Supplementary Material

Characteristic Curves of Polar Fluids: (I) The Two-Center Lennard-Jones Plus Dipole Fluid

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SUPPLEMENTARY MATERIAL

The Supplementary Material for the publication *Characteristic Curves of Polar Fluids: (I) The Two-Center Lennard-Jones Plus Dipole Fluid* contains:

I. Details on the empirical correlation

II. A comparison of the empirical correlation results with molecular-based EOS results for selected real substances

III. Electronic Supplementary Material

I. PARAMETERS FOR THE CORRELATION OF CHARACTERISTIC CURVES IN $\rho - T$ PROJECTION

The reduced characteristic curve results of the $\rho - T$- projection were described by an empirical correlation. The reduced density $\rho^* = \rho/\rho_\mathrm{c}$ was correlated as a function of the model parameters L and μ as

$$\begin{aligned}\rho^* = \quad & a\,(T^* - T^*_{\mathrm{char},i}) \\ & + b\,(T^* - T^*_{\mathrm{char},i})^2 \\ & + c\,(T^* - T^*_{\mathrm{char},i})^3 \\ & + d\,\tanh(0.1(T^* - T^*_{\mathrm{char},i})) \\ & + e\,(\exp(0.1(T^* - T^*_{\mathrm{char},i})) - 1)\ ,\end{aligned} \tag{1}$$

where T^* is the reduced temperature and $T^*_{\mathrm{char},i}$ the reduced temperature of the zero-density limit characteristic point for a given curve i. All properties are reduced with respect to the critical point data as described by the correlation of *Stoll et al.*[1]. The parameters a to e, denoted as y, were described as

$$\begin{aligned}y(L,\mu) = \quad & (d_1 + d_2 L + d_3 L^2 + d_4 L^3 + d_5 L^4) \\ & + \mu((f_1 + f_2 L + f_3 L^2) \\ & + (f_4 + f_5 L + f_6 L^2)\mu \\ & + (f_7 + f_8 L + f_9 L^2)\mu^2 \\ & + (f_{10} + f_{11} L + f_{12} L^2)\mu^3)\ ,\end{aligned} \tag{2}$$

where the parameters d_i and f_i indicate the actual fitted parameters. The results of the parameters d_i and f_i for all a to e are presented in Table S1. Although the reduced density of the Zeno curve can be described adhering to the thermodynamic consistency by using the correlation of $p^*(L,\mu)$ and the condition $Z = 1$, the parameters for the corresponding empirical correlation are presented as well.

TABLE S1: Parameters d_i and f_i for the correlation of the reduced characteristic curves for the 2CLJD fluids in the $\rho - T$ projection, cf. Eqs. (1) and (2).

