

# Creating EOS tables for mixtures in MEOS: uniform strain and pressure mixing

Philip C. Myint, Christine J. Wu, Ryan W. Long, James R. Leek  
Lawrence Livermore National Laboratory, Livermore, CA 94550

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Our goal is to examine the effect of impurities on the EOS of a particular material by mixing together the EOS tables of that material with those of the impurities to create an EOS table for the resulting mixture. The table will be an array representing the Helmholtz energy  $F$  of the mixture vs. temperature  $T$  and density  $\rho$ . We present step-by-step recipes to create EOS tables under two different scenarios: 1) uniform strain and 2) pressure mixing. In both scenarios, we consider a mixture of  $c$  different components in which the impurities are labeled with the indices  $j = 2, 3, \dots, c$ , and  $j = 1$  refers to the main material (the one that is present in excess amounts).

## 1 Uniform strain

### 1.1 User inputs

Inputs required from the user:

- Specification of some arbitrary reference temperature  $T_{\text{ref}}$  and pressure  $P_{\text{ref}}$ . Usually  $T_{\text{ref}}$  and  $P_{\text{ref}}$  will be chosen to be room temperature (295 K) and ambient pressure, respectively, but they are not required to be these values.
- A pressure offset (e.g., a Laplace pressure)  $\Delta P_j$  for each of the components  $j = 1, 2, \dots, c$  that make up the mixture. In most applications, the user will want to set the pressure offset  $\Delta P_1$  of the main material to be zero, but may choose nonzero values for the  $\Delta P_j$  of the impurities  $j = 2, 3, \dots, c$ .
- Out of the  $c - 1$  impurities in the mixture, some of them will actually be dissolved in component 1 (the main material), while others will segregate out to form a separate phase. The user must specify whether each impurity is dissolved or forms a separate phase. This choice will affect how the Helmholtz energy  $F$  of the mixture is calculated, as described below.
- Specification of EOS tables (e.g., L20, L311, etc.) that will be used to model each of the components  $j = 1, 2, \dots, c$  that make up the mixture.
- The mole fraction  $x_1, x_2, \dots, x_c$  of each component, in which  $\sum_{j=1}^c x_j = 1$ .
- The molar mass  $M_1, M_2, \dots, M_c$  of each component. The average molar mass of the mixture is  $\bar{M} = \sum_{j=1}^c x_j M_j$ .

- The temperature and density range covered by the mixture's EOS table, the number of temperature and density points, and the spacing of these points.

## 1.2 Construction of EOS tables

Given this input, perform the following steps to produce the EOS table for the mixture:

1. For each of the components  $j = 1, 2, \dots, c$ :
  - (a) Find the density  $\rho_j = \rho_j(T_{\text{ref}}, P_{\text{ref}} + \Delta P_j)$  and molar volume  $V_j = M_j / \rho_j$  that corresponds to  $T_{\text{ref}}$  and pressure  $P_{\text{ref}} + \Delta P_j$  using the EOS table for that component.
  - (b) Calculate the ratio  $\eta_j = V_j / V_1$ . Under uniform-strain mixing, we assume that this ratio remains fixed for all points on the table so that all the components in the mixture always undergo the same relative degree of compression. Note that  $\eta_1 = V_1 / V_1 = 1$ , but the expressions below appear in a simpler, more systematic form if we do not explicitly separate out the  $j = 1$  case from the  $j \neq 1$  case, so we do not explicitly make this identification in those expressions.
2. Produce the EOS table for the mixture by performing the following for each temperature  $T$  and density  $\rho$  point on the table:

- (a) Translate the density to a molar volume through  $V = \bar{M} / \rho$ .
- (b) Find the volume of component 1 from the fact that  $V = \sum_{j=1}^c x_j V_j = V_1 \sum_{j=1}^c x_j \eta_j$ , which leads to

$$V_1 = \frac{V}{\sum_{j=1}^c x_j \eta_j} = \frac{\eta_1 V}{\sum_{j=1}^c x_j \eta_j}. \quad (1)$$

