

# Supporting Information: Computation of Partial Molar Properties using Continuous Fractional Component Monte Carlo

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## ABSTRACT

In this Supporting Information, expressions for the computation of the chemical potential, partial molar excess enthalpy and partial molar volume of a component in a mixture are derived both for the *NPT* ensemble and the expanded version of the *NPT* ensemble (*CFCNPT*). The partition function of the *CFCNPT* ensemble is presented and partial molar properties are derived from derivatives of the chemical potential. It is shown that partial molar properties and chemical potentials in the *CFCNPT* ensemble are equivalent to those computed in the conventional *NPT* ensemble. Details about Peng-Robinson Equation of State (PR-EoS) and PC-SAFT EoS modeling are also provided. Computed chemical potentials and partial molar properties of NH<sub>3</sub>, N<sub>2</sub>, and H<sub>2</sub> are listed. We also provide additional details of our simulations.

## 1. Partial Molar Enthalpy in the *NPT* Ensemble

The partition function of a mixture of  $S$  distinguishable types of monoatomic components equals [1, 2]

$$Q_{N_i,P,T} = \beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta P V] \int ds^N \exp[-\beta U(s^N, V)] \quad (\text{S1})$$

This equation can be extended to mixtures of polyatomic molecules by simply multiplying by the ideal gas partition function of each polyatomic molecule (excluding the translational part) [3, 4]. As this only changes the reference state of the ideal gas contribution of partial molar properties, all derivations in this document are based on the formulation of Eq. S1. In this equation,  $U$  is the potential energy of the system,  $\beta = 1/(k_B T)$ ,  $k_B$  is the Boltzmann constant,  $s$  are the reduced coordinates of molecules in the system,  $V$  is the volume of the system,  $\Lambda_i$  is the thermal wavelength of a molecule of type  $i$ ,  $N_i$  is the number of molecules of type  $i$ ,  $P$  is the imposed pressure, and  $N$  is the total number of molecules present in the system:

$$N = \sum_{i=1}^S N_i \quad (\text{S2})$$

Following Frenkel, Ciccotti and co-workers [5, 6], we can compute partial molar properties by calculating the ratio between partition functions with different number of molecules. We can write the partition function of Eq. S1 when one additional molecule of type A is added to the system:

$$Q_{N_A+1, N_{i \neq A}, P, T} = \beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \cdot \frac{1}{\Lambda_A^3 (N_A + 1)} \int dV V^{N+1} \exp[-\beta PV] \quad (S3)$$

$$\times \int ds^N \exp[-\beta U(s^N, V)] \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)]$$

$s^{A+}$  is the reduced coordinate of the additional molecule in the system, and  $\Delta U^{A+}$  is the interaction potential of this molecule with the rest of the system. The ratio between partition functions in Eq. S1 and Eq. S3 equals

$$\frac{Q_{N_A+1, N_{i \neq A}, P, T}}{Q_{N_i, P, T}} = \frac{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \cdot \frac{1/\Lambda_A^3}{N_A + 1} \int dV V^N V \exp[-\beta PV] \times \int ds^N \exp[-\beta U(s^N, V)] \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)]}{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \quad (S4)$$

$$= \frac{1/\Lambda_A^3}{N_A + 1} \frac{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \cdot \int dV V^N V \exp[-\beta PV] \times \int ds^N \exp[-\beta U(s^N, V)] \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)]}{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \quad (S5)$$

In terms of an ensemble average, we have

$$\frac{Q_{N_A+1, N_{i \neq A}, P, T}}{Q_{N_i, P, T}} = \frac{1/\Lambda_A^3}{N_A + 1} \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} \quad (S6)$$

We know that in the  $NPT$  ensemble, the chemical potential of species A equals [1]

$$\mu_A = -\frac{1}{\beta} \ln \left( \frac{Q_{N_A+1, N_{i \neq A}, P, T}}{Q_{N_i, P, T}} \right) \quad (S7)$$

Combining Eq. S7 and Eq. S6 leads to

$$\mu_A = -\frac{1}{\beta} \left[ \ln \left( \frac{\left( \frac{N}{\beta P} \right) / \Lambda_A^3}{N_A + 1} \right) - \frac{1}{\beta} \left[ \ln \left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N, P, T} \right] \right] \quad (S8)$$

The ideal part of the chemical potential equals [1]

$$\mu_A^{\text{id}} = -\frac{1}{\beta} \left[ \ln \left( \frac{\left( \frac{N}{\beta P} \right) / \Lambda_A^3}{N_A + 1} \right) \right] \quad (S9)$$

The excess part of the chemical potential is [1, 5]

$$\mu_A^{\text{ex}} = -\frac{1}{\beta} \left[ \ln \left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N,P,T} \right] \quad (\text{S10})$$

These expressions for the chemical potential are in agreement with Ref. [1]. The partial molar enthalpy  $\hat{h}_A$  and chemical potential of species A are related by

$$\bar{h}_A = \left( \frac{\partial H}{\partial N_A} \right)_{T,P,N_{i \neq A}} = \left( \frac{\partial \beta \mu_A}{\partial \beta} \right)_{P,N_i} \quad (\text{S11})$$

For convenience,  $\bar{h}_A$  is expressed per molecule instead of per mole. In Eq. S11,  $H$  is the enthalpy of the system,  $N_i$  denotes the number of molecules of component  $i$ ,  $\mu_A$  is the chemical potential of component A,  $P$  is the imposed pressure,  $T$  is the temperature of the mixture,  $\beta = 1/(k_B T)$ , and  $k_B$  is the Boltzmann constant. It is important to note that the thermal wavelength (which appears in the ideal gas part of the chemical potential) is a function of  $\beta$  as well [2]:

$$\Lambda = \frac{\beta^{1/2} h}{\sqrt{2\pi m}} \quad (\text{S12})$$

Combining Eqs. S9 and S12 leads to

$$\begin{aligned} \bar{h}_A^{\text{id}} &= -\frac{\partial}{\partial \beta} \left[ \ln \left( \frac{\left( \frac{N}{\beta P} \right)}{N_{A+1}} / \frac{\beta^{3/2} h^3}{\sqrt{8\pi^3 m^3}} \right) \right] \\ &= - \left[ -\frac{5}{2\beta} \right] \\ &= \frac{5}{2\beta} \end{aligned} \quad (\text{S13})$$

For the excess part of the partial molar enthalpy, we combine Eqs. S10 and S11 and take the derivative with respect to  $\beta$

$$\bar{h}_A^{\text{ex}} = \left( \frac{\partial \beta \mu_A^{\text{ex}}}{\partial \beta} \right)_{P,N_i} = -\frac{\frac{\partial}{\partial \beta} \left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i,P,T}}{\left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i,P,T}} \quad (\text{S14})$$

Writing out the ensemble average leads to

$$\bar{h}_A^{\text{ex}} = -\frac{\frac{\partial}{\partial \beta} \left( \frac{\int dV V^N \frac{\beta PV}{N} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)]}{\int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \right)}{\left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i,P,T}} \quad (\text{S15})$$

The configurational part of the partition function of Eq. S1 is defined as

$$q_{N_i,P,T} = \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \quad (\text{S16})$$

Taking the derivative with respect to  $\beta$ , Eq. S15 leads to

$$\bar{h}_A^{\text{ex}} = -\frac{1}{\left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T}} \times \quad (\text{S17})$$

$$\left[ \frac{\frac{\partial}{\partial \beta} \left( \int dV V^N \frac{\beta PV}{N} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \right)}{\left( \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)] \right)} \times q_{N_i, P, T}}{(q_{N_i, P, T})^2} \right. \\ \left. - \frac{\frac{\partial q_{N_i, P, T}}{\partial \beta} \times \left( \int dV V^N \frac{\beta PV}{N} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \right)}{(q_{N_i, P, T})^2} \right]$$

$$= -\frac{1}{\left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T}} \times \quad (\text{S18})$$

$$\left[ \frac{\int dV V^N \frac{\beta PV}{N} \cdot \frac{\partial}{\partial \beta} \left( \frac{\exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]}{\int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)]} \right)}{q_{N_i, P, T}} \right. \\ \left. + \frac{\left( \int dV V^N \frac{\partial \left( \frac{\beta PV}{N} \right)}{\partial \beta} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \right)}{q_{N_i, P, T}} \right. \\ \left. - \frac{\frac{\partial q_{N_i, P, T}}{\partial \beta} \times \left( \int dV V^N \frac{\beta PV}{N} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \right)}{q_{N_i, P, T}} \right]$$

$$= -\frac{1}{\left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T}} \times \frac{1}{q_{N_i, P, T}} \quad (\text{S19})$$

$$\left[ \int dV V^N \frac{\beta PV}{N} \cdot (-\Delta U^{A+} - PV - U(s^N, V)) \times \left( \frac{\exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]}{\int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)]} \right) \right. \\ \left. + \int dV V^N \frac{1}{\beta} \times \frac{\beta PV}{N} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \times \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)] \right. \\ \left. - \int dV V^N (-U(s^N, V) - PV) \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \times \frac{1}{q_{N_i, P, T}} \right. \\ \left. \times \int dV V^N \frac{\beta PV}{N} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \times \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)] \right]$$

$$= - \frac{\left[ \begin{aligned} & \left\langle \frac{\beta PV}{N} [-\Delta U^{A+} - U(s^N, V) - PV] \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T} \\ & + \frac{1}{\beta} \left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T} \\ & - \langle -U(s^N, V) - PV \rangle \times \left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T} \end{aligned} \right]}{\left\langle \frac{\beta PV}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T}} \quad (\text{S20})$$

The partial molar excess enthalpy of component A in the  $NPT$  ensemble of a multicomponent mixture equals

$$\bar{h}_A^{\text{ex}} = -\frac{1}{\beta} + \frac{\langle (\Delta U^{A+} + U(s^N, V) + PV)V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}}{\langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}} - \langle U(s^N, V) + PV \rangle_{N_i, P, T} \quad (\text{S21})$$

The energy of the system with one additional molecule of component A can be expressed as

$$U(s^{N+1}, V) = \Delta U^{A+} + U(s^N, V) \quad (\text{S22})$$

We can write Eq. S21 as

$$\bar{h}_A^{\text{ex}} = -\frac{1}{\beta} + \frac{\langle (U(s^{N+1}, V) + PV)V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}}{\langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}} - \langle U(s^N, V) + PV \rangle_{N_i, P, T} \quad (\text{S23})$$

This is the result that Frenkel, Ciccotti and co-workers previously found [5, 6]. It is instructive to show that  $\bar{h}_A^{\text{ex}}$  equals zero for an ideal gas. Since intermolecular interactions for an ideal gas are zero, for an ideal gas Eq. S23 reduces to

$$\begin{aligned} \bar{h}_A^{\text{ex}} &= -\frac{1}{\beta} + \frac{\langle PV^2 \rangle_{N_i, P, T}}{\langle V \rangle_{N_i, P, T}} - \langle PV \rangle_{N_i, P, T} \\ &= -\frac{1}{\beta} + P \left[ \frac{\langle V^2 \rangle_{N_i, P, T}}{\langle V \rangle_{N_i, P, T}} - \langle V \rangle_{N_i, P, T} \right] \end{aligned} \quad (\text{S24})$$

For the average volume  $\langle V \rangle_{N_i, P, T}$  we can write

$$\langle V \rangle_{N_i, P, T} = \frac{\int_0^\infty V^N V \exp[-\beta PV] dV}{\int_0^\infty V^N \exp[-\beta PV] dV} \quad (\text{S25})$$

Both integrals in the nominator and denominator can be solved analytically according to

$$\int_0^\infty x^N \exp[-ax] dx = \frac{N!}{a^{N+1}} \quad (\text{S26})$$

Therefore, we have

$$\langle V \rangle_{N_i, P, T} = \left( \frac{(N+1)!}{(\beta P)^{N+1}} \right) / \left( \frac{N!}{(\beta P)^N} \right) = \frac{N+1}{\beta P} \quad (\text{S27})$$

Similarly, for the term  $\langle V^2 \rangle_{N_i, P, T}$  we have

$$\begin{aligned}
\langle V^2 \rangle_{N_i, P, T} &= \frac{\int_0^\infty V^N V^2 \exp[-\beta P V] dV}{\int_0^\infty V^N \exp[-\beta P V] dV} \\
&= \left( \frac{(N+2)!}{(\beta P)^{N+2}} \right) / \left( \frac{N!}{(\beta P)^N} \right) \\
&= \frac{(N+2)(N+1)}{(\beta P)^2}
\end{aligned} \tag{S28}$$

Combining Eqs. S24, S27 and S28 leads to

$$\begin{aligned}
\bar{h}_A^{\text{ex}} &= -\frac{1}{\beta} + P \left[ \frac{(N+2)(N+1)/(\beta P)^2}{N+1/\beta P} - \frac{N+1}{\beta P} \right] \\
&= -\frac{1}{\beta} + P \left[ \frac{N+2}{\beta P} - \frac{N+1}{\beta P} \right] \\
&= 0
\end{aligned} \tag{S29}$$

This is the expected result.

