Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for

Classical Harmonic Model for the Behavior of Pure Fluids at the Critical Point

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Chemical potential derivatives at the critical point

Here we present one of our assumptions, that the particle-particle fluctuations dominate the particle-energy fluctuations, in terms of thermodynamic derivatives. Starting from the differential of $\beta\mu_1(\beta,p)$ one can write,

$$T\left(\frac{\partial\beta\mu_1}{\partial T}\right)_{\rho_1} = -\beta H_1 + Z\frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_{\rho_1} \qquad \text{(S1)}$$

The total chemical potential can be written as a sum of several terms, most of which are molecular in nature,

$$\beta\mu_1 = \beta\mu_{ij} + \beta\mu_k + \beta\mu_R + \beta\mu_V + \ln\rho_1 \qquad \text{(S2)}$$

corresponding to a simple factorization of the partition function. The central three terms on the right hand side of Equation (S2) only depend on temperature. Using this for the left hand side of Equation (S1) provides several terms that cancel with the corresponding terms in the molar enthalpy appearing on the right hand side. Hence, after some rearrangement we find,

$$Z\frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_{\rho_1} = T\left(\frac{\partial\beta\mu_{ij}}{\partial T}\right)_{\rho_1} + \beta E_{1,ij} + Z \qquad \text{(S3)}$$

Comparison with Equation (3) after using Equation (7) provides,

$$\begin{aligned} T\left(\frac{\partial\beta\mu_{ij}}{\partial T}\right)_{\rho_1} &= -\frac{\beta}{b_{11}}\frac{\left\langle\delta N_1\delta E_{ij}\right\rangle}{\left\langle N_1\right\rangle} \\ \frac{p}{Z}\left(\frac{\partial\beta\mu_{ij}}{\partial p}\right)_{\rho_1} &= \frac{\beta}{b_{1\varepsilon}}\frac{\left\langle\delta N_1\delta E_{ij}\right\rangle}{\left\langle N_1\right\rangle} \end{aligned} \qquad \text{(S4)}$$

which lead to the results in Equation (14).

Numerical values of CHM limits for 121 fluids

Table S1. Critical Properties and Behavior of NIST REFPROP Fluids Using the Default EOS

ρ_c (mol/L)	p_c (bar)	T_c (K)	Z_c	ℓ_1	ℓ_2	ℓ_3	Molecule
4.240	40.051	419.290	0.271	1.64	1.33	1.09	1BUTENE
4.700	47.000	508.100	0.237	1.55	2.90	2.11	ACETONE
13.212	113.330	405.400	0.255	1.55	2.52	0.98	AMMONIA
13.407	48.630	150.687	0.290	1.42	3.61	1.84	ARGON
3.901	49.073	562.020	0.269	1.64	2.59	2.04	BENZENE
3.923	37.960	425.125	0.274	1.66	1.74	2.13	BUTANE
1.515	19.904	638.800	0.247	2.01	3.18	1.58	C11

