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Combining Equations of State in Kull

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Combining Equations of State in Kull

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1 Introduction

For ICF applications, the temperatures are hot enough that materials can transition to an atomic state or plasma. If we are simulating an ICF capsule, then either thru ALE, physical diffusion, transmutation by nuclear reactions, a mix model, or numerical diffusion (if we are running an Eulerian code), we will generate zones that contain multiple materials. It may be desired to treat certain mixtures of materials or mixed zones as atomic mixtures rather than as chunk mixtures. For example, suppose we have a deuterated material that is initially separated from a tritiated material. As these quantities come into contact at the atomic level, high energy neutrons will be generated from the $D + T$ reaction. However, if we had a chunk of deuterium and a chunk of tritium in the same computational zone, then the $D + T$ reaction would not take place.

In dealing with atomic mixtures, two topics that immediately come to mind are mixed equations of state and mixed opacities. This report will only focus on the equation of state (EOS) aspect and its implementation in the Kull code. Imagine we have a zone that contains an atomic mixture of plastic and steel. If we know the density, temperature, and isotopics of this mixture, then a natural question is how will we compute the pressure and specific internal energy of the mixture as well as the derivatives of these quantities with respect to density and temperature. Let's consider the case where we have tabular thermodynamic data for plastic and steel (as a function of density and temperature), and our goal is to determine how to use these tables to compute the thermodynamic quantities of interest.

The first step is to decide a priori which isotopes should be associated with which table (we will let table 1 refer to the plastic table and table 2 refer to the steel table). This step is necessary so that we can compute mass fractions for each table. Let's assume that the plastic consists of isotopes of hydrogen and carbon, while the steel consists of iron, manganese, and zinc. We can then use a simple Z-range (here, Z refers to the atomic number of the element in question) to decide which isotopes go where. For example, table 1 could have a Z-range of (0, 10.5) so that it captures all of the hydrogen and carbon isotopes and table 2 could have a range of (10.5, 50.5) to capture all of its higher Z elements. Since we have access to the mixture density, number fractions and number density, we can readily convert the number fractions to mass fractions (y_i), where they are defined as $y_1 \equiv M_{plastic}/(M_{plastic} + M_{steel})$ and $y_2 \equiv M_{steel}/(M_{plastic} + M_{steel})$.

The second step is to bring the atomic mixture into equilibrium through a Newton-Raphson iteration scheme and solve for the sub-densities, ρ_i , defined as $\rho_1 \equiv M_{plastic}/V_{plastic}$ and $\rho_2 \equiv M_{steel}/V_{steel}$. In many instances it will be more useful to work with specific volume, v_i , which is simply the reciprocal of the density, and we will use whichever quantity will make a particular derivation more transparent. An important constraint in the Newton-Raphson procedure is that the mixture density remains unchanged by the iteration procedure. Therefore, for an N material example, we would have the specific volumes satisfying:

$$v = \frac{1}{\rho} = \sum_{i=1}^N y_i v_i \quad . \quad (1)$$

By equilibration, we mean that we iterate on the sub-densities until

$$f = f_1(\rho_1, T) = f_2(\rho_2, T) = \dots = f_N(\rho_N, T) \quad , \quad (2)$$

where f is the quantity we want to equilibrate. Here the subscript under the f refers to the particular table that is used to perform the thermodynamic lookup (for notational simplicity, we will usually omit this subscript in future equations). Also, for mathematical well-posedness, $f(\rho_i, T)$ should be monotonic in ρ_i to obtain unique solutions.

In Kull, there are four different equilibrate options. We can let f be the total pressure, chemical potential, analytic electron density, or tabular electron density. The electron density, n_e , is directly related to a quantity known as the effective charge or Z_{eff} by the simple relation $n_e = Z_{eff} * \rho / A$, where A is the average atomic weight. We can compute Z_{eff} using an analytic formula based on Thomas-Fermi theory or we can query

the EOS table to return a value for Z_{eff} . Hence, the two equilibrium options for electron density really refer to how one computes Z_{eff} .