## 2. Partial Molar Volume in the $NPT$ Ensemble

We know from thermodynamic relations that the partial molar volume of component A in a mixture of S components equals [5–7]

$$\bar{v}_A = \left( \frac{\partial V}{\partial N_A} \right)_{T,P,N_{i \neq A}} = \left( \frac{\partial \mu_A}{\partial P} \right)_{T,N_i} \quad (\text{S30})$$

**For convenience**, partial molar properties are considered per molecule instead of per mole. In Eq. S30,  $V$  is the volume of the system,  $N_i$  denotes the number of molecules of component  $i$ ,  $\mu_A$  is the chemical potential of component A,  $P$  is the imposed pressure,  $T$  is the temperature of the mixture,  $\beta = 1/(k_B T)$ , and  $k_B$  is the Boltzmann constant. Following Frenkel, Ciccotti, and co-workers [5, 6], combining Eqs. S8 and S30 leads to

$$\begin{aligned} \bar{v}_A &= -\frac{1}{\beta} \frac{\partial}{\partial P} \left[ \ln \frac{\left( \frac{N}{\beta P} \right) / \Lambda_A^3}{N_A + 1} \right] - \frac{1}{\beta} \frac{\partial}{\partial P} \left[ \ln \left\langle \frac{\beta P V}{N} \exp[-\beta \Delta U^{A+}] \right\rangle_{N_i, P, T} \right] \\ &= \frac{1}{\beta P} - \frac{1}{\beta} \left[ \frac{\frac{\partial}{\partial P} \langle P V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}}{\langle P V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}} \right] \\ &= \frac{1}{\beta P} - \frac{1}{\beta} \left[ \frac{\langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} + P \times \frac{\partial}{\partial P} \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}}{P \times \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}} \right] \\ &= -\frac{1}{\beta} \times \frac{\frac{\partial}{\partial P} \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}}{\langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}} \end{aligned} \quad (\text{S31})$$

Starting from  $\frac{\partial}{\partial P} \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}$ , we write out the ensemble average

$$\begin{aligned} \frac{\partial}{\partial P} \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} &= \quad (\text{S32}) \\ \frac{\partial}{\partial P} \left( \frac{\int dV V^N V \exp[-\beta P V] \int ds^N \exp[-\beta U(s^N, V)] \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)]}{\int dV V^N \exp[-\beta P V] \int ds^N \exp[-\beta U(s^N, V)]} \right) \end{aligned}$$

$$= \left[ \frac{\frac{\partial}{\partial P} \left( \int dV V^N V \exp[-\beta P V] \int ds^N \exp[-\beta U(s^N, V)] \right) \times q_{N_i, P, T}}{(q_{N_i, P, T})^2} - \frac{\frac{\partial q_{N_i, P, T}}{\partial P} \times \left( \int dV V^N V \exp[-\beta P V] \int ds^N \exp[-\beta U(s^N, V)] \right)}{(q_{N_i, P, T})^2} \right] \quad (\text{S33})$$

$$= \left[ \frac{\frac{\partial}{\partial P} \left( \int dV V^N V \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \right)}{q_{N_i, P, T}} \right] \left[ - \frac{\frac{\partial q_{N_i, P, T}}{\partial P}}{q_{N_i, P, T}} \times \frac{\left( \int dV V^N V \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \right)}{q_{N_i, P, T}} \right] \quad (\text{S34})$$

$$= \frac{1}{q_{N_i, P, T}} \times \left[ \int dV V^N (-\beta V^2) \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \times \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)] \right. \\ \left. - \int dV V^N (-\beta V) \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \times \frac{1}{q_{N_i, P, T}} \right. \\ \left. \times \int dV V^N V \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \times \int ds^{A+} \exp[-\beta \Delta U^{A+}(s^{A+}, s^N, V)] \right] \quad (\text{S35})$$

In terms of ensemble averages, we can write

$$\frac{\partial}{\partial P} \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} \\ = \langle -\beta V^2 \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} - \langle -\beta V \rangle_{N_i, P, T} \times \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} \quad (\text{S36})$$

Combining Eq. S36 and Eq. S31 leads to

$$\bar{v}_A = -\frac{1}{\beta} \left[ \frac{\langle -\beta V^2 \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} + \langle \beta V \rangle_{N_i, P, T} \times \langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}}{\langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}} \right] \quad (\text{S37})$$

The partial molar volume of component A is [5, 6]

$$\bar{v}_A = \frac{\langle V^2 \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}}{\langle V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}} - \langle V \rangle_{N_i, P, T} \quad (\text{S38})$$

This expression is identical to the one derived by Frenkel, Ciccotti, and co-workers [5, 6]. For an ideal gas, we can calculate the partial molar volume analytically. Since there are no intermolecular interactions between ideal gas molecules, we can write

$$\bar{v}_A = \frac{\langle V^2 \rangle_{N_i, P, T}}{\langle V \rangle_{N_i, P, T}} - \langle V \rangle_{N_i, P, T} \quad (\text{S39})$$



Combining Eqs. S27, S28 and S39 leads to

$$\begin{aligned}\bar{v}_A &= \frac{(N+2)(N+1)/(\beta P)^2}{(N+1)/\beta P} - \frac{N+1}{\beta P} \\ &= \frac{1}{\beta P} \\ &= \frac{V}{N}\end{aligned}\tag{S40}$$

This expression is the well-known result for the partial molar volume of an ideal gas.

### 3. Partial Molar Enthalpy in the Continuous Fractional Component $NPT$ Ensemble

The partition function of the  $NPT$  ensemble of a mixture of  $S$  components, expanded with a fractional molecule of component A equals [8–12]

$$Q_{\text{CFCNPT}} = \beta P \left[ \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \right] \times \frac{1}{\Lambda_A^3} \int_0^1 d\lambda \int dV V^{N+1} \exp[-\beta PV] \quad (\text{S41})$$

$$\times \int ds^N \exp[-\beta U(s^N, V)] \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda, V)]$$

$s$  indicates the scaled coordinates of molecules in the system,  $N$  is the **total** number of whole molecules, and the fractional molecule is distinguishable from whole molecules of the same type.  $U_{\text{frac}}^A$  is the interaction potential of the fractional molecule with the rest of the system, and  $\lambda$  is a scaling factor. The value  $\lambda = 0$  means that the fractional molecule of type A has no interactions with the surrounding molecules, and at  $\lambda = 1$  the fractional molecule has full interactions with other molecules in the system *i.e.* the fractional molecule behaves as a whole molecule. Before deriving expressions for partial molar enthalpy and partial molar volume, we show that the chemical potential of component A corresponding to the conventional  $NPT$  ensemble (Eq. S7) can be computed in the  $\text{CFCNPT}$  ensemble and the result is identical. Following Refs. [8, 9], we can write

$$\left\langle \frac{\delta_{\lambda=0}}{V/\Lambda_A^3} \right\rangle_{\text{CFCNPT}} = \frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} \left( \frac{1}{V/\Lambda_A^3} \right) \exp[-\beta PV] \quad (\text{S42})$$

$$\times \int ds^N \exp[-\beta U(s^N, V)] \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, \lambda \downarrow 0, s^N, V)]$$

$$= \frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]$$

and

$$\left\langle \frac{\delta_{\lambda=1}}{N_A + 1} \right\rangle_{\text{CFCNPT}} = \frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} \frac{1}{N_A + 1} \exp[-\beta PV] \quad (\text{S43})$$

$$\times \int ds^N \exp[-\beta U(s^N, V)] \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \uparrow 1, V)]$$

$\delta_{\lambda=1}$  denotes the probability of  $\lambda$  approaching one, and  $\delta_{\lambda=0}$  the probability of  $\lambda$  approaching zero. Combining the ensemble averages from Eqs. S42 and S43, we have

$$\frac{\left\langle \frac{\delta_{\lambda=1}}{N_A + 1} \right\rangle_{\text{CFCNPT}}}{\left\langle \frac{\delta_{\lambda=0}}{V/\Lambda_A^3} \right\rangle_{\text{CFCNPT}}} = \frac{\prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \times \frac{1}{\Lambda_A^{3(N_A+1)}} \int dV V^{N+1} \exp[-\beta PV] \int ds^{N+1} \exp[-\beta U(s^{N+1}, V)]}{\prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \quad (\text{S44})$$

The ratio between these ensemble averages equals the ratio between the partition functions of the conventional  $NPT$  ensemble in which one ensemble has an additional molecule of type A

$$\frac{\left\langle \frac{\delta_{\lambda=1}}{N_A + 1} \right\rangle_{\text{CFCNPT}}}{\left\langle \frac{\delta_{\lambda=0}}{V/\Lambda_A^3} \right\rangle_{\text{CFCNPT}}} = \frac{Q_{N_A+1, N_{i \neq A}, P, T}}{Q_{N_i, P, T}} \quad (\text{S45})$$

Therefore, with Eq. S45, we have shown that the chemical potential in the conventional  $NPT$  ensemble and the  $CFCNPT$  ensemble are the same by definition, so we have

$$\mu_A = -\frac{1}{\beta} \ln \left( \frac{\langle \frac{\delta_{\lambda=1}}{N_A+1} \rangle_{CFCNPT}}{\langle \frac{\delta_{\lambda=0}}{V/\Lambda_A^3} \rangle_{CFCNPT}} \right) \quad (S46)$$

For sufficiently large systems,  $\lambda_A$ ,  $V$ , and  $N_A$  are uncorrelated [8], so therefore

$$\begin{aligned} \mu_A &\approx -\frac{1}{\beta} \ln \left( \frac{\frac{1}{N_A+1}}{\langle V/\Lambda_A^3 \rangle_{CFCNPT}} \times \frac{\langle \delta_{\lambda=1} \rangle_{CFCNPT}}{\langle \delta_{\lambda=0} \rangle_{CFCNPT}} \right) \\ &\approx -\frac{1}{\beta} \ln \left( \frac{\langle V \rangle_{CFCNPT}}{\Lambda_A^3 (N_A + 1)} \right) - \frac{1}{\beta} \left( \frac{p(\lambda_A \uparrow 1)}{p(\lambda_A \downarrow 0)} \right) \end{aligned} \quad (S47)$$

In the above equations,  $p(\lambda_A \uparrow 1)$  denotes the probability of  $\lambda_A$  approaching one, and  $p(\lambda_A \downarrow 0)$  denotes the probability of  $\lambda_A$  approaching zero. The first term on the right hand side of Eq. S47 is the ideal gas part of the chemical potential of component A, and the second term is the excess chemical potential of component A. Therefore, the excess chemical potential is directly related to the probabilities of  $\lambda_A$  approaching one and zero [8, 9]. Similarly, we can write the partial molar enthalpy and partial molar volume in the conventional  $NPT$  ensemble as averages in the  $CFCNPT$  ensemble. Here, we derive expressions for the ensemble averages of Eq. S21 in terms of averages in the expanded ensemble. Starting from the term  $\langle V \exp(-\beta \Delta U^{A+}) \rangle_{N_i, P, T}$ , we can write

$$\begin{aligned} \frac{\langle \delta_{\lambda=1} \rangle_{CFCNPT}}{\langle \delta_{\lambda=0}/V \rangle_{CFCNPT}} &= \frac{\frac{\beta P}{Q_{CFCNPT}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} \times \left( \frac{\exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]}{\times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \uparrow 1, V)]} \right)}{\frac{\beta P}{Q_{CFCNPT}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} V^{-1} \times \left( \frac{\exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]}{\times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \downarrow 0, V)]} \right)} \\ &= \frac{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N V \times \left( \frac{\exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]}{\times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \uparrow 1, V)]} \right)}{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \\ &= \langle V \exp(-\beta \Delta U^{A+}) \rangle_{N_i, P, T} \end{aligned} \quad (S48)$$