The volume of impurity  $j$  is therefore

$$V_j = \eta_j V_1 = \frac{\eta_j V}{\sum_{j=1}^c x_j \eta_j}. \quad (2)$$

- (c) Compute the molar Helmholtz energy  $F_j = F_j(T, M_j / V_j)$  for  $j = 1, 2, \dots, c$ , using the appropriate EOS tables.
- (d) As stated above, a subset of the  $c - 1$  impurities will be dissolved in component 1, while the remainder are assumed to segregate out to form separate phases. Let the index  $k$  denote all the components (include the main material, component 1) that are dissolved together; this index therefore excludes the ones that form separate phases. Define the mole fraction  $z_k$  as

$$z_k = \frac{x_k}{\sum_k x_k}. \quad (3)$$

Note that  $z_k$  will in general be greater than  $x_k$  (since the sum in the denominator will in general be less than 1 since  $k$  does not necessarily include every component that is present in the mixture), unless *all*  $c - 1$  impurities are dissolved in component 1, in which case then  $z_k = x_k$ .

(e) The molar Helmholtz energy  $F$  of the mixture at the given  $T$  and  $\rho$  is

$$F = \sum_{j=1}^c x_j F_j + RT \sum_{k=1}^c z_k \ln z_k, \quad (4)$$

where  $R = 8.31446 \times 10^{-5}$  Mbar cm<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup> is the gas constant. This  $F$  can be converted to a per-mass quantity by dividing it by the average molar mass  $\bar{M}$ .

3. The  $F$  in Equation (4) refers to the total Helmholtz energy. Hydrodynamic simulation codes would also like to have a decomposition of the total pressure  $P = -(\partial F / \partial V)_T$  and total internal energy  $E = -T^2 [\partial(F/T) / \partial T]_V$  into the cold, ion-thermal, and electron-thermal contributions:  $P = P_{\text{cold}} + P_{\text{ion}} + P_{\text{electron}}$  and  $E = E_{\text{cold}} + E_{\text{ion}} + E_{\text{electron}}$ . Towards this purpose, it is useful to have an equation that relates each of these contributions, as well as the total pressure and internal energy, to those of the individual components. The Appendix shows that these equations are

$$P = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_j, \quad (5)$$

$$P_{\text{cold}} = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_{\text{cold},j}, \quad (6)$$

$$P_{\text{ion}} = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_{\text{ion},j}, \quad (7)$$

$$P_{\text{electron}} = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_{\text{electron},j}, \quad (8)$$

$$E = \sum_{j=1}^c x_j E_j, \quad (9)$$

$$E_{\text{cold}} = \sum_{j=1}^c x_j E_{\text{cold},j}, \quad (10)$$

$$E_{\text{ion}} = \sum_{j=1}^c x_j E_{\text{ion},j}, \quad (11)$$

$$E_{\text{electron}} = \sum_{j=1}^c x_j E_{\text{electron},j}. \quad (12)$$

It is important to note that all of the pure-component properties (all quantities that have a subscript  $j$ ) are to be evaluated at a temperature  $T$  and a volume of  $V_j$  (or a density of  $\rho_j = M_j/V_j$ ) instead of a volume (density) of  $V$  ( $\rho = \bar{M}/V$ ). In contrast the mixture properties that appear on the left-hand side in these equations are to be evaluated at  $T$  and  $V$  (or  $\rho$ ). This is consistent with the fact that the  $F_j$  that appear in Equation (4) are evaluated at  $V_j$  or  $\rho_j$ , while  $F$  in that same equation represents a mixture property at  $V$  or  $\rho$ .

### 1.3 Construction of EOS tables that include effects from surface tension

It may be desirable in some cases to include the effect of surface tension. In such cases, Equation (4) for the total Helmholtz energy becomes

$$F = \sum_{j=1}^c x_j F_j + RT \sum_{k=1} z_k \ln z_k + \sum_{l \neq k} \sigma_l A_l, \quad (13)$$

where  $\sigma_l$  is the surface tension of the interface between component  $l$  and component 1 (the main material), and  $A_l$  is the area of that interface per mole of the mixture. Note that  $A_l$  must be a molar quantity and not a per-mass quantity in order to be compatible with all of the other energy terms in Equation (13)—which are also molar quantities—as well as because of the fact that the  $x_k$  and  $z_k$  represent mole fractions. The  $l \neq k$  condition means that the summation over  $l$  denotes all components that are not dissolved in component 1 and are instead segregated out to form separate phases. Recall that we use the index  $k$  to indicate all components that are dissolved in component 1; by definition, no interface exists between components that are dissolved in each other, and so  $l$  represents all elements of the set  $j = 1, 2, 3, \dots, c$  that do not belong to (are mutually exclusive with) the set of integers represented by  $k$ .

