

# CASM Parametric composition

CASM Developers

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## 1 Parametric Composition

- $\vec{\sigma}$ : A configuration of atomic, electronic, magnetic, etc. degrees of freedom.  $\vec{\sigma}$  can be represented as a vector containing all the discrete and/or continuous values representing the degree of freedoms of the microscopic system being modeled.
- $N^{basis}$ : The number of basis sites in the unit cell.
- $N^{unit}$ : The number of unit cells.
- $N_i$ : The total number of species  $i$ .
- $\vec{N}$ : The vector of  $N_i$ .
- $N^{tot}$ : The total number of all species,  $N^{tot} = \sum_i N_i$ .
- $N^{tot \setminus Va}$ : The total number of all species non-vacancy,  $N^{tot \setminus Va} = \sum_{i \neq Va} N_i$ .
- $N^{spec}$ : The number of different species, including vacancies.
- $N^{spec \setminus Va}$ : The number of different species, excluding vacancies.
- $N^{comp}$ : The number of independent composition axes.
- $n_i$ : The number of species  $i$  per unit cell. CASM writes this as `comp_n(A)`, `comp_n(B)`, etc., where A, B, etc. are the names given to species in the `prim.json` input file.
- $\vec{n}$ : The vector of composition values  $n_i$ .  $\vec{n} = \vec{N}/N^{unit}$
- $x_i$ : The value of parametric composition  $i$ . CASM writes this as `comp(a)`, `comp(b)`, etc., where a, b, etc. are names for the independent composition axes.
- $\vec{x}$ : The vector of parametric composition values  $x_i$ .
- $\vec{n}^o$ : The composition corresponding to the origin ( $\vec{x} = [0, 0, \dots]$ ) in parametric composition space.
- $\vec{n}^a, \vec{n}^b, \dots$ : The end members corresponding to  $\vec{x} = [1, 0, \dots], \vec{x} = [0, 1, \dots], \dots$ . The vectors  $\vec{n}^a - \vec{n}^o, \vec{n}^b - \vec{n}^o, \dots$  are the independent composition axes.
- $\mathbf{M}$ : The  $\vec{x} \rightarrow \vec{n}$  conversion matrix, of size  $N^{spec} \times N^{comp}$ .
- $\mathbf{M}^+$ : The  $\vec{n} \rightarrow \vec{x}$  conversion matrix, of size  $N^{comp} \times N^{spec}$ . The left pseudoinverse of  $\mathbf{M}$ ,  $\mathbf{I} = \mathbf{M}^+ \mathbf{M}$ .

## 1.1 Converting between $n$ and $x$

In a lattice model, the composition space spanned by allowed configurations is limited such that  $\sum_i n_i = N^{basis}$ . This means there is at least one more allowed species (including vacancies) than there are dimensions in the allowed composition space.

We define the parametric composition space by specifying the origin,  $\vec{n}^o$ , corresponding to  $\vec{x} = [0, 0, \dots]$ , and end members  $\vec{n}^a, \vec{n}^b, \dots$  corresponding to  $\vec{x} = [1, 0, \dots], \vec{x} = [0, 1, \dots], \dots$ . This definition gives:

$$\vec{n} = \vec{n}^o + \mathbf{M}\vec{x}. \quad (1)$$

where the columns of  $\mathbf{M}$  are the independent composition axes  $\vec{n}^a - \vec{n}^o, \vec{n}^b - \vec{n}^o, \dots$

Then re-arranging gives,

$$\vec{x} = \mathbf{M}^+(\vec{n} - \vec{n}^o), \quad (2)$$

where the matrix  $\mathbf{M}^+$  is the left pseudoinverse of  $\mathbf{M}$ ,  $I = \mathbf{M}^+\mathbf{M}$ . Since  $\mathbf{M}$  describes the allowed composition space, it has full column rank and  $\mathbf{M}^+$  can be calculated using:

$$\mathbf{M}^+ = (\mathbf{M}^\top \mathbf{M})^{-1} \mathbf{M}^\top. \quad (3)$$

Changes in  $\vec{n}$  and  $\vec{x}$  are related through:

$$d\vec{n} = \mathbf{M}d\vec{x} \quad (4)$$

$$d\vec{x} = \mathbf{M}^+d\vec{n}. \quad (5)$$

## 1.2 Semi-Grand Canonical Ensemble

In semi-grand canonical ensemble Monte Carlo calculations we control the temperature and chemical potential and allow the distribution and relative number of occupants among the basis sites in the crystal to vary.

