Supplementary Material for: Scaling Towards the Critical Point in the Combined Reaction/Gibbs Ensemble

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Table S1: Values of $\ln\left[\frac{q_i}{\Lambda_i^3 \rho_0}\right]$ for monomer (NO_2 or A) and dimer (N_2O_4 or A_2), and natural logarithms of ideal gas reaction equilibrium constants ($\ln[K_{IG}]$) as a function of temperature for reaction R1 of the main text for systems 1, 2, and 3. The values of $\ln\left[\frac{q_i}{\Lambda_i^3 \rho_0}\right]$ as a function temperature are calculated using the correlation reported by Lasala et al. [1] (Eqs. 10 and 11 of the main text). The ideal gas reaction equilibrium constants for reaction R1 are computed using Eq. 9 of the main text.

T / [K]	$\ln\left[\frac{q_i}{\Lambda_i^3 \rho_0}\right]$		$\ln[K_{IG}]$
	Monomer	Dimer	
180	632.98	1293.17	27.21
190	600.53	1226.33	25.28
200	571.32	1166.17	23.53
210	544.90	1111.75	21.95
220	520.87	1062.27	20.52
230	498.94	1017.09	19.21
240	478.83	975.68	18.01
250	460.34	937.58	16.91
260	443.26	902.41	15.89
270	427.45	869.85	14.94
275	419.98	854.46	14.50
280	412.77	839.61	14.07
290	399.10	811.46	13.25
300	386.35	785.19	12.49
310	374.41	760.61	11.78
320	363.23	737.56	11.11
330	352.72	715.92	10.48
340	342.83	695.54	9.89
350	333.50	676.33	9.34
360	324.69	658.19	8.81
370	316.36	641.03	8.31
380	308.46	624.77	7.84
390	300.98	609.35	7.39
395	297.37	601.93	7.18
400	293.86	594.69	6.97
405	290.44	587.64	6.77
410	287.09	580.75	6.57
415	283.83	574.04	6.37

Table S2: Values of $\ln\left[\frac{q_i}{\Lambda_i^3\rho_0}\right]$ for monomer and dimer, and natural logarithms of ideal gas reaction equilibrium constants ($\ln[K_{\mathrm{IG}}]$) as a function of temperature for reaction R1 of the main text for system 4. Lasala et al. [1] reported two correlations to calculate the isolated molecule partition functions of N_2O_4 and NO_2 (Eqs. 10 and 11 of the main text, respectively). We modified the values computed using the correlations from Lasala et al. [1] by decreasing the isolated molecule partition functions of N_2O_4 by 10 $\ln\left[\frac{q_i}{\Lambda_i^3\rho_0}\right]$ units for each temperature. The ideal gas reaction equilibrium constants for reaction R1 are computed using Eq. 9 of the main text.

T / [K]	$\ln\left[\frac{q_i}{\Lambda_i^3\rho_0}\right]$		$\ln[K_{\mathrm{IG}}]$
	Monomer	Dimer	
180	632.98	1283.17	17.21
190	600.53	1216.33	15.28
200	571.32	1156.17	13.53
210	544.90	1101.75	11.95
220	520.87	1052.27	10.52
230	498.94	1007.09	9.21
240	478.83	965.68	8.01
250	460.34	927.58	6.91
260	443.26	892.41	5.89
270	427.45	859.85	4.94
275	419.98	844.46	4.50
280	412.77	829.61	4.07
290	399.10	801.46	3.25
300	386.35	775.19	2.49
310	374.41	750.61	1.78
320	363.23	727.56	1.11
330	352.72	705.92	0.48
340	342.83	685.54	-0.11
350	333.50	666.33	-0.66
360	324.69	648.19	-1.19
370	316.36	631.03	-1.69
380	308.46	614.77	-2.16
390	300.98	599.35	-2.61
395	297.37	591.93	-2.82
400	293.86	584.69	-3.03
405	290.44	577.64	-3.23
410	287.09	570.75	-3.43
415	283.83	564.04	-3.63

Table S3: Values of $\ln\left[\frac{q_i}{\Lambda_i^3\rho_0}\right]$ for monomer and dimer, and natural logarithms of ideal gas reaction equilibrium constants ($\ln[K_{\mathrm{IG}}]$) as a function of temperature for reaction R1 of the main text for system 5. Lasala et al. [1] reported two correlations to compute the isolated molecule partition functions of N_2O_4 and NO_2 (Eqs. 10 and 11 of the main text, respectively). We scaled up the values of isolated molecule partition functions of N_2O_4 computed by Lasala et al. [1] by 1% for system 5. The ideal gas reaction equilibrium constants for reaction R1 are computed using Eq. 9 of the main text.