			Zeno		
	a	b	c	d	e
d_1	$2.711353208 \cdot 10^{4}$	$8.797462107 \cdot 10^{2}$	-3.694282743	$-9.495472500 \cdot 10^{4}$	$-1.761980377 \cdot 10^{5}$
d_2	$4.935406514 \cdot 10^{4}$	$9.351397035 \cdot 10^{2}$	$-6.985013630 \cdot 10^{1}$	$-3.074009943 \cdot 10^{5}$	$-1.861219756 \cdot 10^{5}$
d_3	$-1.279196087 \cdot 10^{5}$	$-2.321823254 \cdot 10^{3}$	$1.907836351 \cdot 10^{2}$	$8.172564932 \cdot 10^{5}$	$4.618832316 \cdot 10^{5}$
d_4	$3.817535292 \cdot 10^{3}$	$-1.199367039 \cdot 10^{3}$	$-1.253912633 \cdot 10^{2}$	$-2.810181002 \cdot 10^{5}$	$2.429004196 \cdot 10^{5}$
d_5	$9.961634151 \cdot 10^{4}$	$3.390271211 \cdot 10^{3}$	$9.262095303 \cdot 10^{-1}$	$-3.165369421 \cdot 10^{5}$	$-6.796512989 \cdot 10^{5}$
f_1	$8.803949866 \cdot 10^{2}$	$3.508730777 \cdot 10^{1}$	$4.969974288 \cdot 10^{-1}$	$-1.770765530 \cdot 10^{3}$	$-7.035199419 \cdot 10^{3}$
f_2	$1.833923794 \cdot 10^{1}$	$-1.951172146 \cdot 10^{1}$	-2.011270715	$-4.010735034 \cdot 10^{3}$	$3.836217833 \cdot 10^{3}$
f_3	$1.912555257 \cdot 10^{3}$	$7.293842841 \cdot 10^{1}$	$8.433376928 \cdot 10^{-1}$	$-4.583797802 \cdot 10^{3}$	$-1.455225318 \cdot 10^{4}$
f_4	$1.714892644 \cdot 10^{2}$	4.322631914	$-1.420536870 \cdot 10^{-1}$	$-8.491634212 \cdot 10^{2}$	$-8.654451830 \cdot 10^{2}$
f_5	$-7.669912520 \cdot 10^{2}$	$-2.062664107 \cdot 10^{1}$	$5.289647030 \cdot 10^{-1}$	$3.523393333 \cdot 10^{3}$	$4.143955717 \cdot 10^{3}$
f_6	$7.006834814 \cdot 10^{1}$	-3.143784663	$-5.371441707 \cdot 10^{-1}$	$-1.324370660 \cdot 10^{3}$	$6.271122514 \cdot 10^{2}$
f_7	-9.088956510	$-2.035925939 \cdot 10^{-1}$	$1.003248066 \cdot 10^{-2}$	$5.006124140 \cdot 10^{1}$	$4.080948800 \cdot 10^{1}$
f_8	$5.415534977 \cdot 10^{1}$	1.757619745	$-8.571325252 \cdot 10^{-3}$	$-1.882590656 \cdot 10^{2}$	$-3.530416800 \cdot 10^{2}$
f_9	$1.552994741 \cdot 10^{1}$	$6.765133304 \cdot 10^{-1}$	$1.473059150 \cdot 10^{-2}$	$-2.005773031 \cdot 10^{1}$	$-1.355870294 \cdot 10^{2}$
f_{10}	$1.220205477 \cdot 10^{-1}$	$1.600771189 \cdot 10^{-3}$	$-2.445004441 \cdot 10^{-4}$	$-8.979807748 \cdot 10^{-1}$	$-3.217798980 \cdot 10^{-1}$
f_{11}	-1.797909895	$-6.599015232 \cdot 10^{-2}$	$-4.619676994 \cdot 10^{-4}$	4.731768818	$1.323958420 \cdot 10^{1}$
f_{12}	$-2.106457964 \cdot 10^{-1}$	$-4.522747069 \cdot 10^{-3}$	$2.558198574 \cdot 10^{-4}$	1.198705482	$9.184793908 \cdot 10^{-1}$
			Amagat		
	a	b	c	d	e
d_1	1.399039623	$6.365063755 \cdot 10^{-2}$	$9.467547134 \cdot 10^{-4}$	-5.544801672	-9.010637715
d_2	$-3.887013452 \cdot 10^{2}$	$-1.612761048 \cdot 10^{1}$	$-2.666132607 \cdot 10^{-1}$	$7.597947896 \cdot 10^{2}$	$3.097667686 \cdot 10^{3}$
d_3	$1.665950969 \cdot 10^{3}$	$6.924424810 \cdot 10^{1}$	1.150005953	$-3.160384512 \cdot 10^{3}$	$-1.338452369 \cdot 10^{4}$
d_4	$-2.382719179 \cdot 10^{3}$	$-9.908175968 \cdot 10^{1}$	-1.647532952	$4.463465294 \cdot 10^{3}$	$1.921055028 \cdot 10^{4}$
d_5	$1.089505533 \cdot 10^{3}$	$4.530924066 \cdot 10^{1}$	$7.535113806 \cdot 10^{-1}$	$-2.028921750 \cdot 10^{3}$	$-8.799298031 \cdot 10^{3}$
f_1	-3.100188326	$-1.287622812 \cdot 10^{-1}$	$-2.190833321 \cdot 10^{-3}$	3.126171204	$2.837162381 \cdot 10^{1}$
f_2	9.179276890	$3.852713669 \cdot 10^{-1}$	$6.716756330 \cdot 10^{-3}$	-6.760831310	$-8.684042329 \cdot 10^{1}$
f_3	-5.706706928	$-2.499808427 \cdot 10^{-1}$	$-4.780353254 \cdot 10^{-3}$	$5.599617977 \cdot 10^{-2}$	$5.828868154 \cdot 10^{1}$
f_4	$6.238590628 \cdot 10^{-1}$	$2.599416327 \cdot 10^{-2}$	$4.452555904 \cdot 10^{-4}$	$-4.366508519 \cdot 10^{-1}$	-5.946130974
f_5	$-1.187020750 \cdot 10^{-1}$	$-7.596568289 \cdot 10^{-3}$	$-2.736532187 \cdot 10^{-4}$	-3.095863863	4.850983838
f_6	-1.392633117	$-5.301420501 \cdot 10^{-2}$	$-6.589715593 \cdot 10^{-4}$	5.533751483	8.032798600
f_7	$-7.044171266 \cdot 10^{-2}$	$-2.950840404 \cdot 10^{-3}$	$-5.097552340 \cdot 10^{-5}$	$6.194309949 \cdot 10^{-2}$	$6.540377643 \cdot 10^{-1}$
f_8	$-7.399647205 \cdot 10^{-2}$	$-2.753910109 \cdot 10^{-3}$	$-2.928815483 \cdot 10^{-5}$	$4.362631236 \cdot 10^{-1}$	$2.551906753 \cdot 10^{-1}$
f_9	$2.646187895 \cdot 10^{-1}$	$1.050566572 \cdot 10^{-2}$	$1.525006688 \cdot 10^{-4}$	$-7.311309696 \cdot 10^{-1}$	-1.887396112
f_{10}	$2.093322169 \cdot 10^{-3}$	$8.782638744 \cdot 10^{-5}$	$1.520521932 \cdot 10^{-6}$	$-2.065961177 \cdot 10^{-3}$	$-1.914468789 \cdot 10^{-2}$
f_{11}	$3.722991751 \cdot 10^{-3}$	$1.443025451 \cdot 10^{-4}$	$1.883247187 \cdot 10^{-6}$	$-1.485126129 \cdot 10^{-2}$	$-2.115268774 \cdot 10^{-2}$
f_{12}	$-9.856729076 \cdot 10^{-3}$	$-3.946582642 \cdot 10^{-4}$	$-5.894023104 \cdot 10^{-6}$	$2.431702490 \cdot 10^{-2}$	$7.363599932 \cdot 10^{-2}$