To make the problem tractable, we consider only the situation where all components  $l$  form spherical “bubbles” of radius  $R_l$  in which the number density  $n_l$  of these bubbles remains a constant for all conditions. The fact that  $n_l$  is fixed means that we neglect bubble coalescence—which reduces the surface area  $A_l$ —that occurs as the bubbles get compressed, and therefore the scenario we are considering represents an upper bound on the magnitude of the surface area  $A_l$  and energy  $\sigma_l A_l$ . With these simplifications, we have

$$A_l = 4\pi R_l^2 n_l V, \quad (14)$$

in which  $V = \bar{M}/\rho$  is the molar volume of the mixture. Substitution of (14) into (13) yields

$$F = \sum_{j=1}^c x_j F_j + RT \sum_{k=1} z_k \ln z_k + \sum_{l \neq k} P_l V, \quad (15)$$

where the pressure  $P_l$  is defined as  $4\pi R_l^2 \sigma_l n_l$ . For a given  $T$  and  $\rho$ , the radius  $R_l$  may be computed from knowledge of the volume fraction  $\phi_l$  at that  $T$  and  $\rho$ . That is, we use the relation

$$\frac{4\pi R_l^3}{3} n_l = \phi_l = \frac{x_l V_l}{V} = \frac{x_l \eta_l}{\sum_{j=1}^c x_j \eta_j}, \quad (16)$$

where the last equality follows from Equation (2), to get

$$R_l = \left( \frac{3}{4\pi n_l} \frac{x_l \eta_l}{\sum_{j=1}^c x_j \eta_j} \right)^{1/3}. \quad (17)$$

Note that because the volume fraction  $\phi_l$  is fixed for all  $T$  and  $\rho$  under uniform-strain mixing (all the volume ratios  $\eta_j$  are constants), the radius  $R_l$  is a constant as well. The procedure for producing an EOS table that accounts for surface tension is largely the same as the procedure in Section 1.2, except for the following few additional steps:

1. Get user input regarding the bubble number density  $n_l$  for each component  $l$ . Use this information, along with the user-specified mole fractions  $x_l$  and the calculated volume ratios  $\eta_l$  to compute the radius  $R_l$  in Equation (17) for each  $l$ .
2. For each different  $\rho = \bar{M}/V$  point on the table, compute the molar surface area  $A_l$  from (14).
3. Calculate the surface tension  $\sigma_l$  for each  $(T, \rho)$  point on the table, and combine with  $A_l$  to calculate the total Helmholtz energy  $F$  according to (13). If  $\sigma_l$  is treated as a constant, it follows from (5) and (9) that we have the following analytical expressions below for the total pressure  $P = -(\partial F/\partial V)_T$  and total internal energy  $E = -T^2[\partial(F/T)/\partial T]_V$ :

$$P = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \left( \sum_{j=1}^c x_j \eta_j P_j \right) - \sum_{l \neq k} 4\pi R_l^2 \sigma_l n_l, \quad (18)$$

$$E = \sum_{j=1}^c x_j E_j + \sum_{l \neq k} \sigma_l A_l. \quad (19)$$

## 2 Pressure mixing

### 2.1 Construction of EOS tables

Pressure mixing is conceptually more simple than mixing under uniform strain, but it is computationally much more involved. The required input from the user is the same in both scenarios, with the exception that pressure mixing does not require specification of the arbitrary reference temperature  $T_{\text{ref}}$  and pressure  $P_{\text{ref}}$ . We produce the EOS table for the mixture by performing the following for each temperature  $T$  and density  $\rho$  point on the table:

1. Translate the density to a molar volume through  $V = \bar{M}/\rho$ .
2. Apply an iterative numerical method to find the pressure  $P_{\text{base}}$  such that

$$V = \sum_{j=1}^c x_j V_j(T, P_j) = \sum_{j=1}^c x_j V_j(T, P_{\text{base}} + \Delta P_j), \quad (20)$$

in which  $V_j(T, P_j)$  is the molar volume of  $j$  that corresponds to  $T$  and a pressure of  $P_j = P_{\text{base}} + \Delta P_j$ . In this mixing scenario, we treat all the  $\Delta P_j$  (which are specified by the user in the input deck) as constants that are fixed throughout the entire table. This requirement to solve for the pressure  $P_{\text{base}}$  and simultaneously determine the volumes all components in the process of doing so is the computationally expensive step of pressure mixing.