2 Quantities of Interest

Once we have iterated the sub-densities to convergence in the Newton-Raphson solver (subject to the mixture density constraint), we can compute mixture properties using the following formulae:

$$P = \sum_{i=1}^N y_i \frac{\partial v_i}{\partial v} P_i(\rho_i, T) \quad (3)$$

$$e = \sum_{i=1}^N y_i e_i(\rho_i, T) \quad (4)$$

$$\frac{\partial P}{\partial T} = \sum_{i=1}^N y_i \frac{\partial v_i}{\partial v} \frac{\partial P_i(\rho_i, T)}{\partial T} + \sum_{i=1}^N y_i \frac{\partial v_i}{\partial v} \frac{\partial v_i}{\partial T} \frac{\partial P_i(\rho_i, T)}{\partial v_i} \quad (5)$$

$$\frac{\partial e}{\partial T} = \sum_{i=1}^N y_i \frac{\partial e_i(\rho_i, T)}{\partial T} + \sum_{i=1}^N y_i \frac{\partial v_i}{\partial T} \frac{\partial e_i(\rho_i, T)}{\partial v_i} \quad (6)$$

$$\frac{\partial P}{\partial v} = \sum_{i=1}^N y_i \left(\frac{\partial v_i}{\partial v} \right)^2 \frac{\partial P_i(\rho_i, T)}{\partial v_i} \quad (7)$$

$$\frac{\partial e}{\partial v} = \sum_{i=1}^N y_i \frac{\partial v_i}{\partial v} \frac{\partial e_i(\rho_i, T)}{\partial v_i} , \quad (8)$$

where P is the mixture pressure and e is the mixture specific internal energy (energy/mass). Eqs. 3 and 4 constitute the physics, while eqs. 5–8 follow purely from the functional dependence of P and e on the independent variables. Also, since the thermodynamic tables use ρ_i as an independent variable, rather than v_i , the following formulas can be substituted above:

$$\frac{\partial X_i}{\partial v_i} = \frac{\partial X_i}{\partial (1/\rho_i)} = -v_i^2 \frac{\partial X_i}{\partial \rho_i} \quad (9)$$

$$\frac{\partial X}{\partial v} = \frac{\partial X}{\partial (1/\rho)} = -v^2 \frac{\partial X}{\partial \rho} . \quad (10)$$

Let us consider for a moment how we would derive equations for $\partial P/\partial T$ and $\partial P/\partial v$. The derivations for $\partial e/\partial T$ and $\partial e/\partial v$ will follow by analogy. Since P_i is a function of ρ_i (or v_i) and T , we have

$$\Delta P_i = \frac{\partial P_i}{\partial T} \Delta T + \frac{\partial P_i}{\partial v_i} \Delta v_i \quad (11)$$

Using the definition of pressure given by eq. 3, we see that if we multiply eq. 11 by $y_i \partial v_i / \partial v$ and sum over all tables, the result is

$$\Delta P = \Delta T \sum_{i=1}^N y_i \frac{\partial v_i}{\partial v} \frac{\partial P_i}{\partial T} + \sum_{i=1}^N y_i \frac{\partial v_i}{\partial v} \frac{\partial P_i}{\partial v_i} \Delta v_i . \quad (12)$$

Dividing this last equation by ΔT and taking the limit as the different Δ 's $\rightarrow 0$ gives eq. 5. Note that we can't simply drop the second term on the right hand side of 5. That is, even though $\partial P/\partial T$ is taken at constant v , the constituent specific volumes can still have changes with respect to temperature. On the other hand, $\partial P/\partial v$ is taken at constant temperature. Thus, when we divide eq. 12 by Δv , we can set $\Delta T = 0$. Taking the limit as the remaining Δ 's $\rightarrow 0$ gives the desired expression for $\partial P/\partial v$.

The final result we need is to develop expressions for $\partial v_i/\partial v$ and $\partial v_i/\partial T$. We begin by assuming $f_j = f_j(v_j, T)$. What follows is

$$\Delta f_j = \frac{\partial f_j}{\partial T} \Delta T + \frac{\partial f_j}{\partial v_j} \Delta v_j . \quad (13)$$

Since $\sum_{j=1}^N y_j v_j = v$, we also have that

$$\Delta v = \sum_{j=1}^N y_j \Delta v_j . \quad (14)$$

Solving eq. 13 for Δv_j and inserting this into eq. 14 gives:

$$\Delta v = \sum_{j=1}^N \frac{y_j \Delta f_j}{\frac{\partial f_j}{\partial v_j}} - \Delta T \sum_{j=1}^N \frac{y_j \frac{\partial f_j}{\partial T}}{\frac{\partial f_j}{\partial v_j}} . \quad (15)$$

