_x atoms of mass m, η_{x_2} diatomic molecules of mass $2m$ and η_i inert atoms of mass m_i in a volume V. At every given temperature T and mass density ρ, assuming that the dissociation reaction has arrived a steady state, the number of atoms and molecules in every volume element is determined by the law of mass action 14. In the present section We shall use the law of mass action 14 and the interpolated partition functions derived in section 3.2 and derive an equation for the densities of atoms and molecules, $n_x \equiv \frac{\eta_x}{V}$, $n_{x_2} \equiv \frac{\eta_{x2}}{V}$; In terms of the total mass density;

$$\rho = \frac{\eta_x m + 2\eta_{x_2} m + \eta_i m_i}{V} \tag{23}$$

and the temperature T.

Clearly, the ratio between the number of inert atoms and number of reacting atoms;

$$a = \frac{\eta_i}{\eta_x + 2\eta_{x_2}} \tag{24}$$

and the total number of reacting atoms

$$\eta = \eta_x + 2\eta_{x_2} \tag{25}$$

are fixed. The mass density ρ in terms of these parameters reads:

$$\begin{aligned} \rho &= \frac{\eta_x m + 2\eta_{x_2} m + \eta_i m_i}{V} \\ &= \frac{(\eta_x + 2\eta_{x_2})(m + a * m_i)}{V} \\ &= \frac{\eta(m + a * m_i)}{V} = \lambda(m + a * m_i) \end{aligned} \tag{26}$$

Where We have defined an effective density

$$\lambda = \frac{\eta}{V}$$

By equation 25:

$$\lambda = n_x + 2n_{x_2} \tag{27}$$

Using equations 16,17,18,21,20,19 in the law of mass action 14,leads to:

$$\begin{aligned} K &= \frac{(\eta_x/V)^2}{\eta_{x_2}/V} = \frac{(q_x/V)^2}{q_{x_2}/V} \\ &= \left\{ \frac{1}{V} \frac{\eta\left(\frac{T}{\theta}\right)^3}{\left[1 + \left(\frac{\eta_x\left(\frac{T}{\theta}\right)^3}{V\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{\frac{3}{2}}} \right\}^2 \left\{ \frac{V\left[1 + \left(\frac{\eta_{x2}\left(\frac{T}{\theta}\right)^3}{V\left(\frac{4\pi m k_B T}{h^2}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{\frac{3}{2}}}{\eta\left(\frac{T}{\theta}\right)^3} \right\} \frac{1}{q^V} \frac{1}{q^R} e^{-\frac{E_{diss}}{k_B T}} \end{aligned} \tag{28}$$

or:

$$\frac{\left[1+\left(\frac{\eta_{x2}\left(\frac{T}{\theta}\right)^{3}}{V\left(\frac{4\pi mk_{B}T}{h^{2}}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{\frac{3}{2}}}{\left[1+\left(\frac{\eta_{x}\left(\frac{T}{\theta}\right)^{3}}{V\left(\frac{2\pi mk_{B}T}{h^{2}}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{3}}=\frac{V}{\eta}\frac{(\eta_{x}/V)^{2}}{\eta_{x_2}/V}\left(\frac{\theta}{T}\right)^{3}q^{V}q^{R}e^{\frac{E_{diss}}{k_{B}T}} \tag{29}$$

or:

$$\frac{\left[2+\left(n_{x2}\frac{\left(\frac{T}{\theta}\right)^{3}}{\left(\frac{2\pi mk_{B}T}{h^{2}}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]}{\left[1+\left(n_{x}\frac{\left(\frac{T}{\theta}\right)^{3}}{\left(\frac{2\pi mk_{B}T}{h^{2}}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{2}}=\left(\frac{1}{\lambda}\frac{(n_{x})^{2}}{n_{x_2}}\right)^{\frac{2}{3}}2\left(\frac{\theta}{T}\right)^{2}\left(q^{V}q^{R}\right)^{\frac{2}{3}}e^{\frac{2}{3}\frac{E_{diss}}{k_{B}T}} \tag{30}$$

$$\left(\frac{n_{x2}/\lambda}{(n_{x}/\lambda)^{2}}\right)^{\frac{2}{3}}\frac{\left[2+\left(\frac{n_{x2}}{\lambda}\frac{\left(\frac{T}{\theta}\right)^{3}}{\frac{1}{\lambda}\left(\frac{2\pi mk_{B}T}{h^{2}}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]}{\left[1+\left(\frac{n_{x}}{\lambda}\frac{\left(\frac{T}{\theta}\right)^{3}}{\frac{1}{\lambda}\left(\frac{2\pi mk_{B}T}{h^{2}}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}\right]^{2}}=2\left(\frac{\theta}{T}\right)^{2}\left(q^{V}q^{R}\right)^{\frac{2}{3}}e^{\frac{2}{3}\frac{E_{diss}}{k_{B}T}}$$

Equations 30 and 27 are two equations for the atomic density n_x and the molecular density n_{x_2} for given values of mass density ρ and temperature T.