			Boyle		
	a	b	c	d	e
d_1	$-1.591054862 \cdot 10^{4}$	$-4.212490297 \cdot 10^{2}$	$1.114951049 \cdot 10^{1}$	$7.487010631 \cdot 10^{4}$	$8.422651027 \cdot 10^{4}$
d_2	$-1.564401481 \cdot 10^{4}$	$-7.261026039 \cdot 10^{2}$	$-1.825443610 \cdot 10^{1}$	$1.048650270 \cdot 10^{4}$	$1.459719562 \cdot 10^{5}$
d_3	$-4.737273492 \cdot 10^{4}$	$-2.083878170 \cdot 10^{3}$	$-4.995727932 \cdot 10^{1}$	$5.800097454 \cdot 10^{4}$	$4.156838177 \cdot 10^{5}$
d_4	$1.802693456 \cdot 10^{5}$	$7.256900888 \cdot 10^{3}$	$1.166072083 \cdot 10^{2}$	$-3.513948617 \cdot 10^{5}$	$-1.451263565 \cdot 10^{6}$
d_5	$-1.335442788 \cdot 10^{5}$	$-5.108812189 \cdot 10^{3}$	$-5.923143592 \cdot 10^{1}$	$3.132449012 \cdot 10^{5}$	$1.022187934 \cdot 10^{6}$
f_1	$-2.415966382 \cdot 10^{2}$	-5.114638034	$2.610829304 \cdot 10^{-1}$	$1.408417908 \cdot 10^{3}$	$1.007163083 \cdot 10^{3}$
f_2	$-1.755464153 \cdot 10^{3}$	$-5.902532090 \cdot 10^{1}$	$1.961234456 \cdot 10^{-1}$	$5.688024720 \cdot 10^{3}$	$1.186655991 \cdot 10^{4}$
f_3	$-6.841994631 \cdot 10^{2}$	$-2.633568546 \cdot 10^{1}$	$-5.747621127 \cdot 10^{-1}$	$1.649625595 \cdot 10^{3}$	$5.191736054 \cdot 10^{3}$
f_4	$-1.689914994 \cdot 10^{2}$	-4.309749920	$1.439921408 \cdot 10^{-1}$	$8.238307864 \cdot 10^{2}$	$8.661444839 \cdot 10^{2}$
f_5	$3.840501754 \cdot 10^{2}$	3.957924867	$-9.112897313 \cdot 10^{-1}$	$-3.040981630 \cdot 10^{3}$	$-7.994582130 \cdot 10^{2}$
f_6	$5.031263555 \cdot 10^{2}$	$2.502072515 \cdot 10^{1}$	$8.409742775 \cdot 10^{-1}$	$-3.961908385 \cdot 10^{1}$	$-4.991382259 \cdot 10^{3}$
f_7	8.787669866	$8.669701572 \cdot 10^{-2}$	$-2.110075520 \cdot 10^{-2}$	$-7.026019179 \cdot 10^{1}$	$-1.762019413 \cdot 10^{1}$
f_8	$3.840093673 \cdot 10^{1}$	2.625029144	$1.320536137 \cdot 10^{-1}$	$1.410345118 \cdot 10^{2}$	$-5.250460917 \cdot 10^{2}$
f_9	$-1.240237855 \cdot 10^{2}$	-5.384244974	$-1.215887429 \cdot 10^{-1}$	$1.638754363 \cdot 10^{2}$	$1.076330706 \cdot 10^{3}$
f_{10}	$-1.095198320 \cdot 10^{-1}$	$2.897042628 \cdot 10^{-3}$	$6.599880362 \cdot 10^{-4}$	1.668115758	$-5.728244548 \cdot 10^{-1}$
f_{11}	-2.330864067	$-1.252248877 \cdot 10^{-1}$	$-4.606785894 \cdot 10^{-3}$	-1.748438512	$2.505698778 \cdot 10^{1}$
f_{12}	4.807607890	$2.053679368 \cdot 10^{-1}$	$4.343325678 \cdot 10^{-3}$	-7.009818403	$-4.106505197 \cdot 10^{1}$