T / [K]	$\ln\left[\frac{q_i}{\Lambda_i^3\rho_0}\right]$		$\ln[K_{\mathrm{IG}}]$
	Monomer	Dimer	
180	632.98	1306.10	40.14
190	600.53	1238.59	37.54
200	571.32	1177.84	35.19
210	544.90	1122.86	33.07
220	520.87	1072.89	31.14
230	498.94	1027.26	29.38
240	478.83	985.44	27.77
250	460.34	946.96	26.28
260	443.26	911.44	24.91
270	427.45	878.55	23.64
275	419.98	863.00	23.04
280	412.77	848.01	22.46
290	399.10	819.58	21.37
300	386.35	793.04	20.34
310	374.41	768.21	19.38
320	363.23	744.94	18.49
330	352.72	723.08	17.64
340	342.83	702.50	16.85
350	333.50	683.10	16.10
360	324.69	664.77	15.39
370	316.36	647.44	14.72
380	308.46	631.02	14.09
390	300.98	615.44	13.49
395	297.37	607.95	13.20
400	293.86	600.64	12.92
405	290.44	593.51	12.64
410	287.09	586.56	12.37
415	283.83	579.78	12.11

Table S4: Values of $\ln\left[\frac{q_i}{\Lambda_i^3\rho_0}\right]$ for monomer and dimer, and natural logarithms of ideal gas reaction equilibrium constants ($\ln[K_{\mathrm{IG}}]$) as a function of temperature for reaction R1 of the main text for system 6. Lasala et al. [1] reported two correlations to compute the isolated molecule partition functions of N_2O_4 and NO_2 (Eqs. 10 and 11 of the main text, respectively). We scaled down the values of isolated molecule partition functions of N_2O_4 computed by Lasala et al. [1] by 1% for system 6. The ideal gas reaction equilibrium constants for reaction R1 are computed using Eq. 9 of the main text.

T / [K]	$\ln\left[\frac{q_i}{\Lambda_i^3\rho_0}\right]$		$\ln[K_{\mathrm{IG}}]$
	Monomer	Dimer	
180	632.98	1280.24	14.28
190	600.53	1214.07	13.01
200	571.32	1154.51	11.87
210	544.90	1100.63	10.84
220	520.87	1051.65	9.90
230	498.94	1006.92	9.04
240	478.83	965.92	8.25
250	460.34	928.21	7.53
260	443.26	893.39	6.86
270	427.45	861.15	6.25
275	419.98	845.91	5.95
280	412.77	831.22	5.67
290	399.10	803.35	5.14
300	386.35	777.33	4.64
310	374.41	753.00	4.17
320	363.23	730.19	3.73
330	352.72	708.76	3.32
340	342.83	688.59	2.94
350	333.50	669.57	2.57
360	324.69	651.61	2.23
370	316.36	634.62	1.90
380	308.46	618.52	1.59
390	300.98	603.25	1.30
395	297.37	595.91	1.16
400	293.86	588.75	1.02
405	290.44	581.76	0.89
410	287.09	574.95	0.76
415	283.83	568.30	0.63

Table S5: Values of β as a function of dimensionless enthalpy of reaction ($\Delta_r^* H = \frac{\Delta_r H}{RT_{c,\text{monomer}}}$ where $\Delta_r^* H$ is the dimensionless enthalpy of reaction, $\Delta_r H$ is the enthalpy of reaction in real units, R is the gas constant, and $T_{c,\text{monomer}}$ is the critical temperature of pure monomer which is 282.4 K) and pre-exponential factor for ideal gas reaction equilibrium constants ($\ln[K_0]$, Eq. 13 of the main text).

		$\ln[K_0]$								
		-9.59	-8.34	-7.09	-5.84	-4.59	-3.34	-2.09	-0.84	0.41
	-36.24	0.279	0.284	0.283	0.283	0.281	0.282	0.286	0.280	0.279
	-33.04	0.275	0.279	0.280	0.283	0.283	0.284	0.285	0.284	0.282
	-29.85	0.274	0.279	0.279	0.280	0.281	0.282	0.282	0.281	0.282
	-26.65	0.267	0.275	0.277	0.281	0.284	0.281	0.285	0.283	0.282
	-23.46	0.256	0.268	0.276	0.277	0.279	0.283	0.281	0.283	0.281
	-20.26	0.243	0.258	0.270	0.276	0.278	0.281	0.283	0.284	0.285
$\Delta_r^* H$	-17.07	0.224	0.248	0.260	0.272	0.278	0.282	0.281	0.283	0.283
	-34.64	0.204	0.228	0.249	0.263	0.272	0.276	0.281	0.281	0.283
	-31.44	0.191	0.208	0.230	0.250	0.263	0.273	0.279	0.282	0.279
	-28.25	0.169	0.189	0.211	0.236	0.257	0.267	0.272	0.279	0.279
	-25.06	0.143	0.173	0.194	0.217	0.238	0.255	0.270	0.276	0.278
	-21.86	0.141	0.165	0.177	0.198	0.221	0.244	0.259	0.270	0.274
	-18.67	0.122	0.149	0.168	0.196	0.205	0.227	0.246	0.261	0.269

Table S6: Values of the normalized critical temperature (T_c^*) as a function of dimensionless enthalpy of reaction ($\Delta_r^* H = \frac{\Delta_r H}{R T_{c,\text{monomer}}}$ where $\Delta_r^* H$ is the dimensionless enthalpy of reaction, $\Delta_r H$ is the enthalpy of reaction in real units, R is the gas constant, and $T_{c,\text{monomer}}$ is the critical temperature of pure monomer which is 282.4 K) and pre-exponential factor for ideal gas reaction equilibrium constants ($\ln[K_0]$, Eq. 13 of the main text). The values of T_c^* are computed as $T_c^* = T_{c,\text{mixture}}/T_{c,\text{monomer}}$ where $T_{c,\text{mixture}}$ is the critical temperature of the reactive binary mixture.