As we are iterating until all the f 's are equal, we can pull the Δf_j out of the summation, call it Δf , and then re-express this using eq. 13 where we let $j \rightarrow i$. The result of these manipulations is:

$$\Delta v = \left(\frac{\partial f_i}{\partial T} \Delta T + \frac{\partial f_i}{\partial v_i} \Delta v_i \right) \sum_{j=1}^N \frac{y_j}{\frac{\partial f_j}{\partial v_j}} - \Delta T \sum_{j=1}^N \frac{y_j \frac{\partial f_j}{\partial T}}{\frac{\partial f_j}{\partial v_j}} . \quad (16)$$

Now divide eq. 16 by Δv (assuming temperature is constant) and solve for $\partial v_i / \partial v$. Then divide eq. 16 by ΔT and solve for $\partial v_i / \partial T$. The desired quantities are:

$$\left(\frac{\partial v_i}{\partial v} \right)_T \equiv \frac{\partial v_i}{\partial v} = \frac{\left(\frac{\partial f_i}{\partial v_i} \right)^{-1}}{\sum_{j=1}^N y_j \left(\frac{\partial f_j}{\partial v_j} \right)^{-1}} \quad (17)$$

$$\left(\frac{\partial v_i}{\partial T} \right)_v \equiv \frac{\partial v_i}{\partial T} = \frac{\partial v_i}{\partial v} \sum_{j=1}^N y_j \frac{\partial f_j}{\partial T} \left(\frac{\partial f_j}{\partial v_j} \right)^{-1} - \frac{\partial f_i}{\partial T} \left(\frac{\partial f_i}{\partial v_i} \right)^{-1} . \quad (18)$$

As a sanity check, we observe from the previous two equations that

$$\sum_{i=1}^N y_i \left(\frac{\partial v_i}{\partial v} \right)_T = \left(\frac{\partial v}{\partial v} \right)_T = 1 , \quad (19)$$

as well as

$$\sum_{i=1}^N y_i \left(\frac{\partial v_i}{\partial T} \right)_v = \left(\frac{\partial v}{\partial T} \right)_v = 0 . \quad (20)$$

The reason we can take y_i inside the differential is that the isotopics are fixed during the Newton-Raphson procedure. Hence, the masses of the different isotopes (and therefore the y_i 's) are constant.

3 Application

The above discussion has shown at a high level how to bring an atomic mixture with a known mixture density, temperature, and isotopics into thermodynamic equilibrium and how to compute mixture thermodynamic quantities of interest. For example, using eqs. 5–8 we can construct derived quantities like sound speed, bulk modulus, etc. . We will not delve into the minutiae of how the Newton-Raphson procedure conducts its iterations, however, the choice of quantities to iterate on warrants some discussion. The EOS tables are constructed using density and temperature as independent variables and so the straightforward approach is to do forward lookups of f using the current values for the sub-densities (ρ_i 's) and the known temperature. Then we develop a way of adjusting the changes in the sub-densities to arrive at better guesses for the next iteration. An alternative procedure is to iterate on the single quantity f by performing reverse or inverse lookups. By reverse lookups, we mean that we interrogate the table for $\rho_i(f, T)$ instead of the forward lookup procedure which gives $f(\rho_i, T)$. The advantage with the reverse lookups is that we are only iterating on a single quantity, f , which is adjusted until the mixture density constraint is satisfied. The disadvantage is that iteration is necessary to provide the reverse lookup from the table. Also, forward and reverse lookups are not necessarily compatible or consistent. Therefore, we have decided in the current implementation to iterate on more quantities by using forward lookups, even though when more than two tables are involved, it may be more difficult to reach a converged equilibrium state.

It is often desired to compute the temperature from the mixture internal energy and density. For simplicity, let's assume that we have modified the internal energy, but the density has remained fixed. The procedure we use for the atomic mixture is to adjust the temperature and do forward lookups of energy until we satisfy the constraint that:

$$e(\rho, T) = \sum_{i=1}^N y_i e_i(\rho_i, T) . \quad (21)$$

In the Lagrange hydro, we have the more complicated circumstance where both the material density and internal energy are being updated in the 3^{rd} order Runge-Kutta time integration scheme. The sub-densities that are used in the above constraint, however, will sum to the old mixture density and not the new density. Also, we can't simply re-equilibrate the mixture with the modified density to find the new sub-densities, since the needed temperature is unknown. Fortunately, there are a few ways out of this chicken and egg dilemma. The most computationally expensive way (and probably the most accurate as well) is to do a double iteration on the sub-densities and temperature, such that after we are equilibrated, we also satisfy the density and energy constraints. A simpler procedure would be to only iterate on temperature, but to use a modified sub-density for the table lookups that is consistent with the current mixture density. Thus, we will use the following energy constraint:

$$e(\rho, T) = \sum_{i=1}^N y_i e_i(1/v_i^*, T) . \quad (22)$$

There are two obvious choices for the v_i^* , with the first one given by the simple scaling

$$v_i^* = v_i \left(\frac{v_{new}}{v} \right) = v_i + \frac{v_i}{v} (v_{new} - v) . \quad (23)$$