Then, by the first and second laws of thermodynamics, the fundamental equation is

$$dU = TdS + \vec{\mu}^\top d\vec{N}, \quad (6)$$

but with the constraint that:

$$\sum_i N_i = N^{basis} N^{unit}. \quad (7)$$

Because Monte Carlo calculations are typically performed at constant  $N^{unit}$ , we separate  $\vec{\mu}d\vec{N}$  into components accounting for change in composition and change in number of unit cells (and composition):

$$\vec{\mu}^\top d\vec{N} = N^{unit} \vec{\mu}^\top d\vec{n} + \vec{\mu}^\top \vec{n} dN^{unit} \quad (8)$$

$$= N^{unit} \vec{\mu}^\top \mathbf{M}d\vec{x} + \vec{\mu}^\top \vec{n} dN^{unit} \quad (9)$$

We define:

$$\vec{\xi} \equiv \mathbf{M}^\top \vec{\mu} \quad (10)$$

$$\xi^o \equiv \vec{\mu}^\top \vec{n}^o, \quad (11)$$

for the parametric chemical potentials along the chosen composition axes, and the unit cell reference potential, respectively.

Then:

$$\vec{\mu}^\top d\vec{N} = N^{unit} \vec{\xi}^\top d\vec{x} + \vec{\xi}^\top \vec{x} dN^{unit} + \xi^o dN^{unit}. \quad (12)$$

Therefore:

$$dU = TdS + N^{unit} \vec{\xi}^\top d\vec{x} + \vec{\xi}^\top \vec{x} dN^{unit} + \xi^o dN^{unit}. \quad (13)$$

A useful characteristic potential,  $\Phi$ , for this system when the number of unit cells is fixed is:

$$\Phi = U - TS - N^{unit} \vec{\xi}^T \vec{x}. \quad (14)$$

$$= U - TS - N^{unit} \vec{\mu}^T (\vec{n} - \vec{n}^o). \quad (15)$$

The associated partition function is:

$$Z = \sum_{\vec{\sigma}} \exp \left( -\frac{e^f(\vec{\sigma}) - \vec{\xi}^T \vec{x}(\vec{\sigma})}{kT} N^{unit} \right) \quad (16)$$

$$= \sum_{\vec{\sigma}} \exp \left( -\frac{e^f(\vec{\sigma}) - \vec{\mu}^T (\vec{n}(\vec{\sigma}) - \vec{n}^o)}{kT} N^{unit} \right). \quad (17)$$

In terms of  $\vec{\xi}$ ,  $\Phi$  has the differential form:

$$d\Phi = dU - TdS - SdT - N^{unit} d\vec{\xi}^T \vec{x} - N^{unit} \vec{\xi}^T d\vec{x} - \vec{\xi}^T \vec{x} dN^{unit} \quad (18)$$

$$= -SdT - N^{unit} d\vec{\xi}^T \vec{x} + \xi^o dN^{unit}. \quad (19)$$

And equations of state:

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\vec{\xi}, N^{unit}} \quad (20)$$

$$N^{unit} x_i = - \left( \frac{\partial \Phi}{\partial \xi_i} \right)_{T, \mu_{j \neq i}, N^{unit}} \quad (21)$$

$$\xi^o = \left( \frac{\partial \Phi}{\partial N^{unit}} \right)_{T, \vec{\xi}} \quad (22)$$

In terms of  $\vec{\mu}$ ,  $\Phi$  has the differential form:

$$d\Phi = -SdT - N^{unit} d\vec{\mu}^T (\vec{n} - \vec{n}^o) + \vec{\mu}^T \vec{n}^o dN^{unit}, \quad (23)$$

And equations of state:

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\vec{\mu}, N^{unit}} \quad (24)$$

$$N_i - N_i^o = - \left( \frac{\partial \Phi}{\partial \mu_i} \right)_{T, \mu_{n_j \neq i}, N^{unit}} \quad (25)$$

$$\vec{\mu}^T \vec{n}^o = \left( \frac{\partial \Phi}{\partial N^{unit}} \right)_{T, \vec{\mu}} \quad (26)$$

**Example 1.1. Binary alloy with single basis site, no vacancies.** There is only one independent parametric composition:  $a$ . There are two standard ways to define the parametric composition axes with  $x_a \in [0, 1]$ :

1)  $n_B = x_a$  and  $n_A = 1 - x_a$ . (Pure A is the origin)

- $\vec{n}^o = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ ,  $\vec{n}^a = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$
- $\mathbf{M}^+ = \begin{bmatrix} -0.5 & 0.5 \end{bmatrix}$ ,  $\mathbf{M} = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$
- $\xi_a = \vec{\mu}^T \mathbf{M}_{:0} = \mu_{n_B} - \mu_{n_A}$ .
- $\xi^o = \vec{\mu}^T \vec{n}^o = \mu_{n_A}$ .

2)  $n_A = x_a$  and  $n_B = 1 - x_a$ . (Pure B is the origin)

- $\vec{n}^o = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$ ,  $\vec{n}^a = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$
- $\mathbf{M}^+ = \begin{bmatrix} 0.5 & -0.5 \end{bmatrix}$ ,  $\mathbf{M} = \begin{bmatrix} 1 \\ -1 \end{bmatrix}$
- $\xi_a = \vec{\mu}^\top \mathbf{M}_{:0} = \mu_{n_A} - \mu_{n_B}$ .
- $\xi^o = \vec{\mu}^\top \vec{n}^o = \mu_{n_B}$ .

**Example 1.2. Binary alloy with two basis sites, no vacancies.** There is only one independent parametric composition:  $a$ . There are two standard ways to define the parametric composition axes with  $x_a \in [0, 1]$ :

1)  $n_B = 2x_a$  and  $n_A = 2 - 2x_a$ . (Pure A is the origin)

- $\vec{n}^o = \begin{bmatrix} 2 \\ 0 \end{bmatrix}$
- $\vec{n}^a = \begin{bmatrix} 0 \\ 2 \end{bmatrix}$
- $\mathbf{M} = \begin{bmatrix} -2 \\ 2 \end{bmatrix}$
- $\mathbf{M}^+ = \begin{bmatrix} -1/4 & 1/4 \end{bmatrix}$
- $\xi_a = \vec{\mu}^\top \mathbf{M}_{:0} = 2(\mu_{n_B} - \mu_{n_A})$ .
- $\xi^o = \vec{\mu}^\top \vec{n}^o = 2\mu_{n_A}$ .

2)  $n_A = 2x_a$  and  $n_B = 2 - 2x_a$ . (Pure B is the origin)

**Example 1.3. Ternary alloy with one basis site, no vacancies.** There are two independent parametric compositions:  $a$ , and  $b$ . There are three standard ways to define the parametric composition axes with  $x_a, x_b \in [0, 1]$ .

1)  $n_A = 1 - x_a - x_b$ ,  $n_B = x_a$ , and  $n_C = x_b$ . (Pure A is the origin)

- $\vec{n}^o = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$ ,  $\vec{n}^a = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$ ,  $\vec{n}^b = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$
- $\mathbf{M}^+ = \begin{bmatrix} -1/3 & 2/3 & -1/3 \\ -1/3 & -1/3 & 2/3 \end{bmatrix}$ ,  $\mathbf{M} = \begin{bmatrix} -1 & -1 \\ 1 & 0 \\ 0 & 1 \end{bmatrix}$
- $\xi_a = \vec{\mu}^\top \mathbf{M}_{:0} = \mu_{n_B} - \mu_{n_A}$ .
- $\xi_b = \vec{\mu}^\top \mathbf{M}_{:1} = \mu_{n_C} - \mu_{n_A}$ .
- $\xi^o = \vec{\mu}^\top \vec{n}^o = \mu_{n_A}$ .