		$\ln[K_0]$								
		-9.59	-8.34	-7.09	-5.84	-4.59	-3.34	-2.09	-0.84	0.41
$\Delta_r^* H$	-36.24	0.279	0.284	0.283	0.283	0.281	0.282	0.286	0.280	0.279
	-33.04	0.275	0.279	0.280	0.283	0.283	0.284	0.285	0.284	0.282
	-29.85	0.274	0.279	0.279	0.280	0.281	0.282	0.282	0.281	0.282
	-26.65	0.267	0.275	0.277	0.281	0.284	0.281	0.285	0.283	0.282
	-23.46	0.256	0.268	0.276	0.277	0.279	0.283	0.281	0.283	0.281
	-20.26	0.243	0.258	0.270	0.276	0.278	0.281	0.283	0.284	0.285
	-17.07	0.224	0.248	0.260	0.272	0.278	0.282	0.281	0.283	0.283
	-34.64	0.204	0.228	0.249	0.263	0.272	0.276	0.281	0.281	0.283
	-31.44	0.191	0.208	0.230	0.250	0.263	0.273	0.279	0.282	0.279
	-28.25	0.169	0.189	0.211	0.236	0.257	0.267	0.272	0.279	0.279
	-25.06	0.143	0.173	0.194	0.217	0.238	0.255	0.270	0.276	0.278
	-21.86	0.141	0.165	0.177	0.198	0.221	0.244	0.259	0.270	0.274
	-18.67	0.122	0.149	0.168	0.196	0.205	0.227	0.246	0.261	0.269

Table S7: Values of the normalized critical density (ρ_c^*) as a function of dimensionless enthalpy of reaction ($\Delta_r^* H = \frac{\Delta_r H}{RT_{c,monomer}}$ where $\Delta_r^* H$ is the dimensionless enthalpy of reaction, $\Delta_r H$ is the enthalpy of reaction in real units, R is the gas constant, and $T_{c,monomer}$ is the critical temperature of pure monomer which is 282.4 K) and pre-exponential factor for ideal gas reaction equilibrium constants ($\ln[K_0]$, Eq. 13 of the main text). The values of ρ_c^* are computed as $\rho_c^* = \rho_{c,mixture}/\rho_{c,monomer}$ where $\rho_{c,mixture}$ and $\rho_{c,monomer}$ are the critical densities of the reactive binary mixture and pure monomer, respectively.

		$\ln[K_0]$								
		-9.59	-8.34	-7.09	-5.84	-4.59	-3.34	-2.09	-0.84	0.41
$\Delta_r^* H$	-36.24	1.1778	1.1756	1.1760	1.1711	1.1778	1.1808	1.1785	1.1756	1.1759
	-33.04	1.1760	1.1944	1.1794	1.1768	1.1766	1.1769	1.2159	1.1904	1.1797
	-29.85	1.1759	1.1761	1.2383	1.2119	1.1893	1.1782	1.1779	1.2612	1.2335
	-26.65	1.2057	1.1831	1.1780	1.2815	1.2492	1.2287	1.2008	1.1856	1.1745
	-23.46	1.1747	1.1763	1.1767	1.1810	1.1780	1.1769	1.1757	1.1755	1.1742
	-20.26	1.1724	1.1744	1.1743	1.1774	1.1786	1.1754	1.1761	1.1858	1.1808
	-17.07	1.1796	1.1761	1.1734	1.1777	1.1726	1.1753	1.1758	1.1850	1.1796
	-34.64	1.1750	1.1741	1.2029	1.1920	1.1851	1.1797	1.1777	1.1758	1.1753
	-31.44	1.1738	1.1741	1.1991	1.1828	1.1743	1.1729	1.2280	1.2119	1.1989
	-28.25	1.1901	1.1829	1.1792	1.1770	1.1752	1.1746	1.2255	1.1975	1.1811
	-25.06	1.1750	1.2473	1.2372	1.2243	1.2088	1.1935	1.1862	1.1822	1.1777
	-21.86	1.1773	1.2458	1.2208	1.1954	1.1804	1.2673	1.2394	1.2460	1.2331
	-18.67	1.2187	1.2025	1.1925	1.1849	1.1817	1.2673	1.2353	1.2152	1.1902

