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Complex Non-monotonic Thermal Response of Volumetric Space of Simple Liquids

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SUPPLEMENTARY INFORMATION

The Supplementary Information includes experimental isothermal data of the isobaric thermal expansivities α_p for 1,3-dichloropropane and 1,5-dichloropentane (details of the materials are given at the end of the document) measured by the scanning trasitiometry (Table 1) as well as values of the parameters (collected in Tables 2 and 3) for their fits (for which the reference state has been fixed at the melting temperature at ambient pressure (i.e., p_0=0.1MPa, and respectively T_0=174.15K and T_0=201.15K) to the temperature-pressure functions $\alpha_p(T,p)$ given in the main text by Eqs. (5) and (6), which are also presented below

$$\alpha_p(T,p)=\alpha_p(T,p_0)+\frac{p-p_0}{B_T(p_0)+\gamma(p-p_0)}\left(\frac{\partial \ln B_T(p_0)}{\partial T}\right)_p \tag{5}$$

$$\alpha_p(T,p)=\frac{\gamma(\rho_0)}{\gamma(\rho)}\left[\alpha_p(T,p_0)+\frac{p-p_0}{B_T(p_0)+\gamma(\rho_0)(p-p_0)}\left(\frac{\partial}{\partial T}\ln\left(\frac{B_T(p_0)}{\gamma(\rho_0)}\right)\right)_p\right] \tag{6}$$

The functions $\alpha_p(T,p)$ result respectively from the equations of state given in the main text by Eqs. (1) and (3), which belong to a class of equations of state formulated in the density scaling regime for simple liquids, the molecular dynamics of which obey a strong linear isochoric correlation between the total instantaneous virial and the total instantaneous potential energy. The equations of state can be also considered only in terms of their limitations. The equation of state given by Eq. (1), which is also displayed here

$$\upsilon(T,p)=\upsilon(T,p_0)\left[1+\frac{\gamma}{B_T(p_0)}(p-p_0)\right]^{-1/\gamma} \tag{1a}$$

$$\upsilon(T,p_0)=\sum_{l=0}^{k}A_l(T-T_0)^l \tag{1b}$$

$$B_T(p_0)=b_0\exp(-b_2(T-T_0)) \tag{1c}$$

where $b_0=B_{T_0}(p_0)$, $b_2=b_2(p_0)=-\partial\ln B_T(p_0,T)/\partial T\big|_{T=T_0}$, $A_0=\upsilon(T_0,p_0)$, and $A_l=(1/l!)\partial^l\upsilon(p_0,T)/\partial T^l\big|_{T=T_0}$ for l=1,2,.. . , is valid if the isothermal bulk modulus obeys the following linear pressure dependence

$$B_T(p)=B_T(p_0)+\gamma(p-p_0) \tag{2}$$

However, the equation of state given by Eq. (3), which is also shown below

$$p=p_0+\frac{B_T(p_0)}{\gamma(\rho_0)}\left(\frac{h(\rho)}{h(\rho_0)}-1\right) \tag{3a}$$

$$h(\rho)=\exp\left(C_1\ln\rho+C_2\ln^2\rho\right) \tag{3b}$$

$$\gamma(\rho)=C_1+2C_2\ln\rho \tag{3c}$$

$$\rho_0=\upsilon^{-1}(T,p_0)=\left(\sum_{l=0}^{k}A_l(T-T_0)^l\right)^{-1} \tag{3d}$$

$$B_T(p_0)=b_0\exp(-b_2(T-T_0)) \tag{3e}$$

can be used to describe volumetric date in an extremely wide range of densities ($\rho=\upsilon^{-1}$) and is not limited only to a linear dependence $B_T(p)$, because Eq. (3) implies the following equation for the isothermal bulk modulus

$$B_T(p)=\frac{\gamma(\rho)}{\gamma(\rho_0)}[B_T(p_0)+\gamma(\rho_0)(p-p_0)] \tag{4}$$

Table 1. Results of transitiometric measurements[a] of the high pressure isobaric thermal expansivities α_p of 1,3-dichloropropane and 1,5-dichloropentane