For the second ensemble average  $\langle U(s^N, V) + PV \rangle_{N_i, P, T}$  in Eq. S21, we can start from

$$\begin{aligned}
\frac{\langle \delta_{\lambda=0} (U/V + P) \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0}/V \rangle_{\text{CFCNPT}}} &= \frac{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_i^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} \left( \begin{array}{l} (U(s^N, V)/V + P) \exp[-\beta PV] \\ \times \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \downarrow 0, V)] \end{array} \right)}{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_i^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} \left( \begin{array}{l} V^{-1} \exp[-\beta PV] \\ \times \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \downarrow 0, V)] \end{array} \right)} \\
&= \frac{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \left( \begin{array}{l} (U(s^N, V) + PV) \exp[-\beta PV] \\ \times \int ds^N \exp[-\beta U(s^N, V)] \end{array} \right)}{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \\
&= \langle U(s^N, V) + PV \rangle_{N_i, P, T} \tag{S49}
\end{aligned}$$

For the third ensemble average  $\langle (\Delta U^{A+} + U(s^N, V) + PV)V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T}$  in Eq. S21, we have

$$\frac{\langle \delta_{\lambda=1} (U_{\text{frac}}^A + U + PV) \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0}/V \rangle_{\text{CFCNPT}}} = \tag{S50}$$

$$\begin{aligned}
&\frac{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_i^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} \times \left( \begin{array}{l} (U_{\text{frac}}^A + U(s^N, V) + PV) \exp[-\beta PV] \\ \times \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \uparrow 1, V)] \end{array} \right)}{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_i^3}{\Lambda_i^{3N_i} N_i!} \int dV V^{N+1} \left( \begin{array}{l} V^{-1} \exp[-\beta PV] \\ \times \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \downarrow 0, V)] \end{array} \right)} \tag{S51}
\end{aligned}$$

$$\begin{aligned}
&\frac{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \left( \begin{array}{l} (U_{\text{frac}}^A + U(s^N, V) + PV) V \exp[-\beta PV] \\ \times \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \uparrow 1, V)] \end{array} \right)}{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i} N_i!} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \tag{S52}
\end{aligned}$$

Similar to Eq. S22, we can define the total energy of the system at  $\lambda = 1$

$$U(s^{N+1}, V) = U_{\text{frac}}^A + U(s^N, V) \tag{S53}$$

$U_{\text{frac}}^A$  is the interaction potential of the fractional molecule with the surrounding molecules.  $U$  is the total energy of the system including the fractional molecule which has full interactions with the rest of the system at  $\lambda = 1$ . The ratio in Eq. S52 equals the ensemble average in the

conventional  $NPT$  ensemble as shown in Eq. S21. Combining Eqs. S50 and S52 leads to

$$\frac{\langle \delta_{\lambda=1} (U + PV) \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0}/V \rangle_{\text{CFCNPT}}} = \langle (U(s^{N+1}, V) + PV)V \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} \quad (\text{S54})$$

Therefore, the two ensemble averages yield identical results. Combining Eqs. S48, S49 and S54 with Eq. S21 yields

$$\bar{h}_A^{\text{ex}} = -\frac{1}{\beta} + \frac{\frac{\langle \delta_{\lambda=1} (U + PV) \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0}/V \rangle_{\text{CFCNPT}}}}{\frac{\langle \delta_{\lambda=1} \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0}/V \rangle_{\text{CFCNPT}}}} - \frac{\langle \delta_{\lambda=0} (U/V + P) \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0}/V \rangle_{\text{CFCNPT}}} \quad (\text{S55})$$

$$= -\frac{1}{\beta} + \frac{\langle \delta_{\lambda=1} (U + PV) \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=1} \rangle_{\text{CFCNPT}}} - \frac{\langle \delta_{\lambda=0} (U/V + P) \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0}/V \rangle_{\text{CFCNPT}}} \quad (\text{S56})$$

$$= -\frac{1}{\beta} + \langle H(\lambda_A \uparrow 1) \rangle_{\text{CFCNPT}} - \frac{\langle H/V(\lambda_A \downarrow 0) \rangle_{\text{CFCNPT}}}{\langle 1/V(\lambda_A \downarrow 0) \rangle_{\text{CFCNPT}}} \quad (\text{S57})$$

$\langle H(\lambda_A \uparrow 1) \rangle_{\text{CFCNPT}}$  is ensemble average enthalpy of the system in the limit at which  $\lambda_A$  approaches one.  $\langle H/V(\lambda_A \downarrow 0) \rangle_{\text{CFCNPT}}$  is ensemble average of the ratio between the total enthalpy and the volume of the system in the limit at which  $\lambda_A$  approaches zero. Note assuming that  $\langle H(\lambda_A \downarrow 0) \rangle \approx \langle H/V(\lambda_A \downarrow 0) \rangle / \langle 1/V(\lambda_A \downarrow 0) \rangle$  leads to a wrong answer for an ideal gas as can be seen from Eqs. S24 and S29.

#### 4. Partial Molar Volume in the Continuous Fractional Component $NPT$ Ensemble

Similar to the partial molar enthalpy, we can write the averages of Eq. S38 in terms of averages in the expanded  $NPT$  ensemble. We already know that the denominator of Eq. S38 can be expressed as an ensemble average in the expanded  $NPT$  ensemble, as shown in Eq. S48. For the ensemble average in the nominator of equation Eq. S38, we can start from

$$\begin{aligned}
\frac{\langle \delta_{\lambda=1} V \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0} / V \rangle_{\text{CFCNPT}}} &= \frac{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i N_i!}} \int dV V^{N+1} V \left( \begin{array}{l} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \uparrow 1, V)] \end{array} \right)}{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i N_i!}} \int dV V^{N+1} V^{-1} \left( \begin{array}{l} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \downarrow 0, V)] \end{array} \right)} \\
&= \frac{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i N_i!}} \int dV V^N V^2 \times \left( \begin{array}{l} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \uparrow 1, V)] \end{array} \right)}{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i N_i!}} \int dV V^N \times (\exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)])} \\
&= \langle V^2 \exp[-\beta \Delta U^{A+}] \rangle_{N_i, P, T} \tag{S58}
\end{aligned}$$

For the second term on the right hand side of Eq. S38, we can start from

$$\begin{aligned}
\frac{\langle \delta_{\lambda=0} \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0} / V \rangle_{\text{CFCNPT}}} &= \frac{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i N_i!}} \int dV V^{N+1} \left( \begin{array}{l} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \downarrow 0, V)] \end{array} \right)}{\frac{\beta P}{Q_{\text{CFCNPT}}} \prod_{i=1}^S \frac{1/\Lambda_A^3}{\Lambda_i^{3N_i N_i!}} \int dV V^{N+1} V^{-1} \left( \begin{array}{l} \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)] \\ \times \int ds_{\text{frac}}^A \exp[-\beta U_{\text{frac}}^A(s_{\text{frac}}^A, s^N, \lambda \downarrow 0, V)] \end{array} \right)} \tag{S59} \\
&= \frac{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i N_i!}} \int dV V^N V \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]}{\beta P \prod_{i=1}^S \frac{1}{\Lambda_i^{3N_i N_i!}} \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta U(s^N, V)]} \\
&= \langle V \rangle_{N_i, P, T}
\end{aligned}$$

Substituting Eqs. S48, S58 and S59 in Eq. S38 leads to

$$\begin{aligned}
\bar{v}_A &= \frac{\langle \delta_{\lambda=1} V \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0} / V \rangle_{\text{CFCNPT}}} - \frac{\langle \delta_{\lambda=0} \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0} / V \rangle_{\text{CFCNPT}}} \\
&= \frac{\langle \delta_{\lambda=1} V \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=1} \rangle_{\text{CFCNPT}}} - \frac{\langle \delta_{\lambda=0} \rangle_{\text{CFCNPT}}}{\langle \delta_{\lambda=0} / V \rangle_{\text{CFCNPT}}} \tag{S60}
\end{aligned}$$

We can write

$$\bar{v}_A = \langle V(\lambda_A \uparrow 1) \rangle_{\text{CFCNPT}} - \langle 1/V(\lambda_A \downarrow 0) \rangle_{\text{CFCNPT}}^{-1} \tag{S61}$$

$\langle V(\lambda_A \uparrow 1) \rangle_{\text{CFCNPT}}$  is the ensemble average of the volume when  $\lambda_A$  approaches one, and  $\langle 1/V(\lambda_A \downarrow 0) \rangle_{\text{CFCNPT}}$  is the ensemble average of the inverse of the volume when  $\lambda_A$  approaches zero. In Eq. S61, one may be tempted to assume that  $\langle 1/V(\lambda_A \downarrow 0) \rangle_{\text{CFCNPT}}^{-1} \approx \langle V(\lambda_A \downarrow 0) \rangle_{\text{CFCNPT}}$ . However this assumption leads to a wrong answer for an ideal gas as can be seen from Eqs. S38 and S39.

## 5. Equation of State Modeling

### 5.1. Peng-Robinson Equation of State

The Peng-Robinson Equation of State (PR-EoS) [13] is used to compute the partial molar properties

$$P = \frac{RT}{v_m - b_m} - \frac{a_m}{v_m(v_m + b_m) + b_m(v_m - b_m)} \quad (\text{S62})$$

$v_m$  is the molar volume of the mixture per mole of the mixture.  $a_m$  and  $b_m$  are defined based on pure component parameters ( $a_i$  and  $b_i$ ) and van der Waals mixing rules [14, 15]:

$$a_m = \sum_{i=1}^S \sum_{j=1}^S x_i x_j a_{ij} \quad (\text{S63})$$

$$b_m = \sum_{j=1}^S x_j b_j \quad (\text{S64})$$

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{1/2} \quad (\text{S65})$$

$x_i$  is the mole fraction of component  $i$ ,  $k_{ij}$  is a **Binary Interaction Parameter (BIP)** between components  $i$  and  $j$ . Pure component parameters  $a_i$  and  $b_i$  are defined by

$$a_i = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[ 1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2) \left( 1 - T_{r,i}^{1/2} \right) \right]^2 \quad (\text{S66})$$

$$b_i = \frac{0.0778RT_{c,i}}{P_{c,i}} \quad (\text{S67})$$

$\omega_i$  is the acentric factor of a pure component which is usually available for common components in literature [16, 17],  $T_{r,i} = T/T_{c,i}$  is the reduced temperature of component  $i$  at temperature  $T$ ,  $T_{c,i}$  and  $P_{c,i}$  are critical temperature and critical pressure of component  $i$  which are available in literature [18]. To obtain an expression for the partial molar volume of a certain component, we start from the minus 1 rule [19]

$$\left( \frac{\partial V_m}{\partial N_k} \right)_{T,P,N_{i \neq k}} \left( \frac{\partial N_k}{\partial P} \right)_{T,V_m,N_{i \neq k}} \left( \frac{\partial P}{\partial V_m} \right)_{T,N_i} = -1 \quad (\text{S68})$$

$V_m$  is the volume of the mixture,  $N_k$  is the number of moles of component  $k$ , and the notation  $N_{i \neq k}$  means that number of molecules of all components except component  $k$  are kept constant during differentiation. The term  $\left( \frac{\partial V_m}{\partial N_k} \right)_{T,V_m,N_{i \neq k}}$  is the partial molar volume of component  $k$  which equals

$$\bar{v}_k = - \frac{\left( \frac{\partial P}{\partial N_k} \right)_{T,V_m,N_{i \neq k}}}{\left( \frac{\partial P}{\partial V_m} \right)_{T,N_i}} \quad (\text{S69})$$

An analytic expression for the partial molar volume is obtained by applying the derivatives of Eq. S69 to the PR-EoS (Eq. S62). We can write Eq. S62 as

$$P = \frac{RT}{\frac{V_m}{N} - b_m} - \frac{a_m}{\frac{V_m}{N^2}(V_m + Nb_m) + \frac{b_m}{N}(V_m - Nb_m)} \quad (\text{S70})$$

$$= \frac{NRT}{V_m - Nb_m} - \frac{N^2 a_m}{V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)}$$

$N$  is the number of moles of the mixture. Starting from the denominator Eq. S69 and taking the derivative of  $P$  (Eq. S70) with respect to  $V_m$  leads to

$$\left(\frac{\partial P}{\partial V_m}\right)_{T, N_i} = \left(\frac{\partial}{\partial V_m}\right)_{T, N_i} \left(\frac{NRT}{V_m - Nb_m} - \frac{N^2 a_m}{V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)}\right) \quad (\text{S71})$$

$$= -\frac{NRT}{(V_m - Nb_m)^2} + \frac{2N^2 a_m(V_m + Nb_m)}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]^2}$$

The derivative in the nominator of Eq. S69 equals

$$\left(\frac{\partial P}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} = \frac{RT(V_m - Nb_m) + NRT\left(\frac{\partial Nb_m}{\partial N_k}\right)_{T, V_m, N_{i \neq k}}}{(V_m - Nb_m)^2} \quad (\text{S72})$$

$$- \frac{\left(\frac{\partial N^2 a_m}{\partial N_k}\right)_{T, V_m, N_{i, j \neq k}} - \frac{N^2 a_m \left(\frac{\partial}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} [V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]}}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]^2}$$