1.330	18.170	658.100	0.250	2.00	3.56	0.51	C12
2.720	34.700	572.200	0.268	1.70	0.17	0.35	C1CC6
4.244	42.255	435.750	0.275	1.64	1.46	1.06	C2BUTENE
2.060	28.600	630.800	0.265	1.75	0.98	0.44	C3CC6
2.520	23.234	386.326	0.287	1.89	3.23	0.33	C4F10
2.116	20.450	420.555	0.276	1.99	3.61	0.94	C5F12
4.431	39.530	396.440	0.271	1.62	1.51	1.46	CF3I
10.850	34.940	132.860	0.292	1.51	1.37	0.81	CO
10.625	73.773	304.128	0.275	1.66	14.89	-8.19	CO2
7.410	63.700	378.770	0.273	1.55	1.33	0.99	COS
3.224	40.805	553.600	0.275	1.67	1.25	0.76	CYCLOHEX
3.820	45.712	511.720	0.281	1.66	0.77	0.17	CYCLOPEN
6.143	55.797	398.300	0.274	1.55	1.28	0.96	CYCLOPRO
17.230	16.796	38.340	0.306	1.36	-0.60	0.12	D2
17.776	216.710	643.847	0.228	1.59	3.89	2.27	D2O
1.031	13.320	586.500	0.265	1.97	3.64	0.98	D4
0.822	11.600	619.150	0.274	2.30	2.38	0.03	D5
0.627	9.610	645.780	0.285	2.49	2.78	0.93	D6
1.640	21.030	617.700	0.250	1.86	2.95	1.30	DECANE
3.562	36.440	466.700	0.264	1.73	2.28	0.81	DEE
4.000	49.088	557.000	0.265	1.91	5.73	4.35	DMC
5.940	53.368	400.378	0.270	1.61	2.30	1.91	DME
2.741	36.224	617.120	0.258	1.73	3.90	4.06	EBENZENE
6.857	48.722	305.322	0.280	1.53	3.38	1.98	ETHANE
5.930	62.680	514.710	0.247	2.08	7.46	-0.75	ETHANOL
7.637	50.418	282.350	0.281	1.51	3.81	2.43	ETHYLENE
15.603	51.724	144.414	0.276	1.51	1.69	1.78	FLUORINE
10.190	90.000	373.100	0.285	1.56	0.46	0.49	H2S
11.272	82.630	324.550	0.272	1.43	1.11	-0.06	HCL
17.384	2.276	5.195	0.303	0.91	1.41	1.19	HELIUM
2.315	27.360	540.130	0.263	1.77	1.48	0.57	HEPTANE
2.706	30.340	507.820	0.266	1.75	1.45	0.40	HEXANE
15.508	12.964	33.145	0.303	1.17	-0.47	0.53	HYDROGEN
2.715	30.400	497.700	0.271	1.71	1.47	0.86	IHEXANE
2.120	25.720	544.000	0.268	1.80	1.10	0.17	IOCTANE
3.271	33.780	460.350	0.270	1.67	1.80	1.22	IPENTANE
3.880	36.290	407.810	0.276	1.63	2.71	2.60	ISOBUTAN
4.170	40.098	418.090	0.277	1.63	1.44	1.08	IBUTENE
10.850	55.250	209.480	0.292	1.43	1.93	0.52	KRYPTON
0.915	12.270	599.400	0.269	2.36	3.77	0.74	MD2M
0.686	9.450	628.360	0.264	2.14	4.23	1.47	MD3M
0.606	8.770	653.200	0.266	2.48	5.37	0.46	MD4M
1.085	14.150	564.090	0.278	2.03	2.56	0.75	MDM
10.139	45.992	190.564	0.286	1.44	2.39	1.30	METHANE
8.600	81.035	512.600	0.221	1.82	8.48	0.84	METHANOL