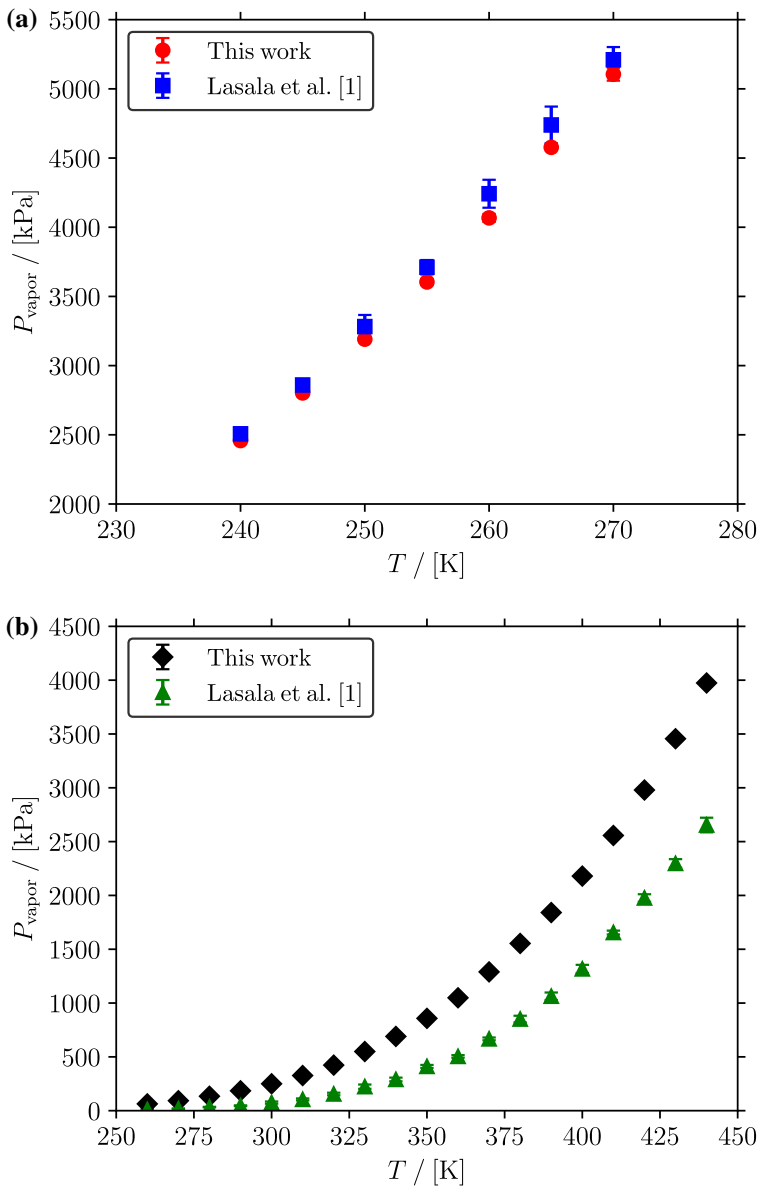

Figure S1: Comparison between the saturated vapor pressures of (a) NO_2 and (b) N_2O_4 computed by representing each molecule as single LJ particles (this work) and using an all-atom force field [1] as a function of temperature.