Taking the derivative on the right hand side and rearranging leads to

$$\left(\frac{\partial P}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} = \frac{RT(V_m - Nb_m) + NRT\left(\frac{\partial Nb_m}{\partial N_k}\right)_{T, V_m, N_{i \neq k}}}{(V_m - Nb_m)^2} \quad (\text{S73})$$

$$- \frac{Na_m \left(\frac{\partial N}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} + N \left(\frac{\partial Na_m}{\partial N_k}\right)_{T, V_m, N_{i, j \neq k}} - \frac{N^2 a_m \left[2v_m \left(\frac{\partial Nb_m}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} - 2Nb_m \left(\frac{\partial Nb_m}{\partial N_k}\right)_{T, V_m, N_{i \neq k}}\right]}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]}}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]}$$

Here, two analytic derivatives of  $a_m$  and  $b_m$  are required which are listed below

$$\left(\frac{\partial Nb_m}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} = \left(\frac{\partial}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} \left(N \sum_{i=1}^S x_i b_i\right) \quad (\text{S74})$$

$$= \left(\frac{\partial}{\partial N_k}\right)_{T, V_m, N_{i \neq k}} \left(N \sum_{i=1}^S \frac{N_i}{N} b_i\right)$$

$$= \sum_{i=1}^S \left(\frac{\partial N_i b_i}{\partial N_k}\right)_{T, V_m, N_{i \neq k}}$$

$$= b_k$$



$$\begin{aligned}
\left(\frac{\partial Na_m}{\partial N_k}\right)_{T,V_m,N_{i,j \neq k}} &= \left(\frac{\partial}{\partial N_k}\right)_{T,V_m,N_{i,j \neq k}} \left(N \sum_{i=1}^S \sum_{j=1}^S x_i x_j a_{ij}\right) \\
&= \left(\frac{\partial}{\partial N_k}\right)_{T,V_m,N_{i,j \neq k}} \left(N \sum_{i=1}^S \sum_{j=1}^S \frac{N_i}{N^2} \cdot N_j a_{ij}\right) \\
&= \left(\frac{\partial}{\partial N_k}\right)_{T,V_m,N_{i,j \neq k}} \left(\sum_{i=1}^S \sum_{j=1}^S \frac{N_i}{N} N_j a_{ij}\right) \\
&= \sum_{i=1}^S \sum_{j=1}^S a_{ij} N_j \left(\frac{\partial \frac{N_i}{N}}{\partial N_k}\right)_{T,V_m,N_{i \neq k}} + \sum_{i=1}^S \sum_{j=1}^S a_{ij} \frac{N_i}{N} \left(\frac{\partial N_j}{\partial N_k}\right)_{T,V_m,N_{i \neq k}} \\
&= \sum_{i=1}^S \sum_{j=1}^S a_{ij} N_j \frac{1}{N} \left(\frac{\partial N_i}{\partial N_k}\right)_{T,V_m,N_{i \neq k}} + \sum_{i=1}^S \sum_{j=1}^S a_{ij} N_i N_j \left(\frac{\partial \frac{1}{N}}{\partial N_k}\right)_{T,V_m,N_{i \neq k}} + \sum_{i=1}^S \sum_{j=1}^S a_{ij} \frac{N_i}{N} \left(\frac{\partial N_j}{\partial N_k}\right)_{T,V_m,N_{i \neq k}} \\
&= \sum_{j=1}^S a_{kj} \frac{N_j}{N} - \sum_{i=1}^S \sum_{j=1}^S a_{ij} \frac{N_i}{N^2} N_j + \sum_{i=1}^S a_{ik} \frac{N_i}{N} \\
&= 2 \sum_{i=1}^S x_i a_{ki} - a_m
\end{aligned} \tag{S75}$$

Replacing Eqs. S74 and S75 in Eq. S73 leads to

$$\left(\frac{\partial P}{\partial N_k}\right)_{T,V_m,N_{i \neq k}} = \frac{RT(V_m - Nb_m) + NRTb_k}{(V_m - Nb_m)^2} - \frac{2N \sum_{i=1}^S x_i a_{i \neq k} - \frac{2a_m b_k N^2 (V_m - Nb_m)}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]}}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]} \tag{S76}$$

Replacing Eqs. S71 and S76 in Eq. S69, the partial molar volume of component  $k$  becomes

$$\bar{v}_k = \frac{\frac{RT(V_m - Nb_m) + NRTb_k}{(V_m - Nb_m)^2} - \frac{2N \sum_{i=1}^S x_i a_{ki} - \frac{2a_m b_k N^2 (V_m - Nb_m)}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]}}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]}}{\left[ \frac{NRT}{(V_m - Nb_m)^2} - \frac{2N^2 a_m (V_m + Nb_m)}{[V_m(V_m + Nb_m) + Nb_m(V_m - Nb_m)]^2} \right]} \tag{S77}$$

Factorizing  $N$  leads to

$$\begin{aligned}
\bar{v}_k &= \frac{\frac{NRT(\frac{V_m}{N} - b_m) + NRTb_k}{N^2(\frac{V_m}{N} - b_m)^2} - \frac{2N \sum_{i=1}^S x_i a_{ki} - \frac{2a_m b_k N^3(\frac{V_m}{N} - b_m)}{[N^2 \frac{V_m}{N}(\frac{V_m}{N} + b_m) + N^2 b_m(\frac{V_m}{N} - b_m)]}}{[N^2 \frac{V_m}{N}(\frac{V_m}{N} + b_m) + N^2 b_m(\frac{V_m}{N} - b_m)]}}{\left[ \frac{NRT}{N^2(\frac{V_m}{N} - b_m)^2} - \frac{2a_m N^3(\frac{V_m}{N} + b_m)}{[N^2 \frac{V_m}{N}(\frac{V_m}{N} + b_m) + N^2 b_m(\frac{V_m}{N} - b_m)]^2} \right]} \\
&= \frac{\frac{1}{N} \left[ \frac{RT(\frac{V_m}{N} - b_m) + RTb_k}{(\frac{V_m}{N} - b_m)^2} \right] - \frac{1}{N} \left[ \frac{2 \sum_{i=1}^S x_i a_{ki} - \frac{2a_m b_k(\frac{V_m}{N} - b_m)}{[\frac{V_m}{N}(\frac{V_m}{N} + b_m) + b_m(\frac{V_m}{N} - b_m)]}}{[\frac{V_m}{N}(\frac{V_m}{N} + b_m) + b_m(\frac{V_m}{N} - b_m)]} \right]}{\frac{1}{N} \left[ \frac{RT}{(\frac{V_m}{N} - b_m)^2} - \frac{2a_m(\frac{V_m}{N} + b_m)}{[\frac{V_m}{N}(\frac{V_m}{N} + b_m) + b_m(\frac{V_m}{N} - b_m)]^2} \right]}
\end{aligned} \tag{S78}$$

$v_m = \frac{V_m}{N}$  is the molar volume of the mixture which is solved directly from Eq. S62. Therefore, partial molar volume of component  $k$  in the mixture equals

$$\bar{v}_k = \frac{\frac{RT(v_m - b_m) + RTb_k}{(v_m - b_m)^2} - \frac{2 \sum_{i=1}^S x_i a_{ki} - \frac{2a_m b_k (v_m - b_m)}{[v_m(v_m + b_m) + b_m(v_m - b_m)]}}{[v_m(v_m + b_m) + b_m(v_m - b_m)]}}{\left[ \frac{RT}{(v_m - b_m)^2} - \frac{2a_m(v_m + b_m)}{[v_m(v_m + b_m) + b_m(v_m - b_m)]^2} \right]} \quad (\text{S79})$$

The partial molar enthalpy of component  $k$  is related to its partial molar volume [20]

$$\left( \frac{\partial \bar{h}_k}{\partial P} \right)_{T, N_i} = \bar{v}_k - T \left( \frac{\partial \bar{v}_k}{\partial T} \right)_{P, N_i} \quad (\text{S80})$$

The right hand side of Eq. S80 is only related to excess partial molar volume as the ideal gas term drops out:

$$\begin{aligned} \bar{v}_k - T \left( \frac{\partial \bar{v}_k}{\partial T} \right)_{P, N_i} &= \left[ \bar{v}_k^{\text{id}} - T \left( \frac{\partial \bar{v}_k^{\text{id}}}{\partial T} \right)_{P, N_i} \right] + \bar{v}_k^{\text{ex}} - T \left( \frac{\partial \bar{v}_k^{\text{ex}}}{\partial T} \right)_{P, N_i} \\ &= \left[ \frac{RT}{P} - T \left( \frac{R}{P} \right) \right] + \bar{v}_k^{\text{ex}} - T \left( \frac{\partial \bar{v}_k^{\text{ex}}}{\partial T} \right)_{P, N_i} \\ &= \bar{v}_k^{\text{ex}} - T \left( \frac{\partial \bar{v}_k^{\text{ex}}}{\partial T} \right)_{P, N_i} \end{aligned} \quad (\text{S81})$$

Given that the ideal part of the enthalpy is only a function of temperature, we can write

$$\left( \frac{\partial \bar{h}_k^{\text{ex}}}{\partial P} \right)_{P, N_i} = \bar{v}_k - T \left( \frac{\partial \bar{v}_k}{\partial T} \right)_{P, N_i} \quad (\text{S82})$$

The partial molar excess enthalpy can be computed numerically from

$$\bar{h}_k^{\text{ex}} = \int_0^P dP \left[ \bar{v}_k - T \left( \frac{\partial \bar{v}_k}{\partial T} \right)_{P, N_i} \right] \quad (\text{S83})$$

Eqs. S79 and S83 were numerically verified with the expressions derived by Michelsen and Mollerup [7]. Exact agreement was found between the results from both methods.

## 5.2. PC-SAFT Equation of State

The Perturbed Chain - Statistical Association Fluid Theory (PC-SAFT) EoS [21–25] is a theoretically derived model, based on statistical mechanics principles. The basis of the model relies on applying rigorous perturbation theory [22, 26–29] for systems which are comprised of a repulsive core and multiple attractive sites, resulting in an expression for the Helmholtz energy. In this way, the Helmholtz energy of a molecular fluid can be obtained as the sum of the Helmholtz energies of a simple reference fluid (which is known accurately) and various perturbation terms. For details **and the exact mathematical relations**, the reader is referred to the original publications [21–25]. **The** calculation of mixture properties requires appropriate mixing and combining rules. In this work, the van der Waals mixing rules, as proposed by Gross and Sadowski [21], were used for the dispersion term, while the Lorentz-Berthelot mixing rules were applied to calculate the segment energy and diameter parameters [2]. The PC-SAFT parameters for the mixtures are therefore

$$\overline{m^2 \frac{\varepsilon}{k_B T} \sigma^3} = \sum_{i=1}^S \sum_{j=1}^S x_i x_j m_i m_j \left[ \frac{\varepsilon_{ij}}{k_B T} \right] \sigma_{ij}^3 \quad (\text{S84})$$

$$\overline{m^2 \left[ \frac{\varepsilon}{k_B T} \right]^2 \sigma^3} = \sum_{i=1}^S \sum_{j=1}^S x_i x_j m_i m_j \left[ \frac{\varepsilon_{ij}}{k_B T} \right]^2 \sigma_{ij}^3 \quad (\text{S85})$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij}) \quad (\text{S86})$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (\text{S87})$$

In these equations,  $m_i$  is the number of spherical segments in component  $i$ ,  $\varepsilon_i$  is the dispersion energy between spherical segments of component  $i$ ,  $\sigma_i$  is the temperature-independent diameter of each spherical segment in component  $i$ , **and**  $k_{ij}$  is the **BIP** between components  $i$  and  $j$ . In this work, the binary interactions parameters  $k_{ij}$  are set to zero. For associating mixtures, two more combining rules have to be applied for the cross-association energy and volume [23]:

$$\varepsilon^{A_i B_j} = \frac{1}{2} (\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}) \quad (\text{S88})$$

$$\kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \left( \frac{\sqrt{\sigma_i \sigma_j}}{\frac{1}{2}(\sigma_i + \sigma_j)} \right)^3 \quad (\text{S89})$$

where  $\varepsilon^{A_i B_i}$  is the association energy and  $\kappa^{A_i B_i}$  is the association volume of component  $i$ . In this work, ammonia was treated as an associating molecule with 4 association sites, as proposed by Mejbri and Bellagi [30, 31]. The PC-SAFT EoS parameters that were used in our calculations are summarized in Table S14.