In the rest of the section We shall simplify the notation of these equations. Define the quantities;

$$\beta(\rho,T)\equiv 2\left(\frac{q^{V}(T)q^{R}(T)}{\frac{1}{\lambda}\left(\frac{2\pi mk_{B}T}{h^{2}}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}}e^{\frac{2}{3}\frac{E_{diss}}{k_{B}T}}, \tag{31}$$

$$R\equiv\frac{n_{x}}{2n_{x_2}+n_{x}}=\frac{n_{x}}{\lambda}, \tag{32}$$

and

$$\xi=\frac{\left(\frac{2\pi mk_{B}T}{h^{2}}\right)}{\lambda^{\frac{2}{3}}\left(\frac{T}{\theta(\rho)}\right)^{2}} \tag{33}$$

In terms of these quantities, equation 30 takes the form:

$$\frac{\left(\frac{1-R}{2}\right)^{\frac{2}{3}}\left[2\xi+\left(\frac{1-R}{2}\right)^{\frac{2}{3}}\right]}{R^{\frac{4}{3}}\left[\xi+R^{\frac{2}{3}}\right]^{2}}=\beta \tag{34}$$

3.4 The procedure for obtaining the atomic and molecular densities for a given state with known total mass density ρ and temperature T.

For given temperature T and mass density ρ , the functions $\theta(\rho), \lambda(\rho), \xi(\rho, T), \beta(\rho, \xi)$ may be evaluated explicitly by using formulas 3,26 33, 31. Thus, the only unknown in equation 34 is R. Solving equation 34, one gets $R(\rho, T)$, the atomic and molecular densities n_x and n_{x_2} are obtained by:

$$n_x = R\lambda \tag{35}$$

$$n_{x_2} = \frac{(1-R)}{2}\lambda \tag{36}$$

In section 4 We will describe a numerical analysis of the equations and an example where the above procedure is applied to the case where $\xi << 1$. In this case the equations may be solved analytically. In section 5 a Fortran routine for applying the procedure and solving for the atomic and molecular densities in the general case is presented.

4 Numerical Examples

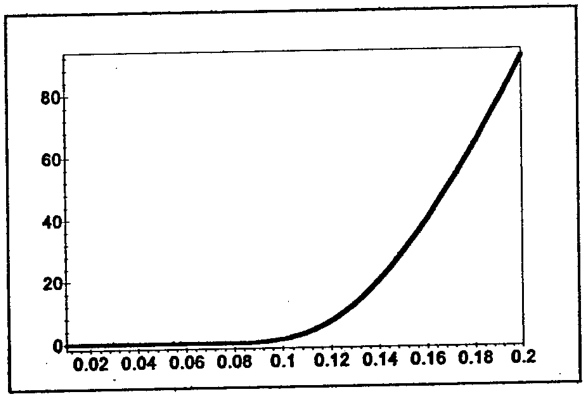
4.0.1 constants and functions definition

$h = 10^{-27}$ erg-sec
$k_B = 1.38 * 10^{-16}$ erg/kelvin
for Deuterium
$m = 2 * 1.67 * 10^{-24}, m = 3.34 \times 10^{-24}$
$\theta_R = 87.5$ k
$\theta_V = 6320$ k
$E_{diss} = 4.48$ eV$= 4.48 * 1.6022 * 10^{-12}$: erg i.e. $E_{diss} = 7.1779 \times 10^{-12}$ erg
take:
$\Gamma_0 = g_0 = 1.8$
$\theta_0 = 240$ Kelvin
$\rho_0 = 0.3017$ g/cc
$m_i = 16 * 1.67 * 10^{-24}$
$m_i = 2.672 \times 10^{-23}$
$a = 0.$
$\theta(\rho) = \theta_0 \left(\frac{\rho_0}{\rho}\right)^{-\frac{3}{2}} e^{g_0\left(1-\frac{\rho_0}{\rho}\right)-\frac{3}{4}\left(3-4\left(\frac{\rho_0}{\rho}\right)+\left(\frac{\rho_0}{\rho}\right)^2\right)}$

$$q_V(T) = \frac{1}{2\sinh(\frac{\theta_V}{2T})}$$
$$q_R(T) = \frac{T}{\theta_R}$$
$$\beta(\rho,T) = 2\left(\frac{q_V(T)q_V(T)}{\frac{1}{\frac{\rho}{(m+a*m_i)}}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}}\right)^{\frac{2}{3}} e^{\frac{2}{3}\frac{E_{diss}}{k_B T}}$$
$$\xi(\rho,T) = \frac{\left(\frac{2\pi m k_B T}{h^2}\right)}{\left(\frac{\rho}{(m+a*m_i)}\right)^{\frac{2}{3}}\left(\frac{T}{\theta(\rho)}\right)^2}$$