2)  $n_B = 1 - x_a - x_b$ ,  $n_A = x_a$ , and  $n_C = x_b$ .

3)  $n_C = 1 - x_a - x_b$ ,  $n_A = x_a$ , and  $n_B = x_b$ .

### 1.3 Relation of $\Phi$ to Helmholtz free energy

At fixed temperature and volume the characteristic potential is the Helmholtz free energy

$$F = U - TS. \quad (27)$$

Therefore, when using an effective Hamiltonian describing a system at fixed volume,

$$\Phi = F - N^{unit} \vec{\xi}^\top d\vec{x}. \quad (28)$$

## 1.4 Relation of $\Phi$ to Gibbs free energy

When using an effective Hamiltonian that explicitly includes volume changes we may perform Monte Carlo calculations that explicitly control the pressure. Also, when using an effective Hamiltonian that is fit to DFT calculations that are allowed to freely relax both atomic coordinates and lattice vectors, we are implicitly allowing the volume to change while controlling the pressure at  $P=0$ . In either case, our fundamental equation, Eq. 13, becomes

$$dU = TdS - PdV + N^{unit}\vec{\xi}^T d\vec{x}, \quad (29)$$

and the characteristic potential,  $\Phi$ , becomes:

$$\Phi = U - TS + PV - N^{unit}\vec{\xi}^T \vec{x}, \quad (30)$$

The Gibbs free energy is defined as:

$$G = U + PV - TS. \quad (31)$$

Therefore,

$$\Phi = G - N^{unit}\vec{\xi}^T \vec{x}. \quad (32)$$

## 1.5 Thermodynamic Integration

- $e^f(\vec{\sigma})$ : The formation energy per unit cell of configuration  $\vec{\sigma}$ . CASM writes this as `formation_energy` (or `clex(formation_energy)` for the cluster expansion predicted formation energy).
- $\Omega = e^f(\vec{\sigma}) - \vec{\xi}^T \vec{x}(\vec{\sigma})$ : the semi-grand canonical potential energy per unit cell. CASM writes this as `potential_energy`.

Recognizing that:

$$\langle X \rangle = \frac{1}{Z} \sum_{\vec{\sigma}} X \exp(-\Omega \beta N^{unit}) \quad (33)$$

First derivatives of the partition function:

$$\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_{\xi_i, N^{unit}} = -N^{unit} \langle \Omega \rangle \quad (34)$$

$$\frac{1}{Z} \left( \frac{\partial Z}{\partial \xi_i} \right)_{\beta, \xi_{j \neq i}, N^{unit}} = \beta N^{unit} \langle x_i \rangle \quad (35)$$

$$\frac{1}{Z} \left( \frac{\partial Z}{\partial \mu_i} \right)_{\beta, \mu_{j \neq i}, N^{unit}} = \beta N^{unit} \langle n_i - n_i^o \rangle \quad (36)$$

$\beta\Phi$ , in terms of the partition function:

$$\beta\Phi = -\ln Z \quad (37)$$

First derivatives of  $\beta\Phi$ :

$$\left( \frac{\partial \beta\Phi}{\partial \beta} \right)_{\xi_i, N^{unit}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = N^{unit} \langle \Omega \rangle \quad (38)$$

$$\left( \frac{\partial \beta\Phi}{\partial \xi_i} \right)_{\beta, \xi_{j \neq i}, N^{unit}} = -\frac{1}{Z} \frac{\partial Z}{\partial \xi_i} = -\beta N^{unit} \langle x_i \rangle \quad (39)$$

$$\left( \frac{\partial \beta\Phi}{\partial \mu_i} \right)_{\beta, \mu_{j \neq i}, N^{unit}} = -\frac{1}{Z} \frac{\partial Z}{\partial \mu_i} = -\beta N^{unit} \langle n_i - n_i^o \rangle \quad (40)$$

$$(41)$$

For changes in  $\beta$ , holding  $\xi_i$  and  $N^{unit}$  constant:

$$\left(\frac{\partial\beta\Phi}{\partial\beta}\right)_{\xi_i, N^{unit}} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial\beta}\right)_{\xi_i, N^{unit}} \quad (42)$$

$$= N^{unit}\langle\Omega\rangle \quad (43)$$

$$\beta^{end}\Phi(\beta^{end}, \xi_i) = \beta^{begin}\Phi(\beta^{begin}, \xi_i) + N^{unit} \int_{\beta^{begin}}^{\beta^{end}} \langle\Omega\rangle d\beta. \quad (44)$$