The second approach is to make a Taylor-series in specific volume. The result is

$$v_i^* = v_i + \frac{\partial v_i}{\partial v} (v_{new} - v) . \quad (24)$$

Note that from eq. 17 and eqs. 9–10, we have the result that

$$\frac{\partial v_i}{\partial v} = \frac{\left(\frac{\partial f_i}{\partial v_i}\right)^{-1}}{\sum_{j=1}^N y_j \left(\frac{\partial f_j}{\partial v_j}\right)^{-1}} = \frac{v_i^2 \left(\frac{\partial f_i}{\partial \rho_i}\right)^{-1}}{\sum_{j=1}^N y_j v_j^2 \left(\frac{\partial f_j}{\partial \rho_j}\right)^{-1}} . \quad (25)$$

Also, since $\partial f_i / \partial \rho_i \geq 0$, we know that $0 \leq \partial v_i / \partial v \leq 1$. This means that all the v_i^* 's will increase or decrease, depending on the sign of $v_{new} - v$. The advantage of the first approach is that the sub-densities will never go negative. The disadvantage to this approach is that it is essentially approximating the derivative $\partial v_i / \partial v$ by v_i / v , which is only zeroth order accurate. The Taylor series approximation is first order accurate, but has the potential of driving the sub-densities negative (particularly in the case of $v_{new} \gg v$).

4 Analytic Z_{eff}

It was noted earlier that there are 2 ways of computing Z_{eff} when we want to use the electron density equilibrate option. One way is to simply do a forward table lookup of Z_{eff} based on ρ_i and T . The table also provides values for $\partial Z_{eff} / \partial \rho$ and $\partial Z_{eff} / \partial T$. The alternative is to use an analytic data fit for Z_{eff} developed by Dick More based on Thomas-Fermi theory. The inputs for the analytic formula are T (KeV), ρ_i (g/cm^3), $\langle z \rangle_i$, and $\langle \hat{z} \rangle_i$. Here, $\langle z \rangle_i$, and $\langle \hat{z} \rangle_i$ are given by

$$\begin{aligned} \langle z \rangle_i &= \sum_j \chi_j Z_j \\ \langle \hat{z} \rangle_i &= \exp \left[\frac{2 \langle z \ln z \rangle_i}{3 \langle z \rangle_i} \right] \\ \langle z \ln z \rangle_i &= \sum_j \chi_j Z_j \ln Z_j , \end{aligned}$$

where it is understood in the above formulas that χ_j are number fractions and the j in the summation refers to all isotopes that are associated with the i^{th} table.

We start the formula for Z_{eff} by defining a scaled temperature \bar{T} and a dimensionless temperature \hat{T} as:

$$\begin{aligned} \bar{T} &= \alpha T \\ \hat{T} &= \frac{\bar{T}}{1 + \bar{T}} , \end{aligned}$$

where $\alpha = 1000 / \langle \hat{z} \rangle^2$. We then define a_Y , a function of scaled temperature and b_Y and c_Y , two functions of dimensionless temperature by the following:

$$\begin{aligned} a_Y &= a_1 \bar{T}^{a_2} + a_3 \bar{T}^{a_4} \\ b_Y &= -\exp \left[b_0 + b_1 \hat{T} + b_2 \hat{T}^7 \right] \\ c_Y &= c_1 \hat{T} + c_2 , \end{aligned}$$

where

$$\begin{aligned} a_1 &= .003323467 \\ a_2 &= .97183224 \\ a_3 &= 9.26148e - 05 \\ a_4 &= 3.1016524 \end{aligned}$$

$$\begin{aligned}
b_0 &= -1.762999 \\
b_1 &= 1.4317567 \\
b_2 &= 0.31546338 \\
c_1 &= -.36666667 \\
c_2 &= .98333333 .
\end{aligned}$$