3. Compute the molar Helmholtz energy  $F_j = F_j(T, M_j/V_j)$  for  $j = 1, 2, \dots, c$ , using the appropriate EOS tables.
4. The molar Helmholtz energy  $F$  of the mixture at the given  $T$  and  $\rho$  is again given by Equation (4). The Appendix shows that the decomposition of this total Helmholtz energy into

cold, ion-thermal, and electron-thermal pieces to the pressure  $P = P_{\text{cold}} + P_{\text{ion}} + P_{\text{electron}}$  and internal energy  $E = E_{\text{cold}} + E_{\text{ion}} + E_{\text{electron}}$  are given by

$$P = \left( \frac{1}{\sum_{j=1}^c x_j V_j / B_j} \right) \sum_{j=1}^c (x_j V_j / B_j) P_j, \quad (21)$$

$$P_{\text{cold}} = \left( \frac{1}{\sum_{j=1}^c x_j V_j / B_j} \right) \sum_{j=1}^c (x_j V_j / B_j) P_{\text{cold},j}, \quad (22)$$

$$P_{\text{ion}} = \left( \frac{1}{\sum_{j=1}^c x_j V_j / B_j} \right) \sum_{j=1}^c (x_j V_j / B_j) P_{\text{ion},j}, \quad (23)$$

$$P_{\text{electron}} = \left( \frac{1}{\sum_{j=1}^c x_j V_j / B_j} \right) \sum_{j=1}^c (x_j V_j / B_j) P_{\text{electron},j}, \quad (24)$$

$$E = \sum_{j=1}^c x_j \left\{ E_j + T \left[ (P_j - P) \left( \frac{\partial V_j}{\partial T} \right)_{P_j} \right] \right\}, \quad (25)$$

$$E_{\text{cold}} = \sum_{j=1}^c x_j \left\{ E_{\text{cold},j} + T \left[ (P_{\text{cold},j} - P_{\text{cold}}) \left( \frac{\partial V_j}{\partial T} \right)_{P_j} \right] \right\}, \quad (26)$$

$$E_{\text{ion}} = \sum_{j=1}^c x_j \left\{ E_{\text{ion},j} + T \left[ (P_{\text{ion},j} - P_{\text{ion}}) \left( \frac{\partial V_j}{\partial T} \right)_{P_j} \right] \right\}, \quad (27)$$

$$E_{\text{electron}} = \sum_{j=1}^c x_j \left\{ E_{\text{electron},j} + T \left[ (P_{\text{electron},j} - P_{\text{electron}}) \left( \frac{\partial V_j}{\partial T} \right)_{P_j} \right] \right\}, \quad (28)$$

where  $B_j = -V_j(\partial P_j / \partial V_j)_T$  is the isothermal bulk modulus of component  $j$ . Like in the case of uniform strain, all pure-component properties (the ones with the subscript  $j$ ) are to be evaluated at  $T$  and a volume of  $V_j$  (or a density of  $\rho_j = M_j / V_j$ ), while the mixture properties (the ones without a subscript of  $j$ ) are to be evaluated at  $T$  and a volume of  $V$  (or  $\rho = \bar{M} / V$ ).

## 2.2 Construction of EOS tables that include effects from surface tension

If we include the effect of surface tension under pressure mixing, the total Helmholtz energy  $F$  is again given by Equation (13), just like in the case of mixing under uniform strain. Likewise, the molar surface area  $A_l$  of the interface between component  $l$  and component 1 may be calculated from Equation (14) so that we again have

$$F = \sum_{j=1}^c x_j F_j + RT \sum_{k=1}^c z_k \ln z_k + \sum_{l \neq k} P_l V, \quad (29)$$

in which  $P_l = 4\pi R_l^2 \sigma_l n_l$ . But the difference with uniform-strain mixing is that the radius  $R_l$  in pressure mixing is not a constant even if the bubble number density  $n_l$  is a constant because

the volumes of the individual components and the volume fraction  $\phi_l$  vary with temperature and pressure. This may be seen from the relations

$$\frac{4\pi R_l^3}{3} n_l = \phi_l = \frac{x_l V_l}{V} = \frac{x_l V_l}{\sum_{j=1}^c x_j V_j}, \quad (30)$$

$$R_l = \left( \frac{3}{4\pi n_l} \frac{x_l V_l}{\sum_{j=1}^c x_j V_j} \right)^{1/3}. \quad (31)$$