For changes in  $\xi_i$ , holding  $\beta$ , other  $\xi_{j\neq i}$ , and  $N^{unit}$  constant:

$$\left(\frac{\partial\beta\Phi}{\partial\xi_i}\right)_{\beta, \xi_{j\neq i}, N^{unit}} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial\xi_i}\right)_{\beta, \xi_{j\neq i}, N^{unit}} \quad (45)$$

$$= -\beta N^{unit}\langle x_i \rangle \quad (46)$$

$$\Phi(\xi_i^{end}, \beta, \xi_{j\neq i}) = \Phi(\xi_i^{begin}, \beta, \xi_{j\neq i}) - N^{unit} \int_{\xi_i^{begin}}^{\xi_i^{end}} \langle x_i \rangle d\xi_i \quad (47)$$

For changes in  $\mu_i$ , holding  $\beta$ , other  $\mu_{j\neq i}$ , and  $N^{unit}$  constant:

$$\left(\frac{\partial\beta\Phi}{\partial\mu_i}\right)_{\beta, \mu_{j\neq i}, N^{unit}} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial\mu_i}\right)_{\beta, \mu_{j\neq i}, N^{unit}} \quad (48)$$

$$= -\beta N^{unit}\langle n_i - n_i^o \rangle \quad (49)$$

$$\Phi(\mu_i^{end}, \beta, \mu_{j\neq i}) = \Phi(\mu_i^{begin}, \beta, \mu_{j\neq i}) - N^{unit} \int_{\mu_i^{begin}}^{\mu_i^{end}} \langle n_i - n_i^o \rangle d\mu_i \quad (50)$$

## 1.6 Hessian of the characteristic potential

Second derivatives of  $\Phi$  with respect to the natural variables,  $Y = T, \xi_i$  correspond to the thermodynamic response functions, such as the extensive heat capacity,  $C_{\mu_x}$ , and extensive susceptibility,  $\chi$ , and can be calculated from covariances of the extensive variables,  $N^{unit}\Omega$ , and  $N^{unit}x_i$ , where  $\Omega = e^f(\vec{\sigma}) - \vec{\xi}^T \vec{x}(\vec{\sigma})$  is the semi-grand canonical potential energy per unit cell.

$$C_{\mu_x} = \left(\frac{\partial Q}{\partial T}\right)_{\vec{\xi}} = T\left(\frac{\partial S}{\partial T}\right)_{\vec{\xi}} = -T\left(\frac{\partial^2\Phi}{\partial T^2}\right)_{\vec{\xi}} \quad (51)$$

$$\chi_{ii}^{\vec{x}} = \left(\frac{\partial N^{unit}x_i}{\partial\xi_i}\right)_{T, \xi_{j\neq i}} = -\left(\frac{\partial^2\Phi}{\partial\xi_i^2}\right)_{T, \xi_{j\neq i}} \quad (52)$$

$$\chi_{ij}^{\vec{x}} = \left(\frac{\partial N^{unit}x_i}{\partial\xi_j}\right)_{T, \xi_{k\neq i, j}} = -\left(\frac{\partial^2\Phi}{\partial\xi_i\partial\xi_j}\right)_{T, \xi_{k\neq i, j}} \quad (53)$$

$$(54)$$

We also include thermo-chemical susceptibilities:

$$\chi_{S, i}^{\vec{x}} = \left(\frac{\partial S}{\partial\xi_i}\right)_{\xi_{j\neq i}} = \left(\frac{\partial N^{unit}x_i}{\partial T}\right)_{\xi_{j\neq i}} = -\left(\frac{\partial^2\Phi}{\partial\xi_i\partial T}\right)_{\xi_{j\neq i}} \quad (55)$$