			Charles		
	a	b	c	d	e
d_1	$1.747656121 \cdot 10^{3}$	$6.768214190 \cdot 10^{1}$	$7.649557434 \cdot 10^{-1}$	$-3.879033405 \cdot 10^{3}$	$-1.360425728 \cdot 10^{4}$
d_2	$-1.092976822 \cdot 10^{4}$	$-4.233602096 \cdot 10^{2}$	-4.822305495	$2.417349718 \cdot 10^{4}$	$8.514370534 \cdot 10^{4}$
d_3	$3.588702167 \cdot 10^{4}$	$1.363206067 \cdot 10^{3}$	$1.342273274 \cdot 10^{1}$	$-8.495597321 \cdot 10^{4}$	$-2.739704834 \cdot 10^{5}$
d_4	$-4.698552970 \cdot 10^{4}$	$-1.770645938 \cdot 10^{3}$	$-1.630579937 \cdot 10^{1}$	$1.141762711 \cdot 10^{5}$	$3.557438718 \cdot 10^{5}$
d_5	$2.096753936 \cdot 10^{4}$	$7.866027445 \cdot 10^{2}$	6.948258706	$-5.168449281 \cdot 10^{4}$	$-1.580180650 \cdot 10^{5}$
f_1	$-1.246914877 \cdot 10^{2}$	-5.088527091	$-7.961048755 \cdot 10^{-2}$	$2.245546003 \cdot 10^{2}$	$1.022383483 \cdot 10^{3}$
f_2	$3.590643413 \cdot 10^{2}$	$1.586319024 \cdot 10^{1}$	$3.325246330 \cdot 10^{-1}$	$-3.904110811 \cdot 10^{2}$	$-3.201260275 \cdot 10^{3}$
f_3	$-2.317092118 \cdot 10^{2}$	$-1.078977715 \cdot 10^{1}$	$-2.640536148 \cdot 10^{-1}$	$1.370736817 \cdot 10^{2}$	$2.180769343 \cdot 10^{3}$
f_4	$4.146078160 \cdot 10^{1}$	1.642341269	$2.194729788 \cdot 10^{-2}$	$-8.492621528 \cdot 10^{1}$	$-3.297111005 \cdot 10^{2}$
f_5	$-9.898203787 \cdot 10^{1}$	-4.350930492	$-8.998448495 \cdot 10^{-2}$	$1.130551679 \cdot 10^{2}$	$8.769742431 \cdot 10^{2}$
f_6	$6.405842357 \cdot 10^{1}$	2.960617476	$7.135043427 \cdot 10^{-2}$	$-4.356836393 \cdot 10^{1}$	$-5.971164772 \cdot 10^{2}$
f_7	-2.546098249	$-1.054473859 \cdot 10^{-1}$	$-1.762027932 \cdot 10^{-3}$	4.278300184	$2.118473201 \cdot 10^{1}$
f_8	3.598357357	$2.014143543 \cdot 10^{-1}$	$7.139511717 \cdot 10^{-3}$	4.783694607	$-4.077916174 \cdot 10^{1}$
f_9	-1.689927188	$-1.200640903 \cdot 10^{-1}$	$-5.665390541 \cdot 10^{-3}$	-7.433946201	$2.433413078 \cdot 10^{1}$
f_{10}	$5.354562689 \cdot 10^{-2}$	$2.298631521 \cdot 10^{-3}$	$4.445873798 \cdot 10^{-5}$	$-7.357210067 \cdot 10^{-2}$	$-4.619181634 \cdot 10^{-1}$
f_{11}	$-1.507286404 \cdot 10^{-2}$	$-2.531102972 \cdot 10^{-3}$	$-1.813407145 \cdot 10^{-4}$	$-3.664611858 \cdot 10^{-1}$	$5.173571036 \cdot 10^{-1}$
f_{12}	$-1.985965814 \cdot 10^{-2}$	$9.276517932 \cdot 10^{-4}$	$1.449216211 \cdot 10^{-4}$	$3.900990043 \cdot 10^{-1}$	$-1.913111662 \cdot 10^{-1}$