The procedure for producing an EOS table is largely the same as in Section 2.1, except for the following few additional steps:

1. Get user input regarding the bubble number density  $n_l$  for each component  $l$ .
2. For each different temperature  $T$  and density  $\rho = \bar{M}/V$  point on the table, calculate the surface tension  $\sigma_l$  with the chosen model for that quantity. In addition, calculate the volumes  $V_j$  of all components according to the procedure in Section 2.1.
3. For each  $(T, \rho)$  point of the table, use the information in the previous two steps to compute the bubble radius  $R_l$ , molar surface area  $A_l$ , and total Helmholtz energy  $F$  from Equations (31), (14), and (13), respectively.
4. If  $\sigma_l$  is treated as a constant, the total pressure  $P = -(\partial F/\partial V)_T$  obeys the analytical expression

$$P = \left( \frac{1}{\sum_{j=1}^c x_j V_j / B_j} \right) \left[ \sum_{j=1}^c (x_j V_j / B_j) P_j \right] - \sum_{l \neq k} 4\pi \sigma_l n_l \left[ R_l^2 + 2R_l V \left( \frac{\partial R_l}{\partial V} \right)_T \right], \quad (32)$$

where

$$\left( \frac{\partial R_l}{\partial V} \right)_T = \frac{1}{3} \left( \frac{3}{4\pi n_l} \frac{x_l V_l}{\sum_{j=1}^c x_j V_j} \right)^{-2/3} \left[ -\frac{3}{4\pi n_l} \frac{x_l V_l}{V^2} + \frac{3}{4\pi n_l} \frac{x_l}{V} \left( \frac{\partial V_l}{\partial V} \right)_T \right], \quad (33)$$

$$\left( \frac{\partial V_l}{\partial V} \right)_T = \frac{1}{\left( \frac{\partial V}{\partial V_l} \right)_T} = \frac{1}{\sum_{j=1}^c x_j \left( \frac{\partial V_j}{\partial P_j} \right)_T \left( \frac{\partial P_l}{\partial V_l} \right)_T} = \frac{1}{\left( \sum_{j=1}^c \frac{x_j V_j}{B_j} \right)} \frac{V_l}{B_l}. \quad (34)$$

The second equality arises from the fact that in the expression  $P_j = P_{\text{base}} + \Delta P_j$ , the pressure offset  $\Delta P_j$  is a constant so that  $(\partial P_j / \partial V_l)_T = (\partial P_l / \partial V_l)_T = (\partial P_{\text{base}} / \partial V_l)_T$ . Moreover, the total internal energy  $E = -T^2 [\partial(F/T) / \partial T]_V$  is

$$E = \sum_{j=1}^c x_j \left\{ E_j + T \left[ (P_j - P) \left( \frac{\partial V_j}{\partial T} \right)_{P_j} \right] \right\} + \sum_{l \neq k} \sigma_l \left[ A_l - 8T\pi R_l n_l V \left( \frac{\partial R_l}{\partial T} \right)_V \right], \quad (35)$$

where

$$\left( \frac{\partial R_l}{\partial T} \right)_V = \frac{1}{3} \left( \frac{3}{4\pi n_l} \frac{x_l V_l}{\sum_{j=1}^c x_j V_j} \right)^{-2/3} \left[ \frac{3}{4\pi n_l} \frac{x_l}{V} \left( \frac{\partial V_l}{\partial T} \right)_V \right], \quad (36)$$

$$\left( \frac{\partial V_l}{\partial T} \right)_V = -\frac{(\partial V_l / \partial V)_T (\partial V / \partial T)_{V_l}}{(\partial T / \partial V)_{V_l}} = -(\partial V_l / \partial V)_T (\partial V / \partial T)_{V_l}. \quad (37)$$

Here, the derivative  $(\partial V_l/\partial V)_T$  is given by Equation (34), and  $(\partial V/\partial T)_{V_l}$  is