Second derivatives of the partition function:

$$\frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \beta^2} \right)_{\xi_i} = \langle (N^{unit} \Omega)^2 \rangle \quad (56)$$

$$\frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \xi_i^2} \right)_{\beta, \xi_{j \neq i}} = \beta^2 \langle (N^{unit} x_i)^2 \rangle \quad (57)$$

$$\frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \xi_i \partial \xi_j} \right)_{\beta, \xi_{k \neq i, j}} = \beta^2 \langle (N^{unit} x_i) (N^{unit} x_j) \rangle \quad (58)$$

$$\frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \beta \partial \xi_j} \right)_{\xi_{j \neq i}} = -\beta \langle (N^{unit} \Omega) (N^{unit} x_i) \rangle + \langle N^{unit} x_i \rangle \quad (59)$$

$$(60)$$

Second derivatives of  $\beta\Phi$ :

$$\begin{aligned} \left( \frac{\partial^2 \beta\Phi}{\partial \beta^2} \right)_{\xi_i} &= - \left[ \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 \right] \\ &= - [\langle \Omega^2 \rangle - \langle \Omega \rangle^2] N^{unit^2} \end{aligned} \quad (61)$$

$$\begin{aligned} \left( \frac{\partial^2 \beta\Phi}{\partial \xi_i^2} \right)_{\beta} &= - \left[ \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi_i^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} \right)^2 \right] \\ &= -\beta^2 [\langle x_i^2 \rangle - \langle x_i \rangle^2] N^{unit^2} \end{aligned} \quad (62)$$

$$\begin{aligned} \left( \frac{\partial^2 \beta\Phi}{\partial \beta \partial \xi_i} \right)_{\xi_{j \neq i}} &= - \left[ \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta \partial \xi_i} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} \right) \right] \\ &= \beta [\langle \Omega x_i \rangle - \langle \Omega \rangle \langle x_i \rangle] N^{unit^2} - \langle N^{unit} x_i \rangle \end{aligned} \quad (63)$$

$$\begin{aligned} \left( \frac{\partial^2 \beta\Phi}{\partial \xi_i \partial \xi_j} \right)_{\beta, \xi_{k \neq i, j}} &= - \left[ \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi_i \partial \xi_j} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} \right) \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_j} \right) \right] N^{unit^2} \\ &= -\beta^2 [\langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle] \end{aligned} \quad (64)$$

From repeated use of the chain rule:

$$\left( \frac{\partial^2 \beta\Phi}{\partial \beta^2} \right)_{\xi_i} = kT^3 \left( \frac{\partial^2 \Phi}{\partial T^2} \right)_{\xi_i} \quad (65)$$

$$\left( \frac{\partial^2 \beta\Phi}{\partial \beta \partial \xi_i} \right)_{\xi_{j \neq i}} = -T \left( \frac{\partial^2 \Phi}{\partial T \partial \xi_i} \right)_{\xi_{j \neq i}} + \left( \frac{\partial \Phi}{\partial \xi_i} \right)_{T, \xi_{j \neq i}} \quad (66)$$

Making the necessary substitutions:

$$\left( \frac{\partial^2 \Phi}{\partial T^2} \right)_{\xi_i} = -\frac{1}{T} \frac{\langle \Omega^2 \rangle - \langle \Omega \rangle^2}{kT^2} N^{unit^2} = -\frac{C_{\vec{\mu}_x}}{T} \quad (67)$$

$$\left( \frac{\partial^2 \Phi}{\partial \xi_i^2} \right)_{T, \xi_{j \neq i}} = -\frac{\langle x_i^2 \rangle - \langle x_i \rangle^2}{kT} N^{unit^2} = -\chi_{ii}^{\vec{x}} \quad (68)$$

$$\left( \frac{\partial^2 \Phi}{\partial T \partial \xi_i} \right)_{\xi_{j \neq i}} = -\frac{\langle \Omega x_i \rangle - \langle \Omega \rangle \langle x_i \rangle}{kT} N^{unit^2} = -\chi_{S,i}^{\vec{x}} \quad (69)$$

$$\left( \frac{\partial^2 \Phi}{\partial \xi_i \partial \xi_j} \right)_{T, \xi_{k \neq i, j}} = -\frac{\langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle}{kT} N^{unit^2} = -\chi_{ij}^{\vec{x}} \quad (70)$$

