Supporting Information: Inaccurate extrapolation toward high pressures using united-atom, Mie λ-6 force fields parameterized with vapor-liquid equilibria properties.

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SI.I Simulation Set-Up

This section is provided to improve the reproducibility of the results presented in this study.

SI.I.1 State Points

Tables SI.I, SI.II, SI.III, SI.IV, SI.V, SI.VI, SI.VII, and SI.VIII contain the state points that were simulated for ethane, propane, *n*-butane, *n*-octane, isobutane, isohexane, isooctane, and neopentane, respectively. The first 10 state points of each table correspond to five isochores while the last 9 points are for the supercritical isotherm. The number of state points, the specified reduced temperatures, and the spacing between neighboring densities were recommended by the developers of the ITIC approach (J. Richard Elliott and Seyed Mostafa Razavi). It has been demonstrated that these points are sufficient for accurate calculation of $\rho_{\mathrm{l}}^{\mathrm{sat}}$, $\rho_{\mathrm{v}}^{\mathrm{sat}}$, and $P_{\mathrm{v}}^{\mathrm{sat}}$.[1] Note that the temperatures (T_{sim}), box lengths (L_{box}), and number of molecules (N_{M}) are the exact values used in simulation while the density (ρ) is approximate (rounded) since it is calculated from L_{box}, N_{M}, and the molecular weight.

SI.I.2 GROMACS Input Files

We have provided example input files for simulating isooctane at 653.0 K with the TraPPE-UA force field in GROMACS (see attached .gro, .top, and .mdp files).

References

(1) Razavi, S. M. Optimization of a Transferable Shifted Force Field for Interfaces and Inhomogenous Fluids using Thermodynamic Integration. M.Sc. thesis, The University of Akron, 2016.

Table SI.I: State points simulated for ethane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
137.0	3.21680	400	600.01
198.5	3.21680	400	600.01
174.0	3.29730	400	557.13
234.6	3.29730	400	557.13
207.0	3.38640	400	514.30
262.9	3.38640	400	514.30
236.0	3.48610	400	471.42
285.1	3.48610	400	471.42
260.0	3.59860	400	428.58
301.9	3.59860	400	428.58
360.0	6.15360	400	85.712
360.0	4.88410	400	171.43
360.0	4.26660	400	257.15
360.0	3.87650	400	342.85
360.0	3.59860	400	428.58
360.0	3.48610	400	471.42
360.0	3.38640	400	514.30
360.0	3.29730	400	557.13
360.0	3.21680	400	600.01

Table SI.II: State points simulated for propane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
166	3.55643	400	651.13
242	3.55643	400	651.13
210	3.64538	400	604.62
285	3.64538	400	604.62
250	3.74395	400	558.11
320	3.74395	400	558.11
285	3.85413	400	511.60
347	3.85413	400	511.60
314	3.97854	400	465.09
368	3.97854	400	465.09
444	6.80321	400	93.019
444	5.39971	400	186.04
444	4.71708	400	279.06
444	4.28575	400	372.08
444	3.97854	400	465.09
444	3.85413	400	511.60
444	3.74395	400	558.11
444	3.64538	400	604.62
444	3.55643	400	651.13

Table SI.III: State points simulated for *n*-butane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
191	3.83864	400	682.53
278	3.83864	400	682.53
241	3.93465	400	633.78
327	3.93465	400	633.78
287	4.04104	400	585.03
367	4.04104	400	585.03
328	4.15997	400	536.28
399	4.15997	400	536.28
361	4.29425	400	487.52
423	4.29425	400	487.52
510	7.34306	400	97.50
510	5.82819	400	195.01
510	5.09140	400	292.51
510	4.62584	400	390.02
510	4.29425	400	487.52
510	4.15997	400	536.28
510	4.04104	400	585.03
510	3.93465	400	633.78
510	3.83864	400	682.53

Table SI.IV: State points simulated for *n*-octane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
285.92	5.98449	800	708.01
387.29	5.98449	800	708.01
347.68	6.13416	800	657.44
440.25	6.13416	800	657.44
404.46	6.30003	800	606.87
483.20	6.30003	800	606.87
451.48	6.48542	800	556.30
515.25	6.48542	800	556.30
490.78	6.69481	800	505.72
539.92	6.69481	800	505.72
600.00	11.44803	800	101.14
600.00	9.08616	800	202.29
600.00	7.93753	800	303.43
600.00	7.21175	800	404.58
600.00	6.69481	800	505.72
600.00	6.48542	800	556.30
600.00	6.30003	800	606.87
600.00	6.13416	800	657.44
600.00	5.98449	800	708.01

Table SI.V: State points simulated for isobutane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
184	4.85814	800	673.40
267	4.85814	800	673.40
232	4.97964	800	625.30
315	4.97964	800	625.30
276	5.11429	800	577.20
353	5.11429	800	577.20
315	5.26480	800	529.10
383	5.26480	800	529.10
347	5.43475	800	481.00
406	5.43475	800	481.00
489	9.29328	800	96.20
489	7.37608	800	192.40
489	6.44360	800	288.60
489	5.85440	800	384.80
489	5.43475	800	481.00
489	5.26480	800	529.10
489	5.11429	800	577.20
489	4.97964	800	625.30
489	4.85814	800	673.40

Table SI.VI: State points simulated for isohexane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
224	5.43297	800	713.86
326	5.43297	800	713.86
282	5.56885	800	662.87
383	5.56885	800	662.87
337	5.71943	800	611.88
431	5.71943	800	611.88
384	5.88774	800	560.89
467	5.88774	800	560.89
423	6.07780	800	509.90
495	6.07780	800	509.90
597	10.39289	800	101.98
597	8.24884	800	203.96
597	7.20603	800	305.94
597	6.54711	800	407.92
597	6.07780	800	509.90
597	5.88774	800	560.89
597	5.71943	800	611.88
597	5.56885	800	662.87
597	5.43297	800	713.86

Table SI.VII: State points simulated for isooctane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
245	5.92132	800	730.91
356	5.92132	800	730.91
309	6.06941	800	678.71
419	6.06941	800	678.71
369	6.23353	800	626.50
472	6.23353	800	626.50
421	6.41697	800	574.29
512	6.41697	800	574.29
464	6.62411	800	522.08
543	6.62411	800	522.08
653	11.32707	800	104.42
653	8.99031	800	208.83
653	7.85376	800	313.25
653	7.13561	800	417.66
653	6.62411	800	522.08
653	6.41697	800	574.29
653	6.23353	800	626.50
653	6.06941	800	678.71
653	5.92132	800	730.91

Table SI.VIII: State points simulated for neopentane.

T_{sim} (K)	L_{box} (nm)	N_{M} (molecules)	$\rho\left(\frac{\mathrm{kg}}{\mathrm{m}^3}\right)$
257	5.34568	800	627.43
344	5.34568	800	627.43
300	5.47938	800	582.61
380	5.47938	800	582.61
337	5.62754	800	537.79
409	5.62754	800	537.79
368	5.79315	800	492.98
431	5.79315	800	492.98
393	5.98015	800	448.16
448	5.98015	800	448.16
520	10.22592	800	89.63
520	8.11632	800	179.26
520	7.09026	800	268.90
520	6.44193	800	358.53
520	5.98015	800	448.16
520	5.79315	800	492.98
520	5.62754	800	537.79
520	5.47938	800	582.61
520	5.34568	800	627.43