We then define two functions p_1 and p_2 by:

$$p_1 = a_Y^{c_Y} Z_R^{b_Y c_Y} \rho^{b_Y c_Y} \quad (26)$$

$$p_2 = Z_R^{c_Y} \rho^{b_Y c_Y} \quad (27)$$

$$Z_R = \frac{\langle z \rangle}{A \langle \hat{z} \rangle^{2/3}} .$$

Finally, the relation for Z_{eff} takes the form:

$$\begin{aligned}
Z_{eff} &= \frac{\langle z \rangle \hat{Z}_{eff}}{x} \\
\hat{Z}_{eff} &= \frac{x}{1 + x + \sqrt{1 + 2x}} \\
x &= 2\gamma_1^2 (p_1 + p_2)^{2\gamma_2/c_Y} \\
\gamma_1 &= 2.6752506 \\
\gamma_2 &= 0.33120023 .
\end{aligned} \quad (28)$$

Now that we have a closed expression for Z_{eff} , we need to take analytic derivatives of Z_{eff} with respect to density and temperature. To this end, we express the density derivative using the chain rule as:

$$\frac{\partial Z_{eff}}{\partial \rho} = \frac{\partial Z_{eff}}{\partial \hat{Z}_{eff}} \frac{\partial \hat{Z}_{eff}}{\partial x} \frac{\partial x}{\partial \rho} . \quad (29)$$

Using simple calculus, we obtain:

$$\begin{aligned}
\frac{\partial \hat{Z}_{eff}}{\partial x} &= x \frac{d}{dx} (1 + x + \sqrt{1 + 2x})^{-1} + (1 + x + \sqrt{1 + 2x})^{-1} \\
&= \frac{\hat{Z}_{eff}}{x} \left[1 - \hat{Z}_{eff} \left(1 + \frac{1}{\sqrt{1 + 2x}} \right) \right] , \\
\frac{\partial x}{\partial \rho} &= \frac{4\gamma_1^2 \gamma_2}{c_Y} (p_1 + p_2)^{2\gamma_2/c_Y - 1} \left(\frac{\partial p_1}{\partial \rho} + \frac{\partial p_2}{\partial \rho} \right) \\
&= \frac{2\gamma_2 x (b_Y p_1 + p_2)}{(p_1 + p_2) \rho} , \\
\frac{\partial Z_{eff}}{\partial \hat{Z}_{eff}} &= \langle z \rangle .
\end{aligned}$$

Therefore we obtain the relatively straightforward result that

$$\frac{\partial Z_{eff}}{\partial \rho} = \frac{2\gamma_2 Z_{eff} (b_Y p_1 + p_2)}{(p_1 + p_2) \rho} \left[1 - \hat{Z}_{eff} \left(1 + \frac{1}{\sqrt{1 + 2x}} \right) \right] . \quad (30)$$

Proceeding in a similar fashion, we can derive the following result for the derivative of Z_{eff} with respect to temperature.

$$\frac{\partial Z_{eff}}{\partial T} = \frac{\partial Z_{eff}}{\partial \hat{Z}_{eff}} \frac{\partial \hat{Z}_{eff}}{\partial x} \frac{\partial x}{\partial T} . \quad (31)$$

If we take the natural log of eq. 28 (the definition for x) and then differentiate both sides with respect to temperature, we obtain:

$$\frac{\partial x}{\partial T} = \frac{2\gamma_2 x}{c_Y} \left[\frac{\partial p_1/\partial T + \partial p_2/\partial T}{p_1 + p_2} - \frac{\ln(p_1 + p_2)}{c_Y} \frac{\partial c_Y}{\partial T} \right] . \quad (32)$$

Equation 31 now assumes the form of:

$$\frac{\partial Z_{eff}}{\partial T} = \frac{2\gamma_2 Z_{eff}}{c_Y} \left[1 - \hat{Z}_{eff} \left(1 + \frac{1}{\sqrt{1+2x}} \right) \right] \left[\frac{\partial p_1/\partial T + \partial p_2/\partial T}{p_1 + p_2} - \frac{\ln(p_1 + p_2)}{c_Y} \frac{\partial c_Y}{\partial T} \right] . \quad (33)$$

To find $\partial p_1/\partial T$ and $\partial p_2/\partial T$, we use the same trick as before. That is, we take the natural log of eqs. 26–27 and differentiate both sides with respect to temperature. The result is:

$$\begin{aligned} \frac{\partial p_1}{\partial T} &= p_1 \left\{ c_Y \left[\frac{1}{a_Y} \frac{\partial a_Y}{\partial T} + \frac{\partial b_Y}{\partial T} \ln \bar{Z}_R \right] + \frac{\partial c_Y}{\partial T} [\ln a_Y + b_Y \ln \bar{Z}_R] \right\} \\ \frac{\partial p_2}{\partial T} &= p_2 \frac{\partial c_Y}{\partial T} \ln \bar{Z}_R \\ \bar{Z}_R &\equiv \rho Z_R . \end{aligned}$$