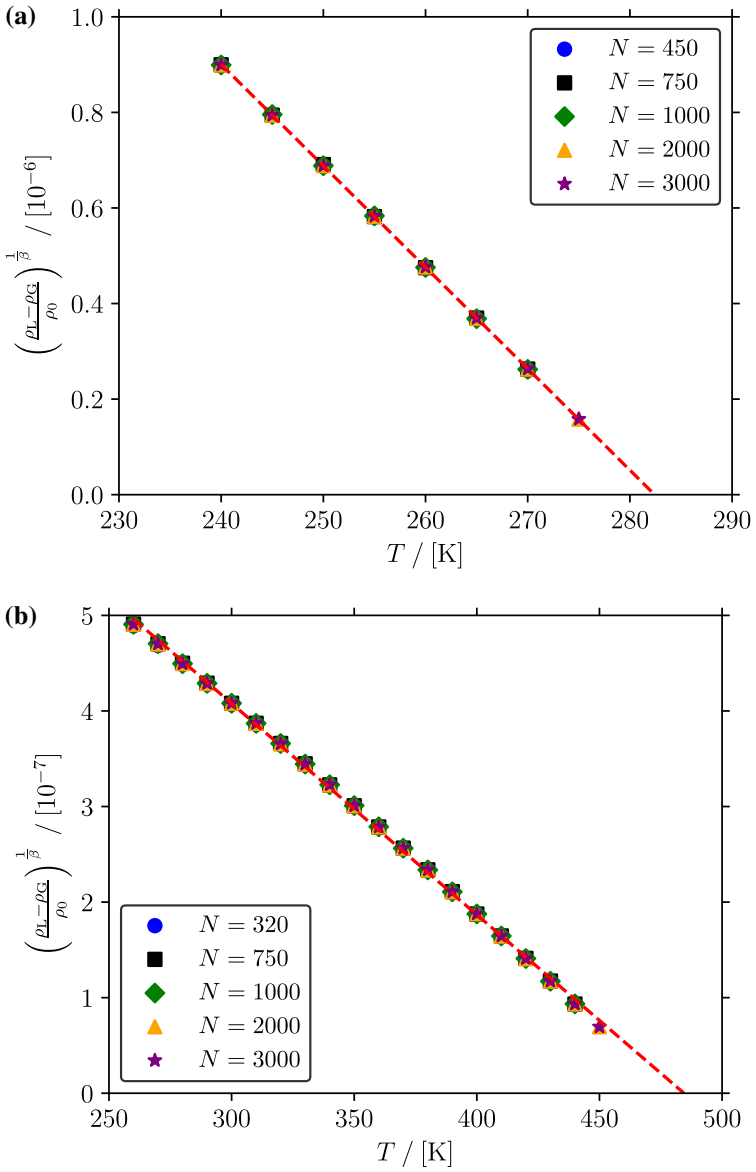

Figure S2: Values of the terms $\left(\frac{\rho_l-\rho_g}{\rho_0}\right)^{\frac{1}{\beta}}$ ($\beta = 0.32$) computed as a function of temperature for (a) pure NO_2 and (b) pure N_2O_4 using the force field parameters listed in Table 1 of the main text. To compute the values of $\left(\frac{\rho_l-\rho_g}{\rho_0}\right)^{\frac{1}{\beta}}$, we used number densities. The dashed lines represent linear regression fits to the values of $\left(\frac{\rho_l-\rho_g}{\rho_0}\right)^{\frac{1}{\beta}}$ as a function of temperature.

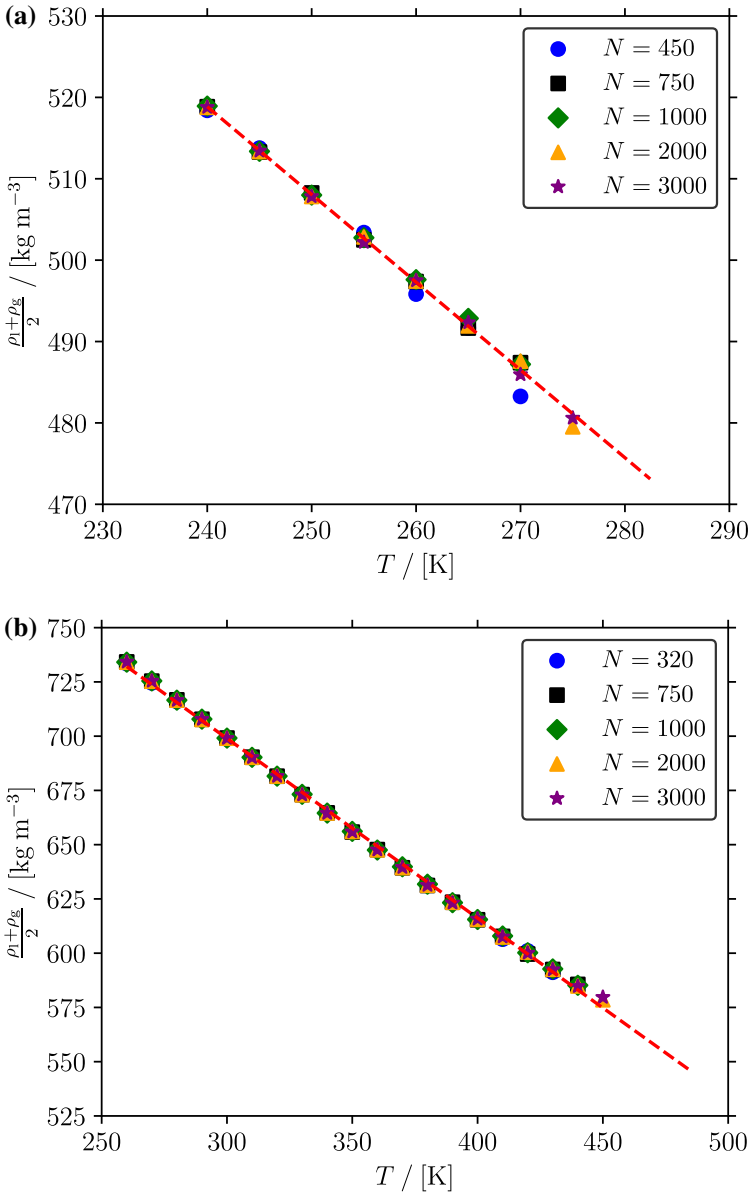

Figure S3: Average liquid and gas phase densities computed as a function of temperature for (a) pure NO_2 and (b) pure N_2O_4 using the force field parameters listed in Table 1 of the main text. The dashed lines represent linear regression fits to the average values of liquid and gas phase densities as a function of temperature.