0.808	13.410	799.000	0.250	2.30	0.39	1.06	MLINOLEA
0.847	13.690	772.000	0.252	3.11	2.19	0.83	MLINOLEN
1.590	19.390	518.750	0.283	1.93	3.86	-0.91	MM
0.813	12.460	782.000	0.236	2.74	3.13	-0.89	MOLEATE
0.897	13.500	755.000	0.240	2.71	3.42	-0.13	MPALMITA
0.794	12.390	775.000	0.242	2.99	2.89	-0.18	MSTEARAT
2.665	35.346	616.890	0.259	1.70	4.19	2.33	MXYLENE
10.270	72.450	309.520	0.274	1.60	1.41	1.06	N2O
23.882	26.786	44.492	0.303	1.41	1.18	0.56	NEON
3.270	31.960	433.740	0.271	1.65	1.61	1.39	NEOPENTN
7.920	44.607	234.000	0.290	1.59	0.60	0.00	NF3
11.184	33.958	126.192	0.289	1.48	2.88	1.97	NITROGEN
1.810	22.810	594.550	0.255	1.85	2.14	0.86	NONANE
1.920	18.690	441.810	0.265	1.96	3.71	2.27	NOVEC649
2.056	24.970	569.320	0.257	1.83	1.77	0.73	OCTANE
15.445	13.107	33.220	0.307	1.16	-0.49	0.68	ORTHOHYD
13.630	50.430	154.581	0.288	1.46	1.70	1.27	OXYGEN
2.685	37.375	630.259	0.266	1.66	7.97	7.66	OXYLENE
15.538	12.858	32.938	0.302	1.16	-0.43	0.58	PARAHYD
3.216	33.700	469.700	0.268	1.68	1.75	1.17	PENTANE
5.000	42.512	369.890	0.276	1.59	3.12	2.40	PROPANE
5.457	45.550	364.211	0.276	1.58	2.78	2.21	PROPYLEN
6.113	56.260	402.380	0.275	1.61	2.33	2.56	PROPYNE
2.694	35.315	616.168	0.256	1.66	7.76	8.20	PXYLENE
4.033	44.076	471.110	0.279	1.65	1.09	0.68	R11
2.989	33.922	487.210	0.280	1.75	2.16	0.80	R113
3.393	32.570	418.830	0.276	1.73	1.59	1.11	R114
3.980	31.290	353.100	0.268	1.78	1.51	1.21	R115
4.444	30.480	293.030	0.282	1.77	1.41	0.78	R116
4.673	41.361	385.120	0.276	1.65	2.06	0.57	R12
3.889	31.495	358.900	0.271	1.88	2.71	1.26	R1216
3.596	36.618	456.831	0.268	1.75	1.53	0.00	R123
3.650	35.709	438.750	0.268	1.75	2.69	1.13	R1233ZD
4.170	33.822	367.850	0.265	1.71	3.39	2.09	R1234YF
4.290	36.349	382.513	0.266	1.76	4.14	3.27	R1234ZE
4.103	36.243	395.425	0.269	1.74	2.96	2.27	R124
4.779	36.177	339.173	0.268	1.77	2.96	1.59	R125
5.580	38.790	302.000	0.277	1.66	0.72	0.00	R13
5.017	40.593	374.210	0.260	1.75	2.92	1.32	R134A
7.109	37.500	227.510	0.279	1.71	0.78	0.29	R14
3.921	42.120	477.500	0.271	1.69	1.12	1.26	R141B
4.438	40.550	410.260	0.268	1.67	1.51	1.06	R142B
5.128	37.610	345.857	0.255	1.64	2.71	1.40	R143A
5.571	45.168	386.411	0.252	1.66	1.46	0.00	R152A
6.280	50.100	375.250	0.256	1.59	4.59	3.09	R161

5.111	51.812	451.480	0.270	1.71	0.41	0.14	R21
3.340	26.400	345.020	0.276	1.83	1.94	1.20	R218
6.058	49.900	369.295	0.268	1.65	2.22	1.74	R22
3.495	29.250	374.900	0.269	1.87	4.26	0.58	R227EA
7.520	48.320	299.293	0.258	1.64	1.99	1.55	R23
3.716	34.200	412.440	0.268	1.83	5.36	1.51	R236EA
3.626	32.000	398.070	0.267	1.83	4.16	1.85	R236FA
3.920	39.407	447.570	0.270	1.82	3.83	3.10	R245CA
3.850	36.510	427.160	0.267	1.82	2.81	2.02	R245FA
8.150	57.820	351.255	0.243	1.59	2.91	1.31	R32
3.200	32.660	460.000	0.267	1.92	4.15	3.46	R365MFC
7.194	66.773	416.300	0.268	1.59	0.90	0.44	R40
9.300	58.970	317.280	0.240	1.49	1.59	1.69	R41
3.099	27.775	388.380	0.278	1.89	1.87	0.62	RC318
4.648	36.350	377.921	0.249	1.71	3.03	0.56	RE143A
3.329	28.864	406.813	0.256	1.75	4.36	2.04	RE245CB2
3.432	34.330	444.880	0.270	1.85	6.31	5.03	RE245FA2
2.620	24.762	437.700	0.260	1.84	4.19	1.54	RE347MCC
5.082	37.550	318.723	0.279	1.69	6.23	4.03	SF6
8.195	78.840	430.640	0.269	1.69	1.58	1.09	SO2
4.213	40.273	428.610	0.268	1.66	1.38	1.15	T2BUTENE
3.169	41.263	591.750	0.265	1.66	1.91	1.03	TOLUENE
17.874	220.640	647.096	0.229	1.57	12.73	-3.40	WATER
8.400	58.420	289.733	0.289	1.42	2.03	0.60	XENON