## 6. Evaluating enthalpies

The reaction enthalpy is defined as the difference between the enthalpy of the reaction products and enthalpy of the reactants, with respect to their stoichiometric coefficients [19]:

$$\Delta\bar{h} = \sum_{\text{P}} \nu_i \bar{h}_i(T, P) - \sum_{\text{A}} \nu_j \bar{h}_j(T, P) \quad (\text{S90})$$

The partial molar enthalpy of a component at temperature  $T$  and pressure  $P$  equals

$$\begin{aligned} \bar{h}_i(T, P) &= \bar{h}_{f,i}^\circ + [\bar{h}_i(T, P_{\text{ref}}) - \bar{h}_i(T_{\text{ref}}, P_{\text{ref}})] + [\bar{h}_i^{\text{ex}}(T, P) - \bar{h}_i^{\text{ex}}(T, P_{\text{ref}})] \\ &= \bar{h}_{f,i}^\circ + [\bar{h}_i(T, P_{\text{ref}}) - \bar{h}_i(T_{\text{ref}}, P_{\text{ref}})] + \bar{h}_i^{\text{ex}}(T, P) \end{aligned} \quad (\text{S91})$$

$T_{\text{ref}}$  and  $P_{\text{ref}}$  are the reference temperature and pressure at 298 K and 1 bar, respectively.  $\bar{h}_{f,i}^\circ$  is the formation enthalpy of component  $i$  at  $(T_{\text{ref}}, P_{\text{ref}})$  and its value can be found in literature [20, 32, 33]. The second term on the right hand side of Eq. S91 is associated with enthalpy difference at  $(T, P_{\text{ref}})$  relative to the reference state at  $(T_{\text{ref}}, P_{\text{ref}})$  and at constant composition. This is often expressed as follows (the Shomate equation [33]):

$$\bar{h}_i(T, P_{\text{ref}}) - \bar{h}_i(T_{\text{ref}}, P_{\text{ref}}) = AT + \frac{BT^2}{2} + \frac{CT^3}{3} + \frac{DT^4}{4} - \frac{E}{T} + F - H \quad (\text{S92})$$

The temperature  $T$  in Eq. S92 is in units of  $\frac{\text{K}}{1000}$ . The coefficients  $A$  to  $H$  for  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{H}_2$  are taken from NIST-JANAF Thermochemical Tables [32, 33]. The coefficients  $A$  to  $H$  and the left hand side of Eq. S92 evaluated at  $T = 573$  K are listed in Table S11 for all components. The third term on the right hand side of Eq. S91 is associated with the enthalpy difference between states  $(T, P)$  and  $(T, P_{\text{ref}})$  which accounts for deviation from ideal gas behavior relative to the standard reference pressure [20]. The term  $\bar{h}_i^{\text{ex}}(T, P_{\text{ref}})$  in Eq. S91 can be considered zero at high temperatures. As explained in the previous sections,  $\bar{h}_i^{\text{ex}}(T, P_{\text{ref}})$  can be obtained either from the PR-EoS (Eq. S83), the PC-SAFT EoS, or MC simulations (Eq. S57).

**Table S1.** Composition of  $[\text{NH}_3, \text{N}_2, \text{H}_2]$  mixtures at  $T = 573$  K and various pressures obtained from chemical equilibrium simulations of the Haber-Bosch reaction. The computed equilibrium compositions are in excellent agreement with experimental data [34–36] as shown in our previous study [9]. These mixture compositions are used as initial parameters for *CFCNPT* ensemble simulations and EoS modeling.  $L_{\text{box}}$  is the initial box size (a cubic simulation box is used),  $N_i$  is the number of molecules of type  $i$ ,  $R_c^{\text{LJ}}$  is the cut off radius for intermolecular Lennard-Jones interactions,  $R_c^{\text{Coul}}$  is the cut off radius for Coulombic interactions, and  $\alpha$  is the damping parameter used in the Wolf method [37–39] to calculate Coulombic interactions. The parameters for the Wolf method were chosen according to the procedure outlined in Ref. [38].

$P/[\text{MPa}]$	$L_{\text{box}}/[\text{\AA}]$	$N_{\text{N}_2}$	$N_{\text{H}_2}$	$N_{\text{NH}_3}$	$R_c^{\text{LJ}}/[\text{\AA}]$	$R_c^{\text{Coul}}/[\text{\AA}]$	$\alpha/[\text{\AA}^{-1}]$
10	75	57	171	306	14	20	0.06
20	57	36	107	349	14	18	0.08
30	49	25	74	371	14	16	0.10
40	43	18	53	385	14	16	0.10
50	40	13	40	394	14	14	0.12
60	37	10	31	400	14	14	0.12
70	35	8	25	404	14	14	0.12
80	34	7	20	407	14	14	0.12

**Table S2.** Force field parameters used for the [NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>] mixture [35, 40, 41]. The Lorentz-Berthelot mixing rules are used for unlike interactions [2]. Cut off radii for Lennard-Jones and Coulombic interactions are specified in Table S1. Analytic tail corrections [1] are used for interactions beyond the cut off radius. Interaction sites are as defined in our previous work [9].

Site	$\sigma/[\text{\AA}]$	$\epsilon/k_B/[\text{K}]$	$q/[e]$
N <sub>N<sub>2</sub></sub>	3.31	36.0	-0.482
M <sub>N<sub>2</sub></sub>	0	0	0.964
H <sub>2</sub>	2.915	38.0	0
N <sub>NH<sub>3</sub></sub>	3.42	185.0	0
H <sub>NH<sub>3</sub></sub>	0	0	0.41
M <sub>NH<sub>3</sub></sub>	0	0	-1.23

**Table S3.** Excess chemical potentials, partial molar excess enthalpies and partial molar volumes of a LJ molecule in a binary color mixture consisting of 200 molecules at  $T^* = 2$  and reduced pressures between  $P^* = 0.1$  and  $P^* = 9$ , using CFCNPT ensemble simulations (Eqs. S57 and S61), and the WTPI method as proposed by Frenkel, Ciccotti, and co-workers [5, 6] (Eqs. S23 and S38) in the conventional NPT ensemble. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

		CFCNPT Method			WTPI method		
$P^*$	$\langle \rho^* \rangle$	$\mu_A^{\text{ex}}$	$\bar{h}_A^{\text{ex}}$	$\bar{v}_A$	$\mu_A^{\text{ex}}$	$\bar{h}_A^{\text{ex}}$	$\bar{v}_A$
0.1	0.052	-0.144(3)	-0.36(5)	19.2(4)	-0.14448(3)	-0.361(5)	19.29(4)
0.5	0.264	-0.369(1)	-1.55(7)	3.75(7)	-0.368(1)	-1.52(4)	3.78(4)
1.0	0.433	0.054(1)	-2.0(1)	2.26(5)	0.067(1)	-1.94(5)	2.32(3)
1.5	0.525	0.709(4)	-1.9(1)	1.89(3)	0.718(1)	-1.8(1)	1.90(3)
2.0	0.586	1.389(3)	-1.61(7)	1.71(1)	1.393(2)	-1.64(4)	1.70(1)
2.5	0.631	2.056(4)	-1.2(1)	1.60(1)	2.070(5)	-1.2(1)	1.59(2)
3.0	0.667	2.715(3)	-0.87(5)	1.517(7)	2.720(4)	-0.8(1)	1.51(3)
3.5	0.697	3.363(3)	-0.5(1)	1.43(1)	3.369(6)	-0.4(1)	1.44(2)
4.0	0.723	3.992(3)	0.0(1)	1.39(1)	4.00(1)	-0.3(2)	1.36(5)
4.5	0.746	4.610(4)	0.4(1)	1.35(2)	4.62(1)	0.1(2)	1.30(3)
5.0	0.766	5.126(7)	0.7(1)	1.30(1)	5.23(1)	0.8(5)	1.31(4)
5.5	0.784	5.824(3)	1.09(8)	1.26(1)	5.81(2)	1.1(4)	1.29(3)
6.0	0.801	6.413(7)	1.53(5)	1.240(5)	6.43(3)	1.6(8)	1.23(5)
6.5	0.817	6.989(4)	2.0(1)	1.22(1)	7.01(3)	2.2(5)	1.25(6)
7.0	0.831	7.567(7)	2.5(1)	1.21(1)	7.59(3)	2.5(7)	1.19(7)
7.5	0.844	8.145(4)	2.9(1)	1.183(6)	8.13(2)	2.8(8)	1.18(7)
8.0	0.857	8.69(1)	3.2(2)	1.15(1)	8.74(3)	4(1)	1.2(1)
8.5	0.869	9.262(8)	3.93(8)	1.15(1)	9.23(4)	4(1)	1.1(1)
9.0	0.880	9.807(4)	4.2(1)	1.14(1)	9.78(5)	5(2)	1.1(1)

**Table S4.** Computed partial molar excess enthalpies and partial molar volumes of  $\text{NH}_3$  in the  $[\text{NH}_3, \text{N}_2, \text{H}_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa, obtained from PR-EoS modeling (using zero BIPs), PC-SAFT EoS modeling (using zero BIPs), direct Numerical Differentiation (ND), and CFCNPT ensemble simulations, respectively. The compositions of the mixtures are obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and are listed in Table S1. Pressures, partial molar (excess) enthalpies and partial molar volumes are reported in units of [MPa], [ $\text{kJ}\cdot\text{mol}^{-1}$ ] and [ $\text{m}^3\cdot\text{kmol}^{-1}$ ], respectively. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

$P$	PR-EoS			PC-SAFT			ND			CFCMC		
	$\bar{h}_{\text{NH}_3}$	$\bar{h}_{\text{NH}_3}^{\text{ex}}$	$\bar{v}_{\text{NH}_3}$	$\bar{h}_{\text{NH}_3}$	$\bar{h}_{\text{NH}_3}^{\text{ex}}$	$\bar{v}_{\text{NH}_3}$	$\bar{h}_{\text{NH}_3}$	$\bar{h}_{\text{NH}_3}^{\text{ex}}$	$\bar{v}_{\text{NH}_3}$	$\bar{h}_{\text{NH}_3}$	$\bar{h}_{\text{NH}_3}^{\text{ex}}$	$\bar{v}_{\text{NH}_3}$
10	-36.61	-1.65	0.441	-36.39	-1.43	0.452	-36.4(4)	-1.40(5)	0.450(4)	-36.4(4)	-1.4(2)	0.455(2)
20	-38.43	-3.47	0.205	-38.14	-3.17	0.210	-38.1(4)	-3.12(4)	0.207(2)	-38.1(5)	-3.1(2)	0.206(2)
30	-40.13	-5.17	0.130	-39.89	-4.92	0.131	-39.7(4)	-4.7(2)	0.129(3)	-39.7(5)	-4.7(2)	0.131(5)
40	-41.56	-6.60	0.096	-41.52	-6.56	0.094	-41.2(4)	-6.2(2)	0.094(2)	-41.5(5)	-6.5(2)	0.090(3)
50	-42.65	-7.70	0.078	-42.92	-7.96	0.073	-42.2(4)	-7.2(2)	0.078(2)	-42.3(6)	-7.3(4)	0.075(5)
60	-43.45	-8.49	0.068	-44.00	-9.04	0.062	-43.7(5)	-8.7(3)	0.062(2)	-43.5(7)	-8.5(6)	0.063(3)
70	-44.02	-9.06	0.061	-44.79	-9.82	0.054	-43.2(5)	-9.3(3)	0.055(2)	-43.9(8)	-9.0(6)	0.058(3)
80	-44.42	-9.46	0.056	-45.35	-10.38	0.049	-44.4(5)	-9.4(2)	0.053(1)	-44.3(7)	-9.4(5)	0.052(2)



**Table S5.** Computed partial molar excess enthalpies and partial molar volumes of  $N_2$  in the  $[NH_3, N_2, H_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa, obtained from PR-EoS modeling (using zero BIPs), PC-SAFT EoS modeling (using zero BIPs), direct Numerical Differentiation (ND), and CFCNPT ensemble simulations, respectively. The compositions of the mixtures are obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and are listed in Table S1. Pressures, partial molar (excess) enthalpies and partial molar volumes are reported in units of [MPa], [ $\text{kJ}\cdot\text{mol}^{-1}$ ] and [ $\text{m}^3\cdot\text{kmol}^{-1}$ ], respectively. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

