

Supplementary Information

Liquid dibromomethane under pressure: A computational study

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Contents

1. Force field parameters.	2
2. Thermodynamic states studied by simulation.	4
3. Isobaric thermal expansion coefficient.	5
4. Isothermal compressibility	6
5. Constant volume heat capacity	6
6. Constant pressure heat capacity	7
7. Speed of sound	8

1. Force field parameters

The atomic charges are ESP/6-31G* charges, fitted to reproduce the electrostatic potential around the molecule as described in the article, are given in Table S1.a.

The Lennard-Jones parameters have been derived from the parameters of the GAFF2 force field¹ of atom types c3, br and hc. Here, the σ parameters are used rather than the R^* ones (for a pair of atoms of the same kind i , $\sigma_{ii} = 2R_i^*/(2^{1/6})$). For c3 atom, a value of 0.1079 kcal/mol for ϵ_{ii} of c3 atom has been used by mistake instead of the exact value of 0.1078 kcal/mol. To try to improve the force field, scaling factors λ_ϵ and λ_σ are introduced to globally scale all the ϵ_{ii} and σ_{ii} parameters, respectively. This choice was made in order to limit the number of tuned parameters. For a given set of Lennard-Jones parameters ($\lambda_\epsilon \epsilon_{ii}$, $\lambda_\sigma \sigma_{ii}$), small MD simulations with experimental densities at 298 and 313 K (2.482 g/cm³ and 2.444 g/cm³, respectively at 1 bar² have been performed to calculate the vaporization enthalpy and the set of two parameters (λ_ϵ , λ_σ) is optimized by a trial-error procedure in order to reproduce as well as possible the experimental values (37.3 kJ/mol and 36.5 kJ/mol, respectively²). Eventually, the parameters of Table S1.a are obtained; they differ from the starting values by a factor 1.1025 for the ϵ_{ii} and by a factor 0.9919012 for the σ_{ii} . This corresponds to a scaling of the attractive terms ($4\epsilon\sigma^6$) by a factor 1.05, keeping the repulsive terms ($4\epsilon\sigma^{12}$) unchanged. The parameters for pairs of dissimilar atoms (i, j) are obtained from the Lorentz-Berthelot combination rules ($\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, $\epsilon_{ij} = \sqrt{\epsilon_{ii} \cdot \epsilon_{jj}}$) which are used in the GAFF2 force field. Table S1.b compares the vaporization enthalpy obtained by MD simulations (original GAFF2 and tuned set of LJ parameters) with the experimental values.

atom type i	$\epsilon_{ii}/\text{kcal.mol}^{-1}$	$\sigma_{ii}/\text{\AA}$	q_i/e (e)
C	0.118960	3.370192	-0.8730
Br	0.433503	3.583337	0.0396
H	0.022932	2.579119	0.3969

Table S1.a: Lennard-Jones parameters and atomic charges used in this study.
 $e = 1.6 \cdot 10^{-19}$ C. 1 kcal = 4.184 kJ.

T / K	ΔH_{vap} / kJ/mol		
	original GAFF2 LJ parameters	final set (Table S1.a)	experiment ²
298.15	34.7	37.4	37.3
313.15	34.1	36.7	36.5

Table S1.b: Vaporization enthalpy at experimental density from MD simulations compared to experimental results.

¹ : <https://github.com/choderalab/ambermini/blob/master/share/amber/dat/leap/parm/gaff2.dat>

² : Lide D.R. Handbook of Chemistry and Physics Web Edition, 92nd Ed. Publisher CRC. (2011-2012). Section 6: Fluid Properties. <http://www.hbcnetbase.com>.