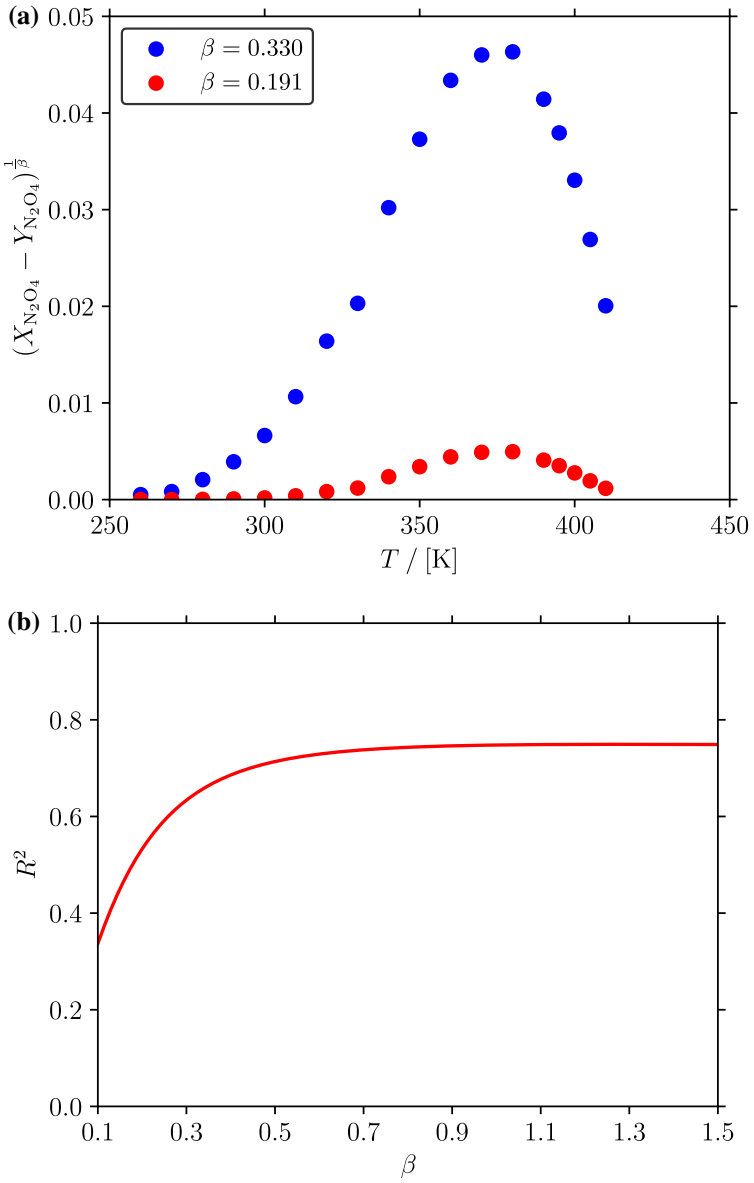

Figure S4: (a) Values of the term $(X_i - Y_i)^{\frac{1}{\beta}}$ (see Eq. 3 of the main text) as a function of temperature for two different values of β, and (b) the coefficients of determination R^2 of the linear regression of the values of $(X_i - Y_i)^{\frac{1}{\beta}}$ as a function of β for the NO_2/N_2O_4 system.

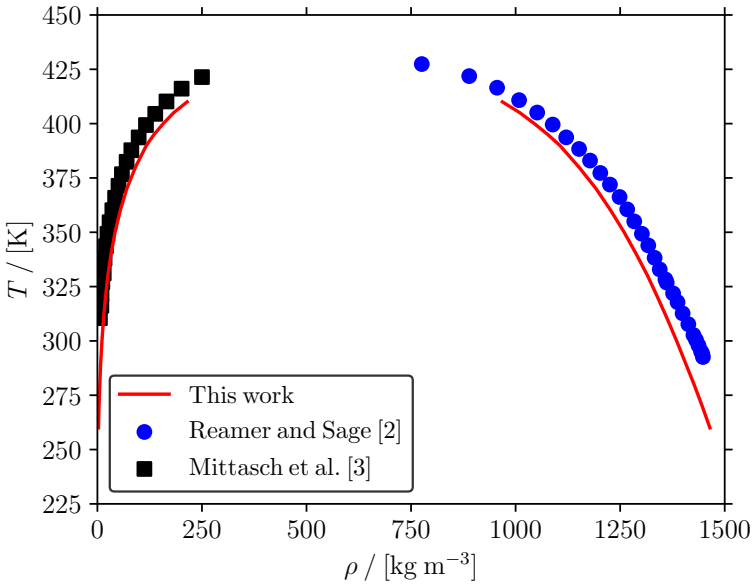

Figure S5: Comparison between the computed densities of the reactive mixture of NO_2 and N_2O_4 (system 1), experimental liquid densities from Reamer and Sage [2], and experimental gas densities from Mittasch et al. [3] as a function of temperature.