Now we simply need derivatives of a_Y , b_Y , and c_Y with respect to temperature to finish the derivation.

$$\begin{aligned} \frac{\partial a_Y}{\partial T} &= \frac{\alpha}{\bar{T}} \left(a_1 a_2 \bar{T}^{a_2} + a_3 a_4 \bar{T}^{a_4} \right) \\ \frac{\partial b_Y}{\partial T} &= \frac{\partial b_Y}{\partial \hat{T}} \frac{\partial \hat{T}}{\partial \bar{T}} \frac{\partial \bar{T}}{\partial T} \\ \frac{\partial c_Y}{\partial T} &= \frac{\partial c_Y}{\partial \hat{T}} \frac{\partial \hat{T}}{\partial \bar{T}} \frac{\partial \bar{T}}{\partial T} \\ \frac{\partial b_Y}{\partial \hat{T}} &= b_Y (b_1 + 7b_2 \hat{T}^6) \\ \frac{\partial c_Y}{\partial \hat{T}} &= c_1 \\ \frac{\partial \hat{T}}{\partial \bar{T}} \frac{\partial \bar{T}}{\partial T} &= \alpha \frac{\hat{T}(1 - \hat{T})}{\bar{T}} . \end{aligned}$$

Finally, recall that it is really the electron density that is put into equilibrium and not the effective charge. Therefore, from the perspective of the Newton-Raphson procedure, what we really need are the derivatives of electron density with respect to density and temperature. Due to the simple relation between n_e and Z_{eff} , the desired derivatives are:

$$\begin{aligned} \frac{\partial n_e}{\partial \rho} &= \frac{\rho}{A} \frac{\partial Z_{eff}}{\partial \rho} + \frac{Z_{eff}}{A} \\ \frac{\partial n_e}{\partial T} &= \frac{\rho}{A} \frac{\partial Z_{eff}}{\partial T} . \end{aligned}$$

5 Thermodynamic Consistency

It was mentioned previously that the relations for expressing the mixture pressure and energy in terms of its constituents come from physics, while their derivatives are purely the result of mathematics. An interesting consequence of a more fundamental approach is that we can check the validity of the relations

for the mixture energy and pressure by working with a , the specific Helmholtz free energy and s , the specific entropy.

For example, the mixture free energy can be expressed as:

$$a = e - T s \quad . \quad (34)$$

Now we assume a specific form for the constituent free energies, a_i , and how they are related to the mixture free energy.

$$a_i = e_i - T s_i \quad (35)$$

$$a = \sum_{i=1}^N y_i a_i = \sum_{i=1}^N y_i (e_i - T s_i) \quad . \quad (36)$$

The first law of thermodynamics can be expressed as

$$de = T ds - P dv \quad . \quad (37)$$

Taking the differential of eq. 34 and making use of the first law relation gives:

$$da = -s dT - P dv \quad , \quad (38)$$

which implies that

$$\begin{aligned} -s &\equiv \left(\frac{\partial a}{\partial T} \right)_v \\ -P &\equiv \left(\frac{\partial a}{\partial v} \right)_T \quad . \end{aligned}$$

Differentiating eq. 36 with respect to temperature gives:

$$-s = \sum_{i=1}^N y_i \left[\left(\frac{\partial e_i}{\partial T} - T \frac{\partial s_i}{\partial T} \right) - s_i + \left(\frac{\partial e_i}{\partial v_i} - T \frac{\partial s_i}{\partial v_i} \right) \frac{\partial v_i}{\partial T} \right] \quad . \quad (39)$$

To simplify this equation for the entropy, let's express the first law for a particular component in the mixture:

$$de_i = T ds_i - P_i dv_i \quad . \quad (40)$$

Dividing eq. 40 by dT (at constant v_i) gives the result

$$\left(\frac{\partial e_i}{\partial T} - T \frac{\partial s_i}{\partial T} \right) = 0 \quad . \quad (41)$$

Similarly, if we divide eq. 40 by dv_i (at constant temperature) we arrive at

$$\left(\frac{\partial e_i}{\partial v_i} - T \frac{\partial s_i}{\partial v_i} \right) = -P_i \quad . \quad (42)$$