2. Thermodynamic states studied by simulation

P_{target}/bar	P_{MD}/bar	T_{MD}/K	$E/\text{kJ.mol}^{-1}$	$L/\text{\AA}$
$T_{target}=268.15\text{ K}$				
1	0.1	267.93	-29.720	48.297901
250	251.6	267.93	-30.143	48.102987
500	500.7	268.02	-30.524	47.927721
750	755.9	268.19	-30.859	47.769139
1000	1008.1	268.42	-31.152	47.624351
1500	1502.6	267.98	-31.701	47.367942
2000	2005.6	268.54	-32.123	47.146391
2500	2485.8	267.98	-32.517	46.951328
3000	2987.1	268.17	-32.818	46.774033
$T_{target}=283.15\text{ K}$				
1	-3.0	282.78	-28.473	48.548252
250	251.5	283.25	-28.913	48.337721
500	497.7	283.24	-29.327	48.147490
750	746.5	283.13	-29.696	47.975408
1000	998.5	283.08	-30.026	47.818870
1500	1501.7	283.39	-30.583	47.543790
2000	1996.4	283.01	-31.056	47.307920
2500	2495.1	283.24	-31.446	47.100833
3000	2982.0	283.23	-31.789	46.915104
$T_{target}=298.15\text{ K}$				
1	-3.4	298.28	-27.201	48.814732
250	249.3	298.08	-27.729	48.572337
500	495.8	298.04	-28.168	48.365720
750	746.9	298.18	-28.557	48.179773
1000	996.1	298.09	-28.913	48.011405
1500	1494.3	297.87	-29.524	47.717273
2000	1993.5	297.86	-30.018	47.466674
2500	2492.1	297.98	-30.429	47.247699
3000	2986.6	297.97	-30.793	47.052040
$T_{target}=313.15\text{ K}$				
1	-1.2	313.10	-25.987	49.077783
250	249.0	313.18	-26.548	48.811442
500	496.5	313.11	-27.021	48.586366
750	749.5	313.21	-27.440	48.384844
1000	1001.2	313.14	-27.817	48.204522
1500	1501.5	313.37	-28.441	47.893498
2000	1992.8	313.33	-28.960	47.630948
2500	2488.8	313.27	-29.395	47.401779
3000	3007.6	313.48	-29.780	47.186333
$T_{target}=328.15\text{ K}$				
1	-1.8	328.16	-24.765	49.355108
250	252.4	328.25	-25.372	49.059708
500	497.9	328.01	-25.908	48.807445
750	750.7	328.04	-26.352	48.590963
1000	998.5	328.12	-26.741	48.399203
1500	1493.0	327.93	-27.415	48.070018
2000	2006.1	328.09	-27.968	47.782903
2500	2496.0	328.11	-28.428	47.542166
3000	2998.2	328.15	-28.818	47.326877

Table S2: Thermodynamic states studied by MD simulation. P_{target} and T_{target} are the desired pressure and temperature. P_{MD} and T_{MD} are the statistical average of the pressure and temperature obtained from the NVE simulations. E is the total energy of each simulation (including the long range correction due to the center of mass-based cutoff of Lennard-Jones interaction at 20 Å). L is the cubic box edge containing N=1000 molecules.

3. Isobaric thermal expansion coefficient

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	1.037	1.059	1.083	1.107	1.132
250	0.956	0.969	0.982	0.996	1.011
500	0.911	0.910	0.909	0.908	0.906
750	0.859	0.856	0.852	0.849	0.845
1000	0.811	0.809	0.806	0.803	0.800
1500	0.735	0.735	0.735	0.735	0.734
2000	0.693	0.683	0.673	0.662	0.651
2500	0.644	0.636	0.628	0.619	0.610
3000	0.593	0.589	0.585	0.581	0.577

Table S3: $\alpha_P / 10^{-3} \text{ K}^{-1}$ from thermodynamic definition and raw MD simulation data.

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	1.049	1.063	1.078	1.094	1.110
250	0.970	0.978	0.986	0.994	1.002
500	0.906	0.910	0.914	0.917	0.920
750	0.853	0.854	0.855	0.855	0.855
1000	0.809	0.808	0.807	0.805	0.802
1500	0.738	0.734	0.730	0.725	0.721
2000	0.683	0.677	0.672	0.666	0.660
2500	0.638	0.632	0.626	0.619	0.612
3000	0.601	0.595	0.588	0.581	0.574

Table S4: $\alpha_P / 10^{-3} \text{ K}^{-1}$ from thermodynamic definition and using a linear fit of α_P^{-2} vs. pressure P.