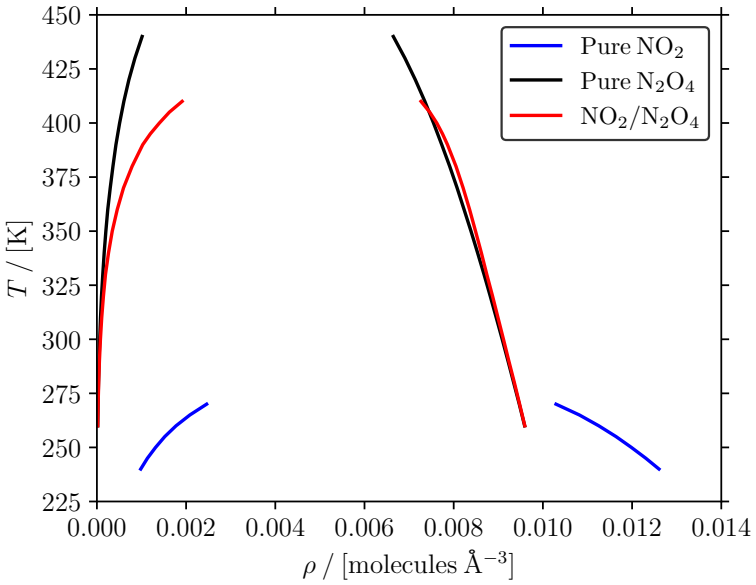

Figure S6: Computed densities of pure NO_2, pure N_2O_4, and the reactive mixture of NO_2 and N_2O_4 (system 1) as a function of temperature. For pure NO_2 and pure N_2O_4, GEMC simulations were used, while for the reactive mixture of NO_2 and N_2O_4, RE/GEMC simulations were used (including reaction R1 of the main text).

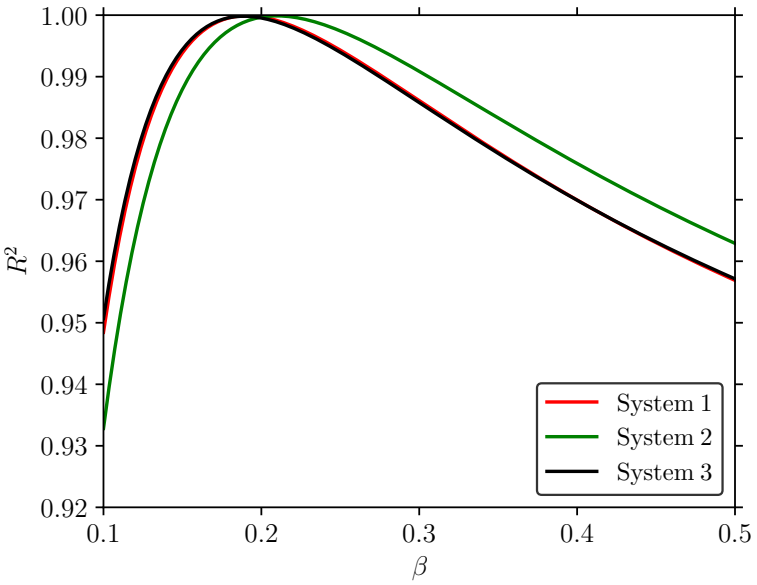

Figure S7: Coefficients of determination (R^2) as a function of β for linear regression fits of the values of $\left(\frac{\rho_l - \rho_g}{\rho_0}\right)^{\frac{1}{\beta}}$ computed as a function of temperature with different force field parameters for the reactive NO_2/N_2O_4 (A/A_2) systems. See Table 2 of the main text for the force field parameters and Table S1 of the Supporting Information for the values of isolated molecule partition functions of monomers and dimers for different systems.

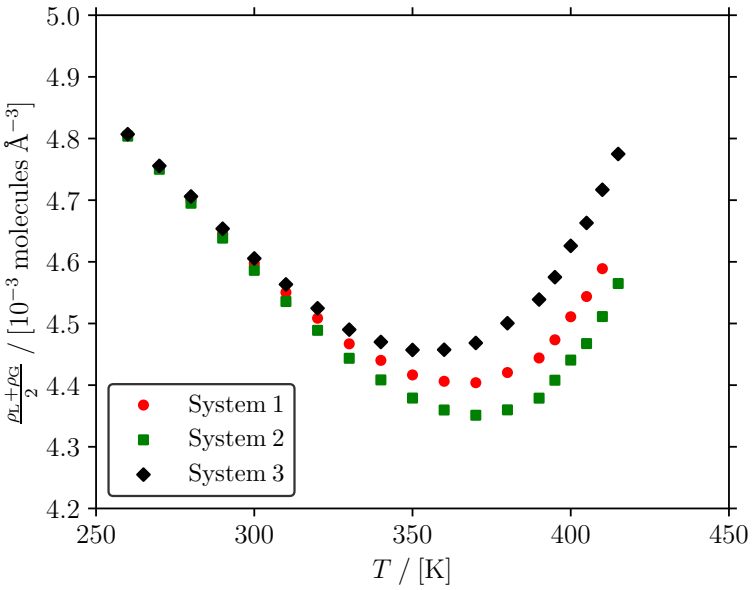

Figure S8: Average number densities of the liquid and gas phases computed using different force fields as shown in Table 2 of the main text with reaction R1 of the main text. See Table 2 of the main text for the force field parameters used in systems 1, 2, and 3.