Inserting these last two results into eq. 39 gives:

$$s = \sum_{i=1}^N y_i \left[s_i + P_i \frac{\partial v_i}{\partial T} \right] \quad . \quad (43)$$

Now that we have relations for a and s in terms of their constituents, we can use eq. 34 to solve for e . The result is:

$$e = \sum_{i=1}^N y_i \left[e_i + T P_i \frac{\partial v_i}{\partial T} \right] . \quad (44)$$

Thus, the specific internal energy is *not* simply a sum of its parts. As John Castor points out in his memo on *Mixing Free-Energy Based EOS Models*, this is probably not a good thing. However, for the case of total pressure equilibration, all of the P_i are equal. This means that the pressure can be pulled out of the above summation and that this term is identically zero, from eq. 20. So for the case of total pressure mixing, we do recover the result that the mixture energy is a simple sum of its parts. Note that by using the fundamental definition for pressure we can show that:

$$P \equiv - \left(\frac{\partial a}{\partial v} \right)_T = \sum_{i=1}^N y_i \frac{\partial v_i}{\partial v} P_i , \quad (45)$$

which is *identical* to eq. 3. Thus, a rigorous derivation of the mixture pressure and energy shows that we have a discrepancy in the energy definition for the case of equilibrating a quantity other than total pressure. We will focus our future work on assessing what consequences there are to omitting this extra term in the mixture energy definition for the cases of electron density and chemical potential equilibration.

6 Test Case

For the case of an atomic mixture of two ideal gases that are equilibrated under the total pressure option, there exists an analytic solution for the sub-densities and the mixture pressure. Thus we can run a simple test case at a variety of densities and temperatures to verify that the Newton-Raphson method converges to the analytic solution. Let the ideal gas mixture have the following number fractions for its isotopics: $n_D = .25$, $n_T = .25$, $n_{N14} = .25$, $n_{O16} = .25$. We will also let the subscript 1 refer to the light gas (the part of the mixture made up of the hydrogen isotopes) and the subscript 2 refer to the heavier isotopes. Converting the number fractions into mass fractions gives $y_1 = .144$ and $y_2 = .856$. Note that for this example, we are using analytic equations of state to represent the two gases, rather than tabular ones. At equilibrium, we will have:

$$P = P_1 = P_2 = \frac{\rho_1 R_u T}{A_1} = \frac{\rho_2 R_u T}{A_2} , \quad (46)$$

where R_u is the universal gas constant and A_i are the average molecular weights of the two sub-gases. Using the mixture density constraint gives 2 equations in 2 unknowns for ρ_1 and ρ_2 . The solution is:

$$\begin{aligned} \rho_1 &= \rho \left(y_1 + y_2 \frac{A_1}{A_2} \right) \\ \rho_2 &= \rho \left(y_2 + y_1 \frac{A_2}{A_1} \right) . \end{aligned}$$

Figure 1 shows the mixture pressure (computed analytically and computed after the Newton-Raphson procedure using the summation formula for the mixture pressure given earlier in the text) as a function of density for a fixed temperature of 1 KeV. Figure 2 shows pressure vs. temperature at a fixed mixture density of $.001 g/cm^3$. In both figures, we see that there is excellent agreement (to approximately 9 decimal places) between the analytically computed pressure and the pressure computed using eq. 3.