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_{V_l} &= \sum_{j=1}^c x_j \left[ \left(\frac{\partial V_j}{\partial T}\right)_{P_j} + \left(\frac{\partial V_j}{\partial P_j}\right)_T \left(\frac{\partial P_l}{\partial T}\right)_{V_l} \right] = \sum_{j=1}^c x_j \left[ \left(\frac{\partial V_j}{\partial T}\right)_{P_j} - \frac{V_j}{B_j} \left(\frac{\partial V_l}{\partial T}\right)_{P_l} \frac{B_l}{V_l} \right] \\ &= \left[ \sum_{j=1}^c x_j \left(\frac{\partial V_j}{\partial T}\right)_{P_j} \right] - \left( \sum_{j=1}^c x_j \frac{V_j}{B_j} \right) \left(\frac{\partial V_l}{\partial T}\right)_{P_l} \frac{B_l}{V_l}. \end{aligned} \quad (38)$$

## Appendix: Decomposition of the mixture pressure and internal energy into cold, ion-thermal, and electron-thermal contributions

### Uniform strain

For uniform-strain mixing, we can express the functional dependence in Equation (4) for the total Helmholtz energy  $F$  of the mixture in terms of its temperature  $T$  and volume  $V = \bar{M}/\rho$  as

$$F = F \{T, F_1[T, V_1(V)], F_2[T, V_2(V)], \dots, F_c[T, V_c(V)]\}. \quad (39)$$

The total pressure  $P$  of the mixture is defined as

$$P = - \left(\frac{\partial F}{\partial V}\right)_T = - \sum_{j=1}^c \left(\frac{\partial F}{\partial F_j}\right)_{T, \mathbf{F}_j} \left(\frac{\partial F_j}{\partial V_j}\right)_T \frac{dV_j}{dV}. \quad (40)$$

The second equality follows from application of the chain rule to Equation (39). The subscripts  $T$  and  $\mathbf{F}_j$  in the derivative  $(\partial F/\partial F_j)_{T, \mathbf{F}_j}$  indicate that the temperature and all of the  $F_i$  except  $F_{i=j}$  are to be held fixed in the evaluation of that derivative. It follows from Equation (4) that

$$\left(\frac{\partial F}{\partial F_j}\right)_{T, \mathbf{F}_j} = x_j, \quad (41)$$

and we also have

$$- \left(\frac{\partial F_j}{\partial V_j}\right)_T = P_j, \quad (42)$$

which is just the familiar definition of the pressure  $P_j$  for a single-component system. From Equations (1) and (2), we have

$$\frac{dV_j}{dV} = \frac{\eta_j}{\sum_{j=1}^c x_j \eta_j}. \quad (43)$$

Substitution of these relations into (40) yields

$$P = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_j. \quad (44)$$

Note that the pressure  $P_j$  is to be evaluated on the EOS table of component  $j$  at a temperature of  $T$  and a volume of  $V_j$  (or a density of  $M_j/V_j$ ); it would be incorrect to evaluate it a volume of  $V$ .



Since  $P_j = P_{\text{cold},j} + P_{\text{ion},j} + P_{\text{electron},j}$  and  $P = P_{\text{cold}} + P_{\text{ion}} + P_{\text{electron}}$ , in which the three terms refer to the cold, ion-thermal, and electron-thermal contributions, we have

$$P_{\text{cold}} = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_{\text{cold},j}, \quad (45)$$

$$P_{\text{ion}} = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_{\text{ion},j}, \quad (46)$$

$$P_{\text{electron}} = \left( \frac{1}{\sum_{j=1}^c x_j \eta_j} \right) \sum_{j=1}^c x_j \eta_j P_{\text{electron},j}. \quad (47)$$

In order to decompose the total internal energy  $E$  into the cold, ion-thermal, and electron-thermal contributions, we use the relation

$$E = -T^2 \left( \frac{\partial F/T}{\partial T} \right)_V = F + TS, \quad (48)$$

where  $S = -(\partial F/\partial T)_V$  is the entropy of the mixture. Let us define  $\mathcal{F} = F/T$  and  $\mathcal{F}_j = F_j/T$  so that from Equation (4), we have

$$\mathcal{F} = \mathcal{F} \{ \mathcal{F}_1[T, V_1(V)], \mathcal{F}_2[T, V_2(V)], \dots, \mathcal{F}_c[T, V_c(V)] \}. \quad (49)$$

Therefore the total internal energy  $E$  is

$$E = -T^2 \left( \frac{\partial \mathcal{F}}{\partial T} \right)_V = -T^2 \sum_{j=1}^c \left( \frac{\partial \mathcal{F}}{\partial \mathcal{F}_j} \right)_{T, \mathcal{F}_j} \left( \frac{\partial \mathcal{F}_j}{\partial T} \right)_{V_j} = \sum_{j=1}^c x_j E_j. \quad (50)$$