4.0.2 Debye temperature

Let us start by plotting the formula for Debye temperature used in reference [1] :

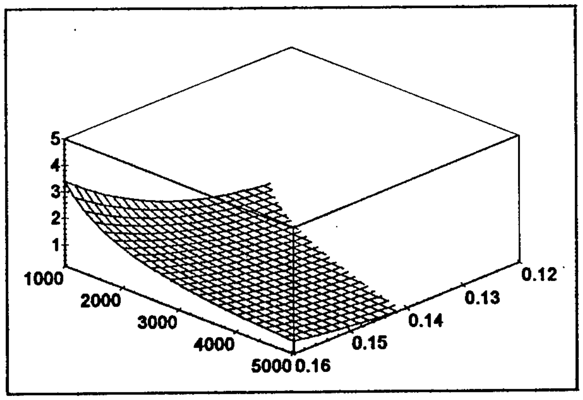


Debye temperature (Kelvin) as a function of the mass density ρ (g/cc)

4.0.3 The interpolation factor, ξ

Notice that at low densities, θ becomes very low, of the order of few degrees. This in turns means that ξ becomes very small. For a single type of atoms, $\xi = \left(\frac{q_G}{q_D}\right)^{\frac{2}{3}}$, when this ratio becomes much smaller than 1, as can be seen immediately from equation 13, the partition function and consequently all the other thermodynamics quantities, reach the limit of ideal gas. The surface $\xi(\rho,T)$ is shown in the figure below. The line, in the ρ, T plane, formed by the intersection between the ξ surface and the bottom of the box ($\xi = 0.2$) determines the region for which $\xi << 1$ and the ideal gas behavior prevails. Similarly ,

The line formed by the intersection between the ξ surface and the top of the box ($\xi = 5$) determines the region for which $\xi >> 1$ and solid state behavior prevails. In the region between these lines the full interpolation formulas 1,4 and 5 should be used.



The interpulation factor ξ as a function of $\rho(g/cc), T(Kelvin)$

4.0.4 Ideal gas case

In the following We shall consider the case $\xi << 1$. This simple analytically solvable case will serve as a test case when solving numerically for the general case. When $\xi << 1$, equation 34 takes the form:

$$\frac{\left(\frac{1-R}{2}\right)^{\frac{2}{3}}\left[\left(\frac{1-R}{2}\right)^{\frac{2}{3}}\right]}{R^{\frac{4}{3}}\left[R^{\frac{2}{3}}\right]^{2}}=\beta \tag{37}$$

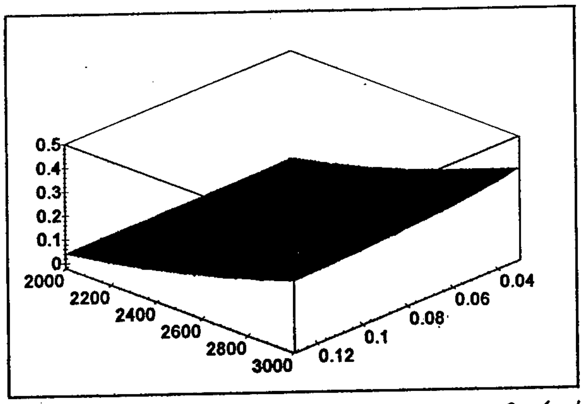
or,

$$R^2+\frac{1}{2\beta^{\frac{3}{4}}}R-\frac{1}{2\beta^{\frac{3}{4}}}=0 \tag{38}$$

The solutions for this equation is:

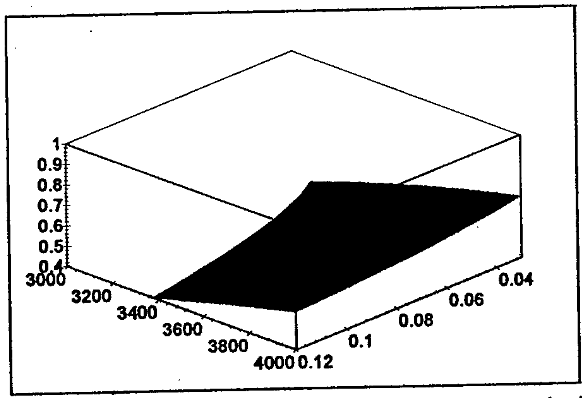
$$R(\rho,T)=-\frac{1}{4}\left(\frac{1}{\beta(\rho,T)}\right)^{\frac{3}{4}}+\frac{1}{4}\sqrt{\left(\frac{1}{\beta(\rho,T)}\right)^{\frac{3}{2}}+8\left(\frac{1}{\beta(\rho,T)}\right)^{\frac{3}{4}}} \tag{39}$$

Only the upper sign solution is physical since this is the only solution which leads to values in the correct range, $0 < R < 1$. The figure below shows the dissociation ratio as a function of ρ and T.