4. Isothermal compressibility

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	502.9	543.9	606.6	670.6	735.6
250	458.6	495.2	546.3	597.0	652.2
500	418.7	451.3	492.9	532.6	579.3
750	383.1	412.0	445.7	476.5	515.9
1000	351.5	377.1	404.3	428.1	461.2
1500	299.5	319.5	337.4	352.7	375.3
2000	261.4	276.9	290.3	303.5	317.9
2500	236.4	248.3	261.5	278.8	287.3
3000	223.7	232.8	250.0	277.0	281.8

Table S5: $\kappa_T / 10^{-12} \text{ J}^{-1} \cdot \text{m}^3$ from thermodynamic definition.

5. Constant volume heat capacity

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	46.62	45.56	44.51	43.03	42.16
250	49.21	46.66	45.44	43.80	42.74
500	48.53	47.29	44.97	44.48	43.63
750	49.87	47.83	47.31	45.49	44.47
1000	49.24	48.32	46.93	45.65	44.21
1500	51.12	49.43	47.81	46.74	45.79
2000	51.32	50.51	48.65	47.36	46.75
2500	52.51	52.17	49.34	48.67	47.48
3000	53.16	51.94	50.78	49.38	48.82

Table S6: $c_V / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ from fluctation formula in NVE ensemble.

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	47.95	47.28	45.91	43.44	38.83
250	48.25	47.25	45.88	43.88	40.78
500	48.80	47.45	46.12	44.41	41.54
750	49.06	47.83	46.51	44.97	42.86
1000	48.92	48.29	46.97	45.55	44.00
1500	50.95	49.32	47.95	46.61	44.91
2000	51.04	50.27	48.90	47.58	46.50
2500	53.05	51.13	49.75	48.44	47.08
3000	52.76	51.84	50.49	49.20	47.94

Table S7: $c_V/ \text{J.mol}^{-1}.\text{K}^{-1}$ from thermodynamic definition. The table includes the thermodynamic states (involving extrapolated values of volume outside the range explored by MD simulations) which have been rejected in the plot of Figure 4.

6. Constant pressure heat capacity

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	84.72	83.68	82.65	81.61	80.57
250	83.12	82.10	81.07	80.04	79.02
500	83.37	81.69	80.02	78.34	76.66
750	82.63	81.03	79.44	77.84	76.25
1000	81.05	79.99	78.92	77.85	76.78
1500	81.51	80.07	78.64	77.20	75.76
2000	80.61	79.33	78.05	76.76	75.48
2500	81.90	80.03	78.15	76.27	74.40
3000	79.93	78.84	77.75	76.65	75.56

Table S8: $c_P/ \text{J.mol}^{-1}.\text{K}^{-1}$ from thermodynamic definition.

7. Speed of sound

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	1209.6	1189.1	1135.1	1091.4	1057.8
250	1229.0	1201.8	1151.0	1111.0	1072.1
500	1251.1	1223.3	1180.9	1149.7	1111.9
750	1287.1	1256.3	1218.6	1192.7	1153.7
1000	1332.9	1297.6	1262.6	1239.7	1198.5
1500	1411.3	1377.5	1354.3	1341.6	1308.3
2000	1489.7	1458.1	1437.8	1419.3	1397.4
2500	1529.4	1507.3	1480.9	1440.0	1436.6
3000	1542.7	1525.1	1470.5	1384.6	1388.0

Table S9: $u/ \text{m.s}^{-1}$ from Eq.(9) of the article.

P/bar	268.15 K	283.15 K	298.15 K	313.15 K	328.15 K
1	1123.4	1094.1	1039.4	993.6	956.2
250	1148.3	1114.9	1063.5	1021.5	981.3
500	1176.4	1142.4	1097.1	1061.5	1021.3
750	1213.5	1177.4	1136.4	1105.5	1064.8
1000	1256.8	1217.9	1180.0	1152.6	1111.2
1500	1336.4	1298.5	1269.9	1250.2	1214.3
2000	1412.6	1376.8	1350.8	1326.8	1300.3
2500	1458.0	1429.7	1398.1	1354.8	1342.9
3000	1474.4	1451.6	1397.5	1317.3	1314.4

Table S10: $u/ \text{m.s}^{-1}$ from Eq.(9) of the article and using the quantum correction for vibrational degrees of freedom (Eq.(6)) for the heat capacity.