This is a consequence of the relations  $(\partial \mathcal{F}/\partial \mathcal{F}_j)_{T, \mathcal{F}_j} = x_j$  and  $-T^2 (\partial \mathcal{F}_j/\partial T)_{V_j} = E_j$ . Like the pressure  $P_j$ , the internal energy  $E_j$  is to be evaluated at a volume of  $V_j$  and not  $V$ . Since  $E_j = E_{\text{cold},j} + E_{\text{ion},j} + E_{\text{electron},j}$  and  $E = E_{\text{cold}} + E_{\text{ion}} + E_{\text{electron}}$ , we obtain

$$E_{\text{cold}} = \sum_{j=1}^c x_j E_{\text{cold},j}, \quad (51)$$

$$E_{\text{ion}} = \sum_{j=1}^c x_j E_{\text{ion},j}, \quad (52)$$

$$E_{\text{electron}} = \sum_{j=1}^c x_j E_{\text{electron},j}. \quad (53)$$

## Pressure mixing

We write the functional dependence of  $F$  under pressure mixing as

$$F = F(T, F_1\{T, V_1[T, P_1(T, V)]\}, F_2\{T, V_2[T, P_2(T, V)]\}, \dots, F_c\{T, V_c[T, P_c(T, V)]\}). \quad (54)$$

That is,  $F$  is an explicit function of  $T$  and the Helmholtz energy  $F_j$  of the individual components. The free energy  $F_j$  is in turn a function of  $T$  and  $V_j$ , where the latter ultimately depends on  $T$

and  $V$  through Equation (20). The pressure  $P_j$  is introduced as an auxiliary variable to aid the derivations. Applying the chain rule, the pressure  $P$  of the mixture is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\sum_{j=1}^c \left(\frac{\partial F}{\partial F_j}\right)_{T, \mathbf{F}_j} \left(\frac{\partial F_j}{\partial V_j}\right)_T \left(\frac{\partial V_j}{\partial P_j}\right)_T \left(\frac{\partial P_j}{\partial V}\right)_T. \quad (55)$$

We know the first two derivatives that appear in the summation on the right from Equations (41) and (42). In addition, we have

$$\left(\frac{\partial V_j}{\partial P_j}\right)_T = -\frac{V_j}{B_j}, \quad (56)$$

where  $B_j = -V_j(\partial P_j/\partial V_j)_T$  is the isothermal bulk modulus of component  $j$  evaluated at  $T$  and a volume of  $V_j$  (or a density of  $M_j/V_j$ ). The last derivative that appears in the summation may be obtained from Equation (20), which tells us that

$$\left(\frac{\partial V}{\partial P_j}\right)_T = \frac{1}{(\partial P_j/\partial V)_T} = \sum_{j=1}^c x_j \left(\frac{\partial V_j}{\partial P_j}\right)_T = -\sum_{j=1}^c x_j \frac{V_j}{B_j}. \quad (57)$$

Substituting all of these different relations into (55) gives

$$P = \left(\frac{1}{\sum_{j=1}^c x_j V_j/B_j}\right) \sum_{j=1}^c (x_j V_j/B_j) P_j, \quad (58)$$

which we may divide into the three contributions as follows

$$P_{\text{cold}} = \left(\frac{1}{\sum_{j=1}^c x_j V_j/B_j}\right) \sum_{j=1}^c (x_j V_j/B_j) P_{\text{cold},j}, \quad (59)$$

$$P_{\text{ion}} = \left(\frac{1}{\sum_{j=1}^c x_j V_j/B_j}\right) \sum_{j=1}^c (x_j V_j/B_j) P_{\text{ion},j}, \quad (60)$$

$$P_{\text{electron}} = \left(\frac{1}{\sum_{j=1}^c x_j V_j/B_j}\right) \sum_{j=1}^c (x_j V_j/B_j) P_{\text{electron},j}. \quad (61)$$

For the total internal energy  $E$ , we again define  $\mathcal{F} = F/T$  and  $\mathcal{F}_j = F_j/T$  and write Equation (54) as

$$\mathcal{F} = \mathcal{F}(\mathcal{F}_1\{T, V_1[T, P_1(T, V)]\}, \mathcal{F}_2\{T, V_2[T, P_2(T, V)]\}, \dots, \mathcal{F}_c\{T, V_c[T, P_c(T, V)]\}). \quad (62)$$