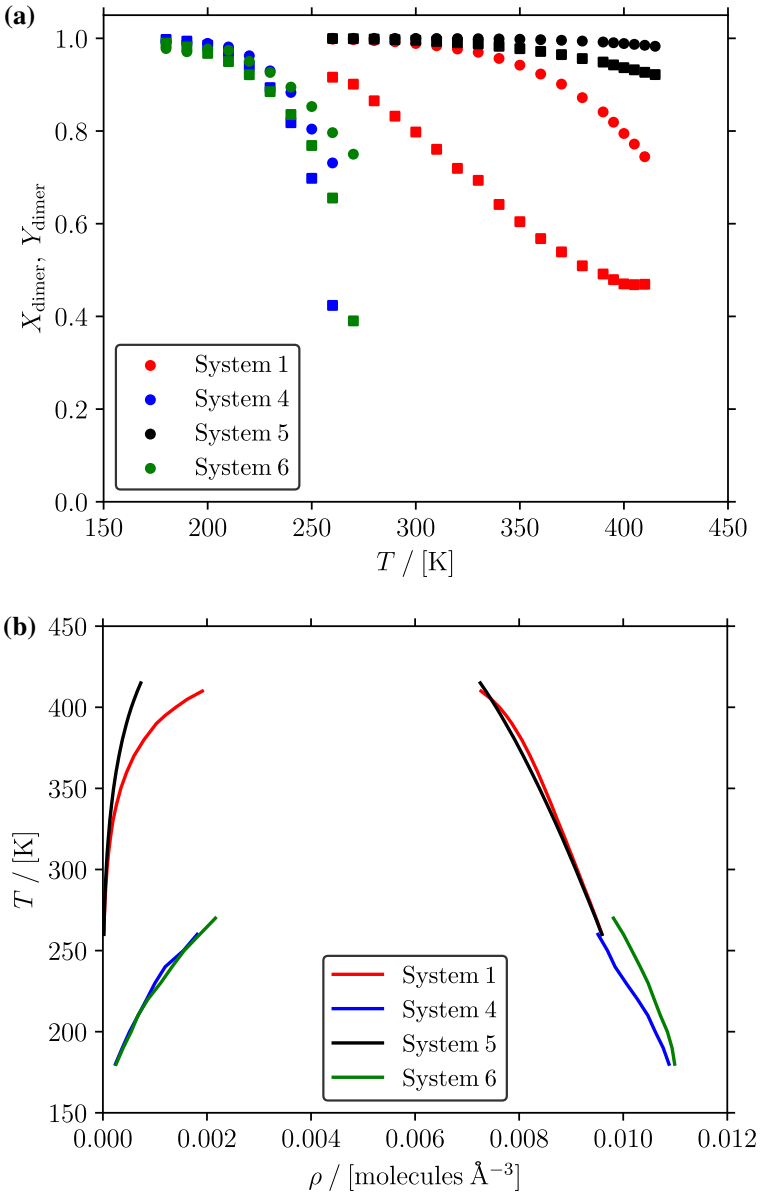

Figure S9: (a) Mole fractions of dimers in the gas (squares, Y_{dimer}) and liquid (circles, X_{dimer}) phases and (b) coexistence densities computed for different values of isolated molecule partition functions for dimers as a function of temperature. In our RE/GEMC simulations, the chemical reaction R1 is included. See Table 2 of the main text for the force field parameters and Tables S1-S4 of the Supporting Information for the values of isolated molecule partition functions of monomers and dimers for different systems.

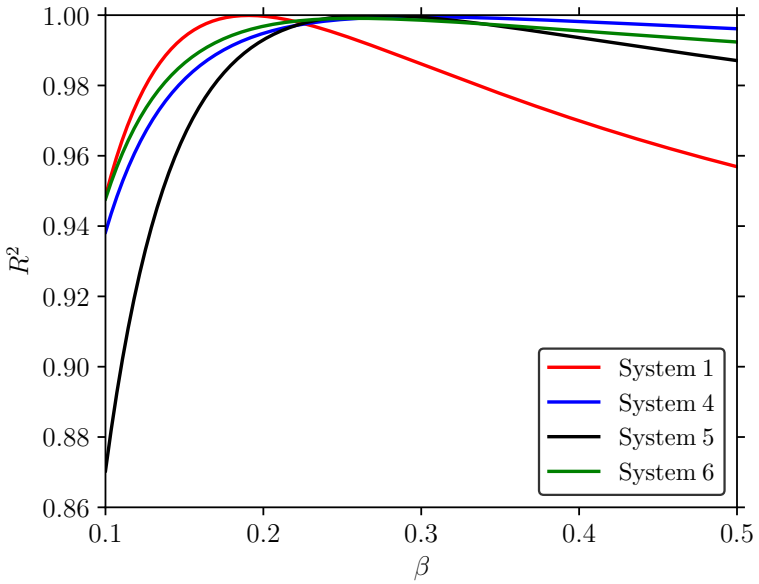

Figure S10: Coefficients of determination (R^2) as a function of the critical exponent β for linear regression fits of the values of $\left(\frac{\rho_l - \rho_g}{\rho_0}\right)^{\frac{1}{\beta}}$ as a function of temperature with different values of isolated molecule partition function for dimers in reactive NO_2/N_2O_4 (A/A_2) systems. See Table 2 of the main text for the force field parameters and Tables S1-S4 of the Supporting Information for the values of isolated molecule partition functions of monomers and dimers for different systems.

References

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