Thedissociation ratio $R(\rho, T) = \frac{\eta_x}{2\eta_{x_2}+\eta_x}$ as a function of $\rho(g/cc)$ and $T(Kelvin)$

and at higher temperatures:



Thedissociation ratio $R(\rho, T) = \frac{\eta_x}{2\eta_{x_2}+\eta_x}$ as a function of $\rho(g/cc)$ and $T(Kelvin)$

At the high density corner of the box $\xi(0.13, 3000) = .26644$ so beyond this density the ideal gas approximation is not valid anymore and we have to solve the more general equation 34

5 The general case: A routine for solving for atomic and molecular densities

5.1 The program

The program for solving the equation for the molecular density n_{x_2} and the atomic density n_{x_2} for the general case, (equation 34) is presented in the Appendix. For given values of a, ρ and T (a,rho and t in the program), the program evaluates the effective density of hydrogen atoms $\lambda(\rho)$ and the coefficients $\xi(\rho, T)$ and $\beta(\rho, T)$ (csi and beta in the program) of equation 34 . Having these coefficients the program calls the routine *rtsafe* which solves equation 34 for R. (The routine *rtsafe* is based on the Newton-Raphson method for finding zeros of functions).

the molecular density n_{x_2} and the atomic density n_{x_2} are evaluated by using equations 35 and 36.

5.2 An example

The routine described above was incorporated into the EOS. Figure (5) describes the results of the application of the improved EOS to measurements described in reference [4] . The squares describe the experimental Hugoniot.The left line ("ion") describes the Hugoniot curve with the EOS without dissociation. The next Hugoniot ("sim") was obtained by using EOS with the assumption that dissociation fraction is just $\exp(-E_{diss}/k_BT)$. The curve "mol" was obtained by using EOS with the model described above but with a constant dissociation energy. The "new model" result was obtained by using the EOS with the complete model. The line "ref 11" corresponds to the model of reference (11) in [4].

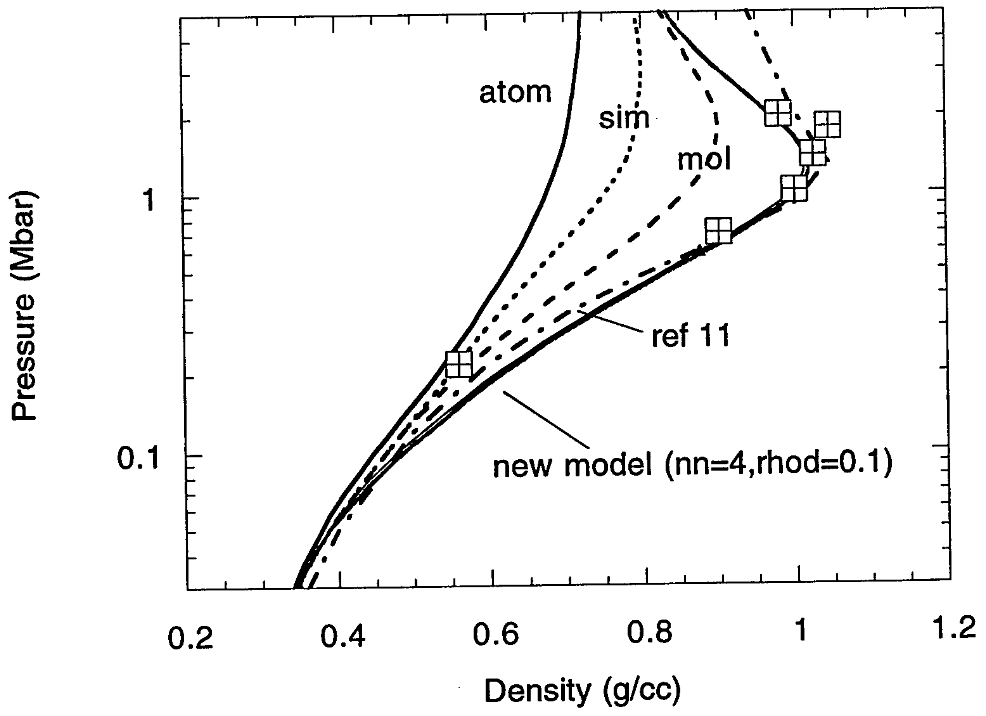


Figure (5): The results of the application of the improved EOS to the measurements described in reference [4].

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