$P$	PR-EoS			PC-SAFT			ND			CFCMC		
	$\bar{h}_{N_2}$	$\bar{h}_{N_2}^{\text{ex}}$	$\bar{v}_{N_2}$	$\bar{h}_{N_2}$	$\bar{h}_{N_2}^{\text{ex}}$	$\bar{v}_{N_2}$	$\bar{h}_{N_2}$	$\bar{h}_{N_2}^{\text{ex}}$	$\bar{v}_{N_2}$	$\bar{h}_{N_2}$	$\bar{h}_{N_2}^{\text{ex}}$	$\bar{v}_{N_2}$
10	8.28	0.20	0.504	8.57	0.49	0.512	8.38(3)	0.30(3)	0.506(3)	8.29(3)	0.2(3)	0.49(3)
20	9.10	1.02	0.274	9.71	1.62	0.284	9.5(1)	1.4(1)	0.284(4)	9.4(4)	1.3(4)	0.28(2)
30	10.45	2.37	0.200	11.37	3.28	0.212	10.8(2)	2.8(2)	0.209(3)	11.0(3)	2.9(3)	0.210(7)
40	12.01	3.93	0.162	13.45	5.36	0.177	12.6(3)	4.5(3)	0.170(3)	13.0(3)	4.9(3)	0.175(3)
50	13.41	5.33	0.136	15.58	7.50	0.154	14.9(2)	6.8(2)	0.152(1)	14.6(6)	6.5(6)	0.150(4)
60	14.46	6.38	0.118	17.30	9.22	0.136	16.50(8)	8.42(8)	0.134(1)	16.5(3)	8.4(3)	0.133(3)
70	15.18	7.10	0.103	18.41	10.33	0.120	18.0(3)	10.0(3)	0.120(1)	17.8(7)	9.7(7)	0.119(4)
80	15.68	7.60	0.093	19.03	10.94	0.107	18.7(2)	10.6(2)	0.107(1)	18.9(7)	10.9(7)	0.108(4)

**Table S6.** Computed partial molar excess enthalpies and partial molar volumes of H<sub>2</sub> in the [NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>] equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa, obtained from PR-EoS modeling (using zero BIPs), PC-SAFT EoS modeling (using zero BIPs), direct Numerical Differentiation (ND), and CFCNPT ensemble simulations, respectively. The compositions of the mixtures are obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and are listed in Table S1. Pressures, partial molar (excess) enthalpies and partial molar volumes are reported in units of [MPa], [kJ.mol<sup>-1</sup>] and [m<sup>3</sup>.kmol<sup>-1</sup>], respectively. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

	PR-EoS			PC-SAFT			ND			CFCMC		
$P$	$\bar{h}_{\text{H}_2}$	$\bar{h}_{\text{H}_2}^{\text{ex}}$	$\bar{v}_{\text{H}_2}$	$\bar{h}_{\text{H}_2}$	$\bar{h}_{\text{H}_2}^{\text{ex}}$	$\bar{v}_{\text{H}_2}$	$\bar{h}_{\text{H}_2}$	$\bar{h}_{\text{H}_2}^{\text{ex}}$	$\bar{v}_{\text{H}_2}$	$\bar{h}_{\text{H}_2}$	$\bar{h}_{\text{H}_2}^{\text{ex}}$	$\bar{v}_{\text{H}_2}$
10	8.57	0.56	0.501	8.77	0.75	0.509	8.73(3)	0.72(3)	0.511(2)	8.9(3)	0.8(3)	0.52(3)
20	9.76	1.74	0.270	10.25	2.23	0.281	10.13(8)	2.12(8)	0.282(3)	10.2(2)	2.2(2)	0.285(6)
30	11.36	3.35	0.193	12.26	4.24	0.209	12.1(1)	4.1(1)	0.209(2)	12.2(4)	4.2(4)	0.212(8)
40	13.02	5.01	0.153	14.58	6.56	0.172	14.4(2)	6.4(2)	0.171(2)	14.3(7)	6.3(7)	0.170(8)
50	14.40	6.38	0.126	16.71	8.69	0.146	16.9(2)	8.9(2)	0.148(1)	16.7(5)	8.7(5)	0.146(4)
60	15.35	7.34	0.107	18.20	10.18	0.125	16.6(2)	8.6(2)	0.134(1)	18.5(5)	10.5(5)	0.126(4)
70	15.97	7.95	0.092	18.97	10.95	0.108	19.4(4)	11.4(4)	0.106(2)	19.3(4)	11.3(4)	0.106(2)
80	16.36	8.34	0.081	19.21	11.19	0.093	20.4(2)	12.4(2)	0.096(1)	20.1(4)	12.1(4)	0.094(2)

**Table S7.** Computed excess chemical potentials of  $\text{NH}_3$  in the  $[\text{NH}_3, \text{N}_2, \text{H}_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa, obtained from PR-EoS modeling (using zero BIPs), PC-SAFT EoS modeling (using zero BIPs), serial Rx/CFC ensemble [9], and CFCNPT ensemble simulations, respectively. The compositions of the mixtures are obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC and are listed in Table S1. Pressures and chemical potentials are reported in units of [MPa], and  $[\text{kJ}\cdot\text{mol}^{-1}]$ , respectively. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

	PR-EoS	PC-SAFT	serial Rx/CFC	CFCMC
$P$	$\mu_{\text{NH}_3}^{\text{ex}}$	$\mu_{\text{NH}_3}^{\text{ex}}$	$\mu_{\text{NH}_3}^{\text{ex}}$	$\mu_{\text{NH}_3}^{\text{ex}}$
10	-0.38	-0.26	-0.36(2)	-0.36(2)
20	-0.79	-0.60	-0.91(3)	-0.901(5)
30	-1.14	-0.94	-1.49(3)	-1.48(2)
40	-1.43	-1.25	-2.00(3)	-2.00(2)
50	-1.65	-1.51	-2.37(2)	-2.39(2)
60	-1.81	-1.73	-2.58(3)	-2.590(7)
70	-1.91	-1.90	-2.63(3)	-2.65(2)
80	-1.97	-2.03	-2.55(6)	-2.59(2)

**Table S8.** Computed excess chemical potentials of  $N_2$  in the  $[NH_3, N_2, H_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa, obtained from PR-EoS modeling (using zero BIPs), PC-SAFT EoS modeling (using zero BIPs), serial Rx/CFC ensemble [9], and CFCNPT ensemble simulations, respectively. The compositions of the mixtures are obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC and are listed in Table S1. Pressures and chemical potentials are reported in units of [MPa], and  $[kJ.mol^{-1}]$ , respectively. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

	PR-EoS	PC-SAFT	serial Rx/CFC	CFCMC
$P$	$\mu_{N_2}^{ex}$	$\mu_{N_2}^{ex}$	$\mu_{N_2}^{ex}$	$\mu_{N_2}^{ex}$
10	0.26	0.36	0.30(2)	0.296(8)
20	0.68	0.91	0.63(4)	0.60(1)
30	1.19	1.57	1.01(3)	1.00(2)
40	1.75	2.31	1.54(3)	1.505(6)
50	2.30	3.09	2.18(4)	2.139(9)
60	2.80	3.83	2.91(2)	2.87(2)
70	3.26	4.52	3.68(2)	3.63(2)
80	3.67	5.14	4.49(6)	4.40(2)

**Table S9.** Computed excess chemical potentials of  $\text{H}_2$  in the  $[\text{NH}_3, \text{N}_2, \text{H}_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa, obtained from PR-EoS modeling (using zero BIPs), PC-SAFT EoS modeling (using zero BIPs), serial Rx/CFC ensemble [9], and CFCNPT ensemble simulations, respectively. The compositions of the mixtures are obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC and are listed in Table S1. Pressures and chemical potentials are reported in units of [MPa], and  $[\text{kJ}\cdot\text{mol}^{-1}]$ , respectively. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

	PR-EoS	PC-SAFT	serial Rx/CFC	CFCMC
$P$	$\mu_{\text{H}_2}^{\text{ex}}$	$\mu_{\text{H}_2}^{\text{ex}}$	$\mu_{\text{H}_2}^{\text{ex}}$	$\mu_{\text{H}_2}^{\text{ex}}$
10	0.25	0.30	0.33(2)	0.33(2)
20	0.64	0.80	0.70(2)	0.71(1)
30	1.11	1.41	1.16(3)	1.17(2)
40	1.59	2.07	1.70(2)	1.73(2)
50	2.03	2.72	2.33(2)	2.36(1)
60	2.42	3.31	2.98(3)	3.04(2)
70	2.76	3.80	3.66(3)	3.70(2)
80	3.05	4.20	4.30(4)	4.35(2)

**Table S10.** Critical temperatures ( $T_c$ ), pressures ( $P_c$ ), acentric factors ( $\omega$ ) and enthalpies of formation ( $\bar{h}_f^\circ$ ) of the components at standard reference state (1 bar) [16, 32, 33].

Component	$T_c$ /[K]	$P_c$ /[Pa]	$\omega$	$\bar{h}_f^\circ$ /[kJ.mol <sup>-1</sup> ]
N <sub>2</sub>	126.19	3395800	0.0372	0
H <sub>2</sub>	33.14	1296400	-0.219	0
NH <sub>3</sub>	405.4	11333000	0.25601	-45.94 ± 0.35

**Table S11.** Calculation of the enthalpy differences for each component at temperature of 573 K relative to the reference temperature ( $T_{\text{ref}} = 298.15\text{K}$ ) at  $P_{\text{ref}} = 0.1\text{MPa}$ , using the Shomate equation (Eq. S92 [33]). The parameters  $A$  to  $H$  were taken from NIST thermochemistry database [32, 33]. The parameters are applicable to the temperature range of 298 K to 1400 K for  $\text{NH}_3$ , 500 K to 2000 K for  $\text{N}_2$  and 298 K to 1000 K for  $\text{H}_2$ . Enthalpies are in units of  $\text{kJ}\cdot\text{mol}^{-1}$ .

Component	$\text{NH}_3$	$\text{N}_2$	$\text{H}_2$
$A$	19.99563	19.50583	33.066178
$B$	49.77119	19.88705	-11.363417
$C$	-15.37599	-8.598535	11.432816
$D$	1.921168	1.369784	-2.772874
$E$	0.189174	0.527601	-0.158558
$F$	-53.30667	-4.935202	-9.980797
$G$	203.8591	212.3900	172.707974
$H$	-45.89806	-	-
$\bar{h}_i(T, P_{\text{ref}}) - \bar{h}_i(T_{\text{ref}}, P_{\text{ref}})$			
$T/[\text{K}]$	$\text{NH}_3$	$\text{N}_2$	$\text{H}_2$
573	10.97	8.08	8.01

**Table S12.** Computed reaction enthalpies of the Haber-Bosch process (per mole of  $\text{N}_2$ ) at  $T = 573$  K and pressures from  $P = 10$  MPa to  $P = 80$  MPa using PR-EoS (using zero BIPs), PC-SAFT (using zero BIPs), the ND method and CFCNPT simulations. The reaction enthalpy at the standard reference pressure ( $T_{\text{ref}} = 298.15\text{K}$ ,  $P_{\text{ref}} = 0.1$  MPa) is  $-102.06/[\text{kJ}\cdot\text{mol}^{-1}]$ . The compositions of the mixtures are obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and are listed in Table S1. Enthalpies in the table are in units of  $\text{kJ}\cdot\text{mol}^{-1}$ .