II. COMPARISON OF THE CORRELATION FOR CHARACTERISTIC CURVES TO THE MOLECULAR-BASED EOS

Fig. S1 shows the results from the empirical characteristic curve correlation in comparison to the predictions from the EOS (cf. main body of this work) for the three substances carbon monoxide (CO), R152a ($C_2H_4F_2$), and R134a ($C_2H_2F_4$). Additionally, molecular simulation data for the Charles curve, as reported by *Vrabec et al.*[2], is shown. Overall, the results are in reasonable agreement. Yet, some deviations are observed, e.g. for the Amagat curve at low temperatures (where usually a solid phase exists) and the zero-density limit temperatures. The latter are not accurately captured by the EOS (see main body of this work). Also for the Charles curve, the empirical correlation provides a slightly better description of the molecular simulation data from *Vrabec et al.*[2] than the EOS predictions.

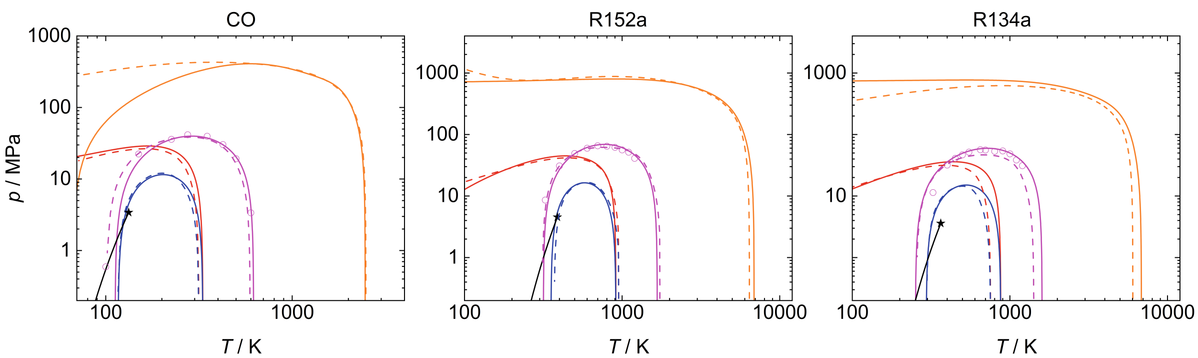

FIG. S1: Characteristic curves in the $p-T$ projection for CO (left), R152a (middle), and R134a (right). Results from the empirical correlation evaluated for the molecular models (solid lines), the EOS as described in the main body of this work (dashed lines) for the Zeno (red), Amagat (orange), Boyle (blue), and Charles curve (pink). Simulation results for the Charles curve from *Vrabec et al.*[2] (circles). Binodal (black) and critical point (star) computed from the correlation proposed by *Stoll et al.*[1].

III. ELECTRONIC SUPPLEMENTARY MATERIAL

The electronic Supplementary Material includes:

- `Results_2CLD.xlsx` containing the results of the characteristic curve state points obtained by MD simulation

- Matlab script `Correlation_CharacteristicCurves.m` for evaluating the empirical correlation for the characteristic curves. The user has to specify the fluid parameters L/σ and the strength of the polarity

REFERENCES

[1]J. Stoll, J. Vrabec, and H. Hasse, "Comprehensive study of the vapour-liquid equilibria of the pure two-centre Lennard-Jones plus pointdipole fluid," Fluid Phase Equilibria **209**, 29–53 (2003).

[2]J. Vrabec, G. K. Kedia, and H. Hasse, "Prediction of Joule-Thomson inversion curves for pure fluids and one mixture by molecular simulation," Cryogenics **45**, 253–258 (2005).