Summarizing:

$$C_{\vec{\mu}_x} = \frac{\langle \Omega^2 \rangle - \langle \Omega \rangle^2}{kT^2} N^{unit2} \quad (71)$$

$$\chi_{ij}^{\vec{x}} = \frac{\langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle}{kT} N^{unit2} \quad (72)$$

$$\chi_{S,i}^{\vec{x}} = \frac{\langle \Omega x_j \rangle - \langle \Omega \rangle \langle x_j \rangle}{kT} N^{unit2}. \quad (73)$$

CASM Monte Carlo outputs the intensive heat capacity,  $C_{\vec{\mu}_x}/N^{unit}$ , as **heat\_capacity**, the intensive parametric susceptibility,  $\chi_{ij}^{\vec{x}}/N^{unit}$ , as **susc\_x(i,j)**, and the intensive thermo-chemical susceptibility,  $\chi_{S,i}^{\vec{x}}/N^{unit}$ , as **susc\_x(S,i)**:

$$\text{heat\_capacity} = C_{\vec{\mu}_x}/N^{unit} = \frac{\langle \Omega^2 \rangle - \langle \Omega \rangle^2}{kT^2} N^{unit} \quad (74)$$

$$\text{susc\_x(i,j)} = \chi_{ij}^{\vec{x}}/N^{unit} = \frac{\langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle}{kT} N^{unit} \quad (75)$$

$$\text{susc\_x(S,i)} = \chi_{S,i}^{\vec{x}}/N^{unit} = \frac{\langle \Omega x_i \rangle - \langle \Omega \rangle \langle x_i \rangle}{kT} N^{unit}. \quad (76)$$

In terms of  $\vec{n}$  and  $\vec{\mu}$ :

$$\chi_{ii}^{\vec{n}} = \left( \frac{\partial N^{unit} n_i}{\partial \mu_i} \right)_{T, \mu_{j \neq i}} = - \left( \frac{\partial^2 \Phi}{\partial \mu_i^2} \right)_{T, \mu_{j \neq i}} \quad (77)$$

$$\chi_{ij}^{\vec{n}} = \left( \frac{\partial N^{unit} n_i}{\partial \mu_j} \right)_{T, \mu_{k \neq i,j}} = - \left( \frac{\partial^2 \Phi}{\partial \mu_i \partial \mu_j} \right)_{T, \mu_{k \neq i,j}} \quad (78)$$

$$\chi_{S,i}^{\vec{n}} = \left( \frac{\partial S}{\partial \mu_i} \right)_{\mu_{j \neq i}} = \left( \frac{\partial N^{unit} n_i}{\partial T} \right)_{\mu_{j \neq i}} = - \left( \frac{\partial^2 \Phi}{\partial \mu_i \partial T} \right)_{\mu_{j \neq i}}. \quad (79)$$

Following the same steps as for  $\vec{x}$  and  $\vec{\xi}$  gives a similar result for the intensive susceptibility  $\chi_{ij}^{\vec{n}}/N^{unit}$ , which CASM writes as **susc\_n(i,j)**, and intensive thermo-chemical susceptibility,  $\chi_{S,i}^{\vec{n}}/N^{unit}$ , as **susc\_n(S,i)**:

$$\text{susc\_n(i,j)} = \chi_{ij}^{\vec{n}}/N^{unit} = \frac{\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle}{kT} N^{unit} \quad (80)$$

$$\text{susc\_n(S,i)} = \chi_{S,i}^{\vec{n}}/N^{unit} = \frac{\langle \Omega n_i \rangle - \langle \Omega \rangle \langle n_i \rangle}{kT} N^{unit}. \quad (81)$$