	PR-EoS	PC-SAFT	ND	CFCNPT
$P$	$\Delta\bar{h}_{T=573\text{K}}$	$\Delta\bar{h}_{T=573\text{K}}$	$\Delta\bar{h}_{T=573\text{K}}$	$\Delta\bar{h}_{T=573\text{K}}$
10	-107.23	-107.68	-107.3(8)	-108(2)
20	-115.26	-116.76	-116.0(8)	-116(2)
30	-124.81	-127.95	-126.6(9)	-127(2)
40	-134.23	-142.24	-138.1(9)	-139(3)
50	-141.94	-151.58	-149.9(9)	-149(2)
60	-147.44	-159.93	-154(2)	-159(2)
70	-151.14	-164.90	-165(2)	-164(2)
80	-153.61	-167.37	-169(1)	-168(2)

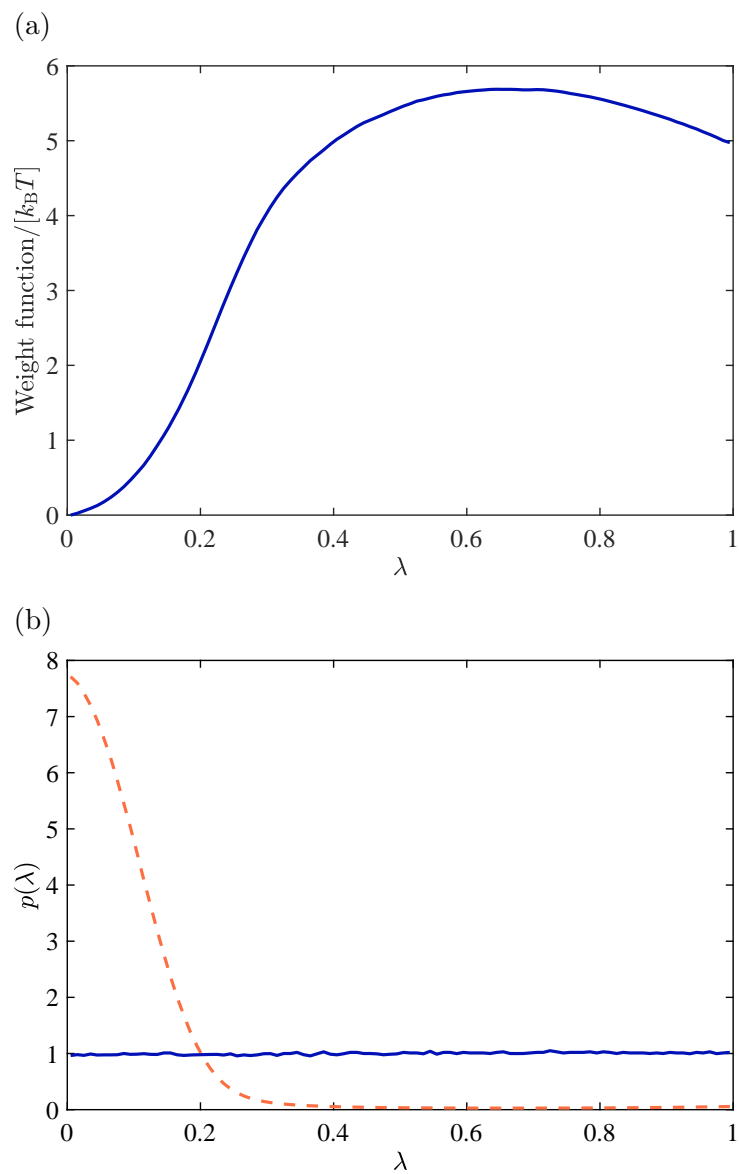


**Table S13.** Computed partial molar excess enthalpies, partial molar volumes and excess chemical potentials of NH<sub>3</sub>, N<sub>2</sub> and H<sub>2</sub> in the [NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>] equilibrium mixture at  $T = 573$  K and pressure  $P = 50$  MPa, obtained from CFCNPT ensemble simulations. The first three columns show the results from simulations where only one fractional molecule per component is used in each simulation. The last three columns show the results from simulations where only a single simulation is performed with three fractional molecules present at the same time (one of each component). The composition of the mixture is obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and is listed in Table S1. Partial molar enthalpies, partial molar volumes and excess chemical potentials are reported in units of [kJ.mol<sup>-1</sup>], [m<sup>3</sup>.kmol<sup>-1</sup>] and [kJ.mol<sup>-1</sup>], respectively. Numbers in brackets are uncertainties in the last digit, *i.e.*, 3.4(2) means  $3.4 \pm 0.2$ .

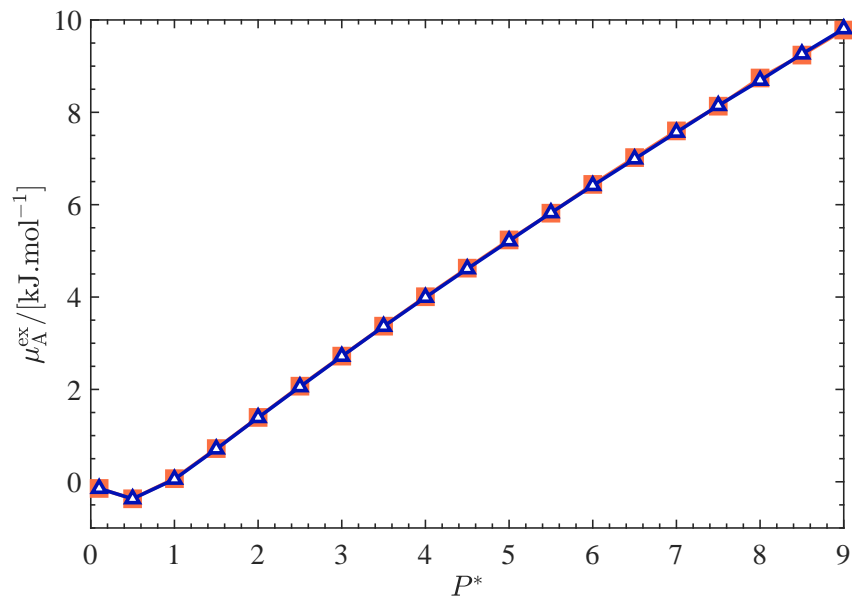
Component	CFCMC (1 fractional molec.)			CFCMC (3 fractional molec.)		
	$\bar{h}^{\text{ex}}$	$\bar{v}$	$\mu^{\text{ex}}$	$\bar{h}^{\text{ex}}$	$\bar{v}$	$\mu^{\text{ex}}$
NH <sub>3</sub>	-7.3(4)	0.075(5)	-2.39(2)	-6.9(9)	0.079(9)	-2.37(2)
N <sub>2</sub>	6.5(6)	0.150(4)	2.139(9)	7.3(9)	0.156(9)	2.13(3)
H <sub>2</sub>	8.7(5)	0.146(4)	2.36(1)	8.7(7)	0.147(6)	2.36(3)

**Table S14.** PC-SAFT EoS parameters for the components studied in this work.

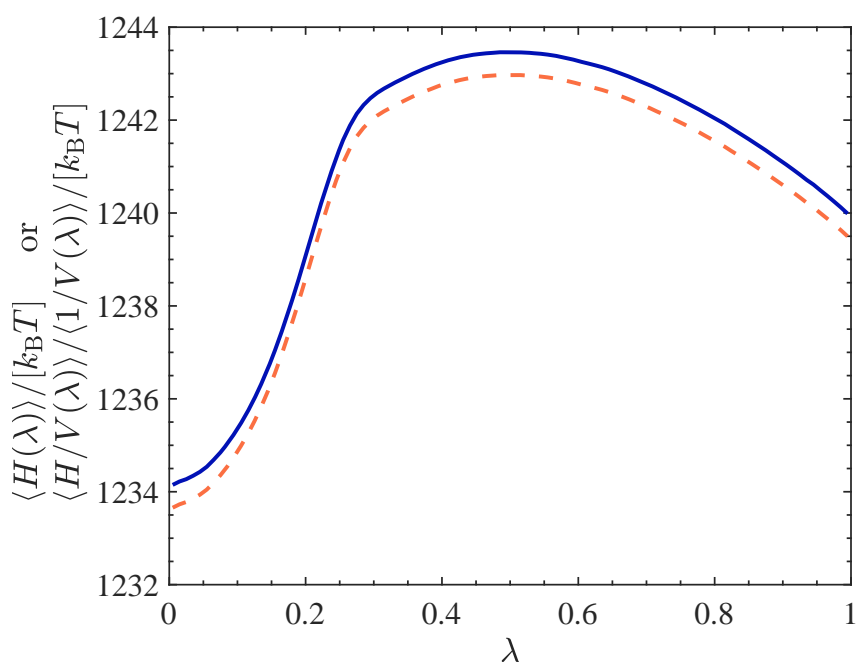
Component	$m$	$\sigma/[\text{\AA}]$	$\epsilon/k_B/[\text{K}]$	$\epsilon^{AB}/k_B/[\text{K}]$	$\kappa^{AB}$	Ref.
H <sub>2</sub>	0.8285	2.973	12.53	-	-	[31]
N <sub>2</sub>	1.2053	3.313	90.96	-	-	[24]
NH <sub>3</sub>	2.5785	2.2677	75.092	1041.5	0.37213	[30]



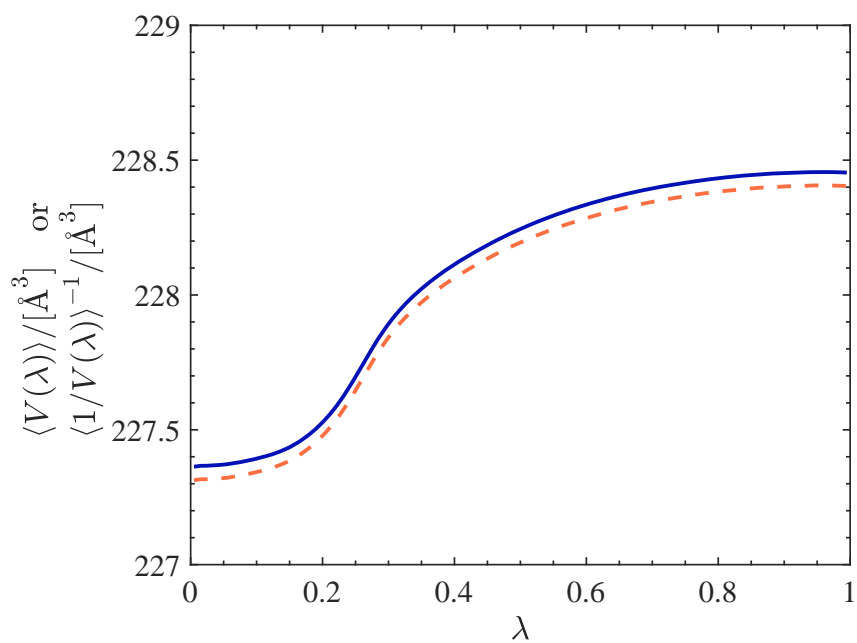
**Figure S1.** (a) Weight function and (b) probability distributions of  $\lambda$  (observed and unbiased) of a LJ molecule in a binary color mixture (50%-50%) consisting of 200 molecules at  $T^* = 2$  and  $P^* = 9$ . In subfigure (b): (---): unbiased probability distribution of lambda. (—): observed probability distribution of lambda.



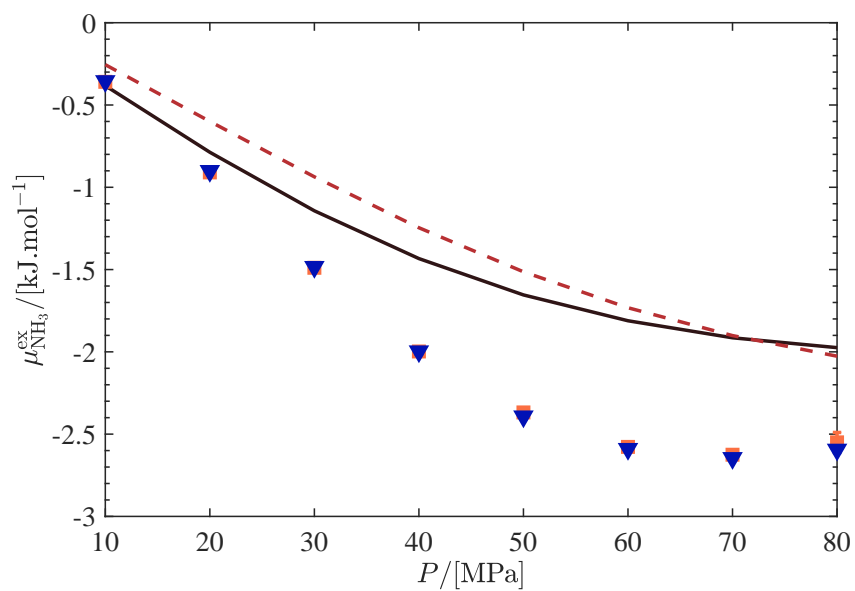
**Figure S2.** Computed excess chemical potentials of a LJ molecule in a binary color mixture (50%-50%) consisting of 200 molecules at a reduced temperature  $T^* = 2$  and reduced pressures between  $P^* = 0.1$  and  $P^* = 9$ .  $\blacktriangle$ : excess chemical potential in the CFCNPT ensemble,  $\blacksquare$ : excess chemical potential computed using WTPI method in the conventional NPT ensemble as proposed by Frenkel, Ciccotti, and co-workers [5, 6]. Raw data are provided in Table S3.