Application of the chain rule gives the following expression for  $E = -T^2(\partial \mathcal{F}/\partial T)_V$ :

$$E = -T^2 \sum_{j=1}^c \left(\frac{\partial \mathcal{F}}{\partial \mathcal{F}_j}\right)_{T, \mathbf{F}_j} \left\{ \left(\frac{\partial \mathcal{F}_j}{\partial T}\right)_{V_j} + \left(\frac{\partial \mathcal{F}_j}{\partial V_j}\right)_T \left[ \left(\frac{\partial V_j}{\partial T}\right)_{P_j} + \left(\frac{\partial V_j}{\partial P_j}\right)_T \left(\frac{\partial P_j}{\partial T}\right)_V \right] \right\}. \quad (63)$$

We know the first two derivatives on the right-hand side through Equation (50). We also know that

$$-T^2 \sum_{j=1}^c \left(\frac{\partial \mathcal{F}}{\partial \mathcal{F}_j}\right)_{T, \mathbf{F}_j} \left(\frac{\partial \mathcal{F}_j}{\partial V_j}\right)_T \left(\frac{\partial V_j}{\partial T}\right)_{P_j} = T \sum_{j=1}^c P_j x_j \left(\frac{\partial V_j}{\partial T}\right)_{P_j}. \quad (64)$$

Applying a basic thermodynamic identity to the last derivative in Equation (63) gives

$$\left(\frac{\partial P_j}{\partial T}\right)_V = -\left(\frac{\partial P_j}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_{P_j} = \left(\frac{1}{\sum_{j=1}^c x_j V_j / B_j}\right) \sum_{j=1}^c x_j \left(\frac{\partial V_j}{\partial T}\right)_{P_j}. \quad (65)$$

Here, the second equality follows from Equations (20) and (57). Therefore

$$\begin{aligned} & -T^2 \sum_{j=1}^c \left(\frac{\partial \mathcal{F}}{\partial \mathcal{F}_j}\right)_{T, \mathcal{F}_j} \left(\frac{\partial \mathcal{F}_j}{\partial V_j}\right)_T \left(\frac{\partial V_j}{\partial P_j}\right)_T \left(\frac{\partial P_j}{\partial T}\right)_V \\ & = -T \left(\frac{1}{\sum_{j=1}^c x_j V_j / B_j}\right) \left[\sum_{j=1}^c (x_j V_j / B_j) P_j\right] \sum_{j=1}^c x_j \left(\frac{\partial V_j}{\partial T}\right)_{P_j} = -TP \sum_{j=1}^c x_j \left(\frac{\partial V_j}{\partial T}\right)_{P_j}. \end{aligned} \quad (66)$$

We have substituted Equation (58) to obtain the last equality. Substituting (50), (64), and (66) into (63) leads to

$$E = \sum_{j=1}^c x_j \left\{ E_j + T \left[ (P_j - P) \left(\frac{\partial V_j}{\partial T}\right)_{P_j} \right] \right\}. \quad (67)$$

We thus have

$$E_{\text{cold}} = \sum_{j=1}^c x_j \left\{ E_{\text{cold},j} + T \left[ (P_{\text{cold},j} - P_{\text{cold}}) \left(\frac{\partial V_j}{\partial T}\right)_{P_j} \right] \right\}, \quad (68)$$

$$E_{\text{ion}} = \sum_{j=1}^c x_j \left\{ E_{\text{ion},j} + T \left[ (P_{\text{ion},j} - P_{\text{ion}}) \left(\frac{\partial V_j}{\partial T}\right)_{P_j} \right] \right\}, \quad (69)$$

$$E_{\text{electron}} = \sum_{j=1}^c x_j \left\{ E_{\text{electron},j} + T \left[ (P_{\text{electron},j} - P_{\text{electron}}) \left(\frac{\partial V_j}{\partial T}\right)_{P_j} \right] \right\}, \quad (70)$$

where  $P_{\text{cold}}$ ,  $P_{\text{ion}}$ , and  $P_{\text{electron}}$  of the mixture are given by Equations (59)–(61). Note that if the pressure were uniform in all components so that all  $\Delta P_j = 0$  and  $P_j = P$ , Equation (67) reduces to  $E = \sum_{j=1}^c x_j E_j$ , much like in the case of uniform strain. Similar simplifications also hold for the three energy contributions in this event.