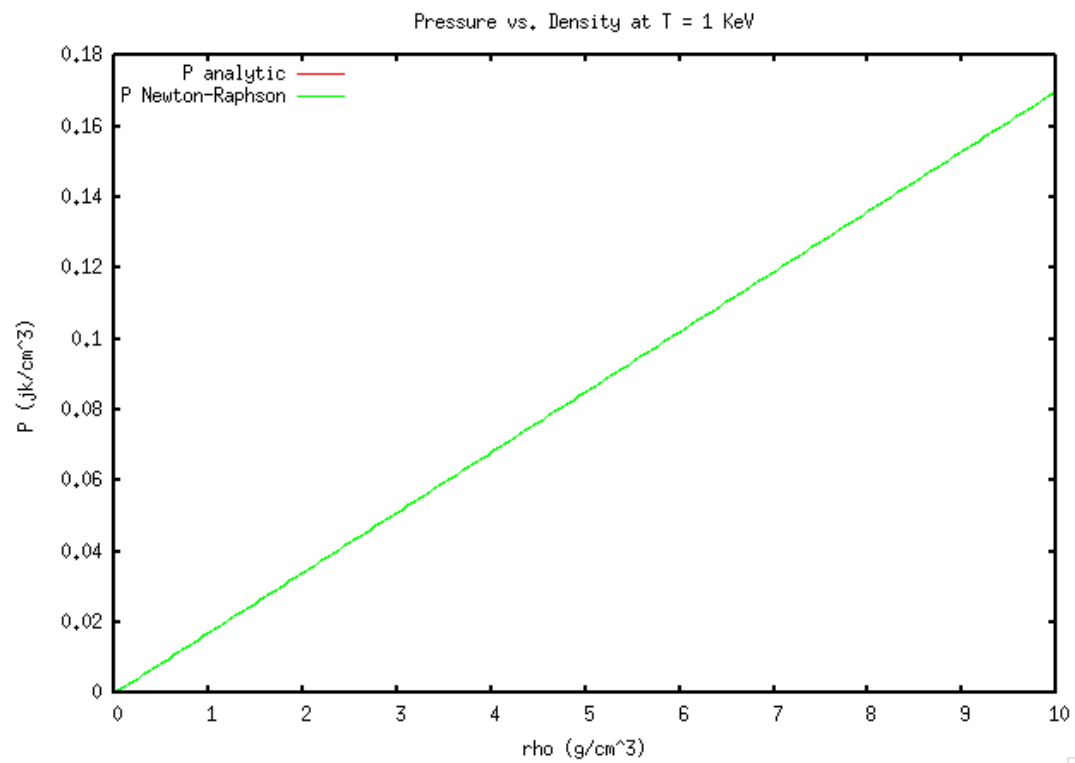


Figure 1: Pressure vs Density at $T = 1 \text{ KeV}$.

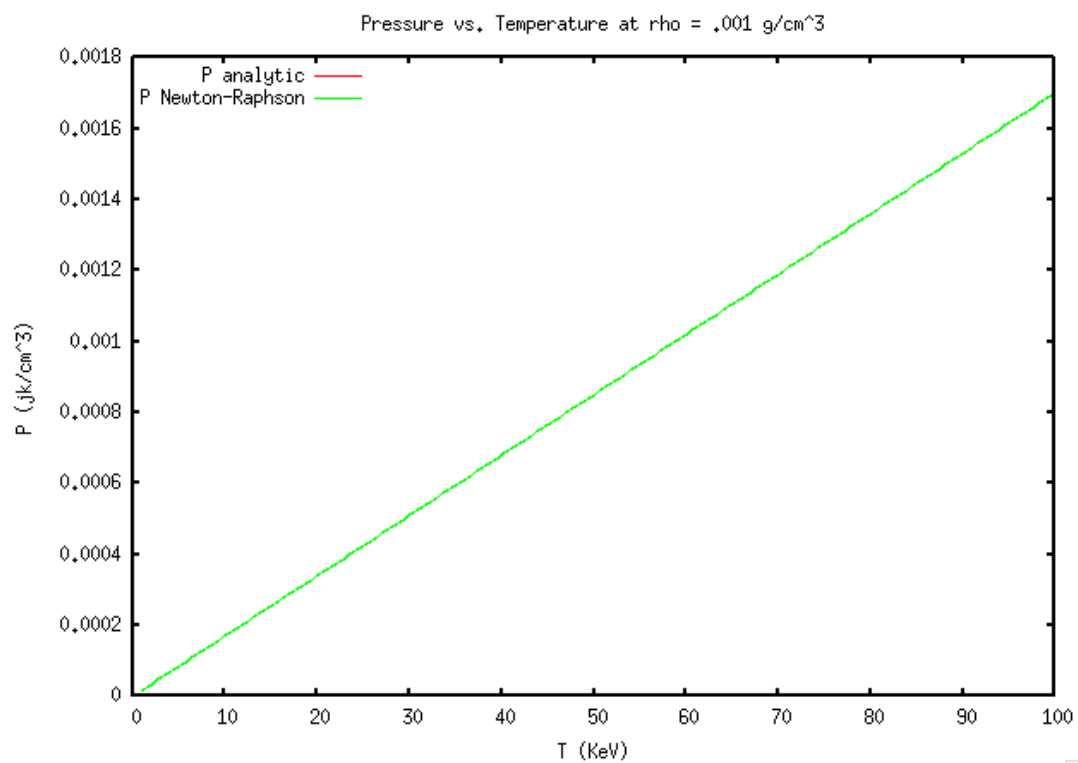


Figure 2: Pressure vs Temperature at $\rho = .001 \text{ g/cm}^3$.