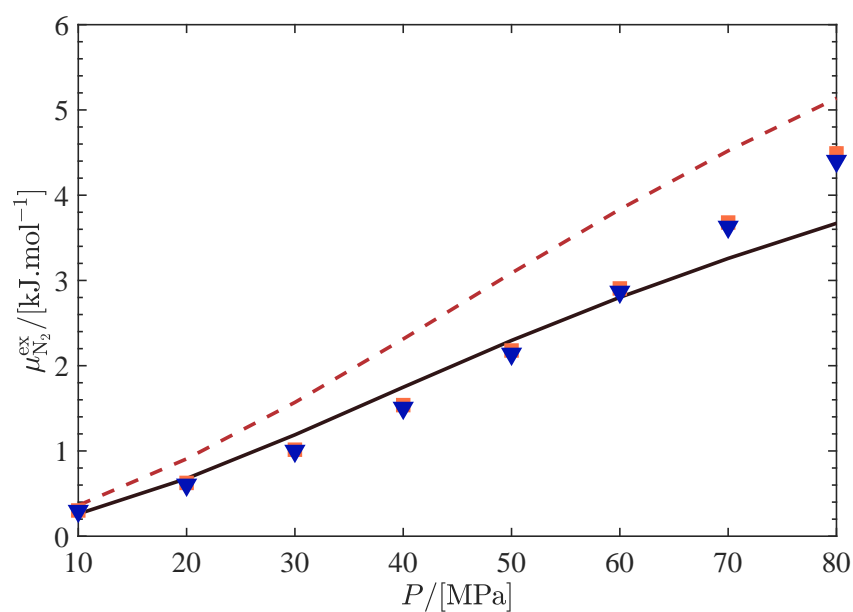
**Figure S3.** Ensemble average  $\langle H(\lambda) \rangle$  (—) and ensemble average  $\langle H/V(\lambda) \rangle / \langle 1/V(\lambda) \rangle$  (- - -) in the CFCNPT ensemble simulation of a binary color mixture (50%-50%) consisting of 200 molecules. Temperature, reduced pressure and reduced density of the mixture are  $T^* = 2$ ,  $P^* = 9$  and  $\langle \rho^* \rangle = 0.880$ , respectively.



**Figure S4.** Ensemble average  $\langle V(\lambda) \rangle$  (—) and ensemble average  $\langle 1/V \rangle^{-1}(\lambda)$  (- - -) in the CFCNPT ensemble simulation of a binary color mixture (50%-50%) consisting of 200 molecules. Temperature, reduced pressure and reduced density of the mixture are  $T^* = 2$ ,  $P^* = 9$  and  $\langle \rho^* \rangle = 0.880$ , respectively.

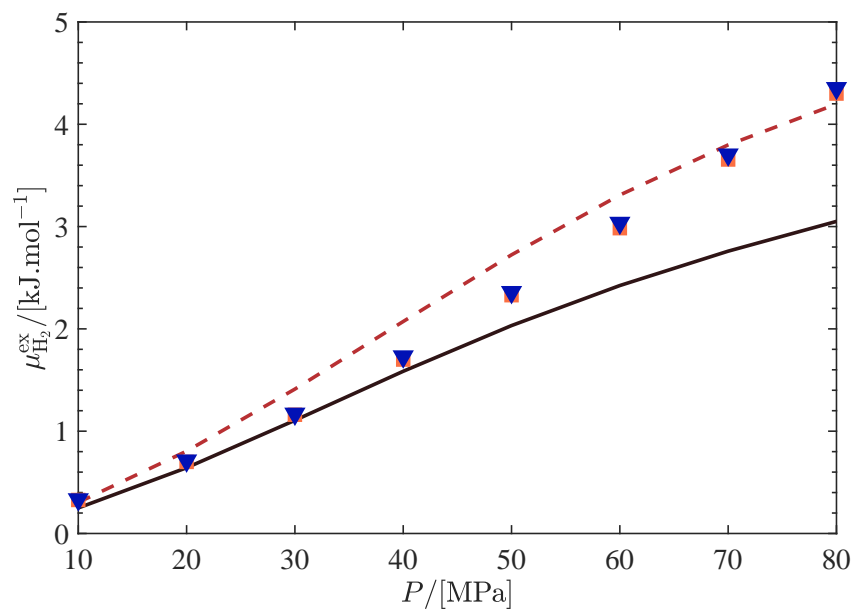


**Figure S5.** Computed excess chemical potentials of  $\text{NH}_3$  in the  $[\text{NH}_3, \text{N}_2, \text{H}_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa. The composition of the mixture is obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and is listed in Table S1. The excess chemical potential is computed using (—):PR-EoS, (---):PC-SAFT, ■: serial RX/CFC ensemble, ▼: CFCNPT ensemble. Zero BIPs were used for the PR-EoS and PC-SAFT EoS modeling. Raw data are listed in Table S7.

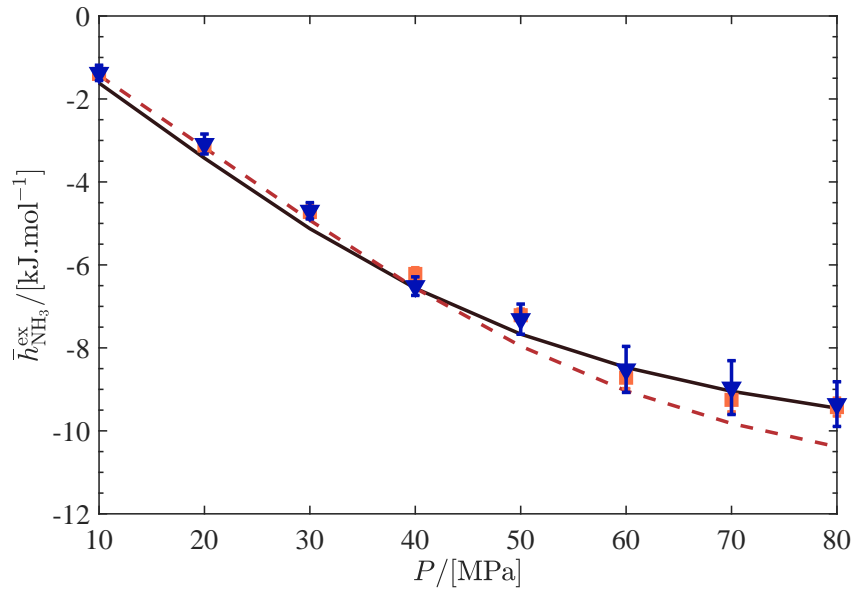


**Figure S6.** Computed excess chemical potentials of  $N_2$  in the  $[NH_3, N_2, H_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa. The composition of the mixture is obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and is listed in Table S1. The excess chemical potential is computed using (—):PR-EoS, (---):PC-SAFT, ■: serial RX/CFC ensemble, ▼: CFCNPT ensemble. Zero BIPs were used for the PR-EoS and PC-SAFT EoS modeling. Raw data are listed in Table S8.

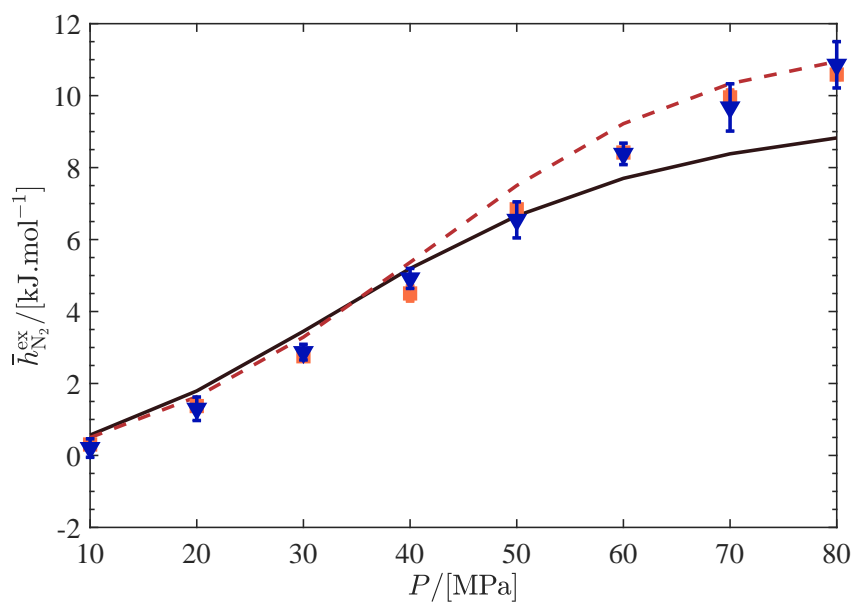




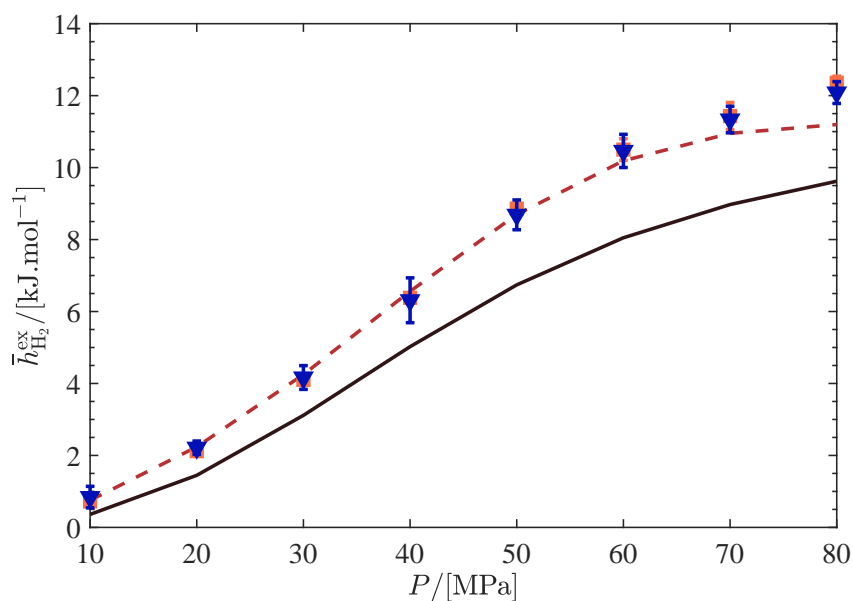
**Figure S7.** Computed excess chemical potentials of  $H_2$  in the  $[NH_3, N_2, H_2]$  equilibrium mixture at  $T = 573$  K and pressures between  $P = 10$  MPa and  $P = 80$  MPa. The composition of the mixture is obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and is listed in Table S1. The excess chemical potential is computed using (—):PR-EoS, (---):PC-SAFT, ■: serial RX/CFC ensemble, ▼: CFCNPT ensemble. Zero BIPs were used for the PR-EoS and PC-SAFT EoS modeling. Raw data are listed in Table S9.



**Figure S8.** Computed partial molar excess enthalpies of  $\text{NH}_3$  in the  $[\text{NH}_3, \text{N}_2, \text{H}_2]$  equilibrium mixture at  $T = 573$  K and pressure range of  $P = 10$  MPa and  $P = 80$  MPa. The composition of the mixture is obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and is listed in Table S1. Partial molar excess enthalpies are computed using: (—): using PR-EoS, (---): PC-SAFT, ■: the ND method, ▼: CFCNPT ensemble simulations. The following BIPs were used for the PR-EoS modeling: ammonia-hydrogen:  $k_{ij} = 0.103$ , nitrogen-ammonia:  $k_{ij} = 0.2193$ , nitrogen-hydrogen:  $k_{ij} = 0$  [42].



**Figure S9.** Computed partial molar excess enthalpies of  $N_2$  in the  $[NH_3, N_2, H_2]$  equilibrium mixture at  $T = 573$  K and pressure range of  $P = 10$  MPa and  $P = 80$  MPa. The composition of the mixture is obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and is listed in Table S1. Partial molar excess enthalpies are computed using: (—): using PR-EoS, (---): PC-SAFT,  $\blacksquare$ : the ND method,  $\blacktriangledown$ : CFCNPT ensemble simulations. The following BIPs were used for the PR-EoS modeling: ammonia-hydrogen:  $k_{ij} = 0.103$ , nitrogen-ammonia:  $k_{ij} = 0.2193$ , nitrogen-hydrogen:  $k_{ij} = 0$  [42].



**Figure S10.** Computed partial molar excess enthalpies of  $H_2$  in the  $[NH_3, N_2, H_2]$  equilibrium mixture at  $T = 573$  K and pressure range of  $P = 10$  MPa and  $P = 80$  MPa. The composition of the mixture is obtained from equilibrium simulations of the Haber-Bosch reaction using serial Rx/CFC [9] and is listed in Table S1. Partial molar excess enthalpies are computed using: (—): using PR-EoS, (- - -): PC-SAFT,  $\blacksquare$ : the ND method,  $\blacktriangledown$ : CFCNPT ensemble simulations. The following BIPs were used for the PR-EoS modeling: ammonia-hydrogen:  $k_{ij} = 0.103$ , nitrogen-ammonia:  $k_{ij} = 0.2193$ , nitrogen-hydrogen:  $k_{ij} = 0$  [42].

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