Temperatures of Experimental Isotherms									
273.15 K		**303.15 K**		**323.15 K**		**373.15 K**		**423.15 K**	
1,3-dichloropropane									
p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$
194.99	0.650	194.99	0.637	193.69	0.623	194.87	0.605	193.55	0.560
169.57	0.672	169.04	0.662	168.55	0.648	169.05	0.639	168.64	0.597
149.48	0.698	149.13	0.692	148.80	0.676	149.23	0.668	148.95	0.625
129.28	0.726	129.14	0.717	128.91	0.710	129.28	0.705	129.05	0.664
109.19	0.749	109.29	0.750	109.01	0.746	109.36	0.746	109.13	0.717
89.14	0.786	89.36	0.791	89.07	0.790	89.43	0.796	89.29	0.768
69.06	0.809	69.40	0.841	69.23	0.835	69.55	0.848	69.44	0.855
54.06	0.846	54.44	0.879	54.37	0.885	54.63	0.903	54.62	0.920
39.12	0.893	39.42	0.927	39.53	0.949	39.69	0.980	39.70	0.991
24.13	0.940	24.32	0.988	24.64	1.006	24.72	1.072	24.82	1.136
8.70	0.970	9.05	1.019	9.28	1.053	9.64	1.149	9.93	1.270
0.10	1.010	0.10	1.064	0.10	1.103				
1.5-dichloropentane									
p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$	p/ MPa	$\alpha_p \times 10^3$ / K $^{-1}$
194.38	0.579	194.99	0.582	194.62	0.565	194.99	0.530	194.34	0.504
168.40	0.599	169.09	0.597	168.83	0.579	169.01	0.560	168.91	0.523
148.56	0.621	149.12	0.615	148.78	0.602	149.13	0.584	149.04	0.549
128.65	0.645	129.12	0.640	128.88	0.634	129.12	0.612	129.23	0.589
108.62	0.672	109.13	0.672	109.14	0.661	109.16	0.646	109.30	0.626
88.52	0.710	89.12	0.707	89.24	0.705	89.25	0.679	89.35	0.668
68.55	0.744	69.17	0.742	69.29	0.743	69.29	0.727	69.45	0.710
53.74	0.770	54.29	0.776	54.41	0.778	54.40	0.762	54.59	0.787
38.83	0.793	39.34	0.817	39.40	0.822	39.45	0.830	39.64	0.860
23.91	0.833	24.29	0.869	24.41	0.877	24.49	0.895	24.71	0.941
8.40	0.861	8.94	0.893	9.13	0.903	9.36	0.919	9.66	1.053
0.10	0.896	0.10	0.930	0.10	0.954				

[a] Standard uncertainties: u(T)= ±0.05 K, u(p)=± 0.07 MPa, and $u_{relative}(\alpha_p)$ = ±2%.

Table 2. Values of the fitting parameters of Eq. (1) found from fitting the experimental isothermal pressure dependences of thermal expansivity to Eq. (5)

Material	*Fitting parameters*						
	A_0 / cm^3g^{-1}	A_1 / $cm^3g^{-1}K^{-1}$	A_2 / $cm^3g^{-1}K^{-2}$	A_3 / $cm^3g^{-1}K^{-3}$	b_0 / MPa	b_2 / K^{-1}	γ
1,3-dichloropropane	0.7631±0.0014	$(6.51\pm0.21)\times10^{-4}$	$(5.76\pm0.45)\times10^{-7}$	$(2.31\pm0.36)\times10^{-9}$	12000±1700	0.0114±0.0007	11.83±0.83
1,5-dichloropentane	0.8354±0.0005	$(6.99\pm0.54)\times10^{-4}$	$(4.82\pm0.43)\times10^{-7}$	$(1.46\pm0.28)\times10^{-9}$	6370±590	0.0089±0.0003	11.39±0.96

Table 3. Values of the fitting parameters of Eq. (3) found from fitting the experimental isothermal pressure dependences of thermal expansivity to Eq. (6)

Material	*Fitting parameters*							
	A_0 / cm^3g^{-1}	A_1 / $cm^3g^{-1}K^{-1}$	A_2 / $cm^3g^{-1}K^{-2}$	A_3 / $cm^3g^{-1}K^{-3}$	b_0 / MPa	b_2 / K^{-1}	C_1	C_2
1,3-dichloropropane	0.7631±0.0015	$(6.77\pm0.16)\times10^{-4}$	$(3.60\pm0.89)\times10^{-7}$	$(2.90\pm0.26)\times10^{-9}$	10300±1100	0.0108±0.0005	7.37 ±0.67	10.00±0.94
1,5-dichloropentane	0.8354±0.0007	$(7.04\pm0.15)\times10^{-4}$	$(4.21\pm0.82)\times10^{-7}$	$(1.76\pm0.34)\times10^{-9}$	5820±950	0.0086±0.0007	8.16 ±0.89	10.01±0.92

Details of the examined materials: 1,3-dichloropropane was supplied by Aldrich with a stated mass-fraction purity 0.99, 1,5-dichloropentane had a mass-fraction purity of 0.99 and was supplied by Avocado. Both liquids were purified by fractional distillation. Only the middle fractions were collected, resulting in a liquid sample with a purity of more than 99 % (by gas-liquid chromatography). The mass fraction of water as determined by the Karl-Fischer-method was less than 5×10^{-5} for tested compounds. Before their use, the liquids were dried over grade 3Å molecular sieve (Lancaster) and stored in the dark. Prior to the experiments, they were degassed ultrasonically. In order to check the purity of tested liquids, theirs densities with a vibrating-tube densimeter (Anton Paar DMA 500) were determined. In Table 4, the measured densities of 1,3-dichloropropane and 1,5-dichloropentane at 298.15 K are compared with literature values. Our experimental results are in good agreement with the literature values. Small differences in densities may result from differences in the purity of the chemicals.

Table 4. Comparison of the densities for 1,3-dichloropropane and 1,5-dichloropentane measured by us at temperature T = 298.15K and atmospheric pressure with those previously reported[64-68]

Material	ρ / (kg/m^3)	
	this work[a]	literature
1,3-dichloropropane	1179.15	1179.56,[64] 1180.10,[65] 1178.32,[66] 1178.66[67]
1,5-dichloropentane	1095.01	1095.16,[66] 1095.11[68]

[a] Standard uncertainties: u(ρ) = ±0.05 kg/m^3 and u(T) = ±0.01K.

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