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Comment on "Anti-cooperativity in hydrophobic interactions: A simulation study of spatial dependence of three-body effects and beyond" [J. Chem. Phys. 115, 1414 (2001)]

J. Chem. Phys. **116**, 2665 (2002); 10.1063/1.1434994

Comment on "Anisotropic intermolecular interactions in van der Waals and hydrogen-bonded complexes: What can we get from density-functional calculations?" [J. Chem. Phys. 111, 7727 (1999)]

J. Chem. Phys. **113**, 1666 (2000); 10.1063/1.481955

Complex photothermal refractive index change in host-guest liquid crystals determined with a novel interferometric method

Appl. Phys. Lett. **70**, 2544 (1997); 10.1063/1.118915

Response to “Comment on ‘Refractive index change by photothermal effect with a constant density detected as temperature grating in various fluids’” [J. Chem. Phys. 106, 1296 (1997)]

J. Chem. Phys. **106**, 1298 (1997); 10.1063/1.473969

Refractive index change by photothermal effect with a constant density detected as temperature grating in various fluids

J. Chem. Phys. **104**, 4988 (1996); 10.1063/1.471129

[illegible]

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Comment on “Refractive index change by photothermal effect with a constant density detected as temperature grating in various fluids” [J. Chem. Phys. 104, 4988 (1996)]

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Much more experimental evidence for nonpolar liquids is in favor of $(\partial n/\partial T)_V > 0$ than $(\partial n/\partial T)_V < 0$. None of these facts has been mentioned by Terazima in his article¹ as if they were not existing at all. We will point out then the main of them to complete the issue.

A simple way to determine $(\partial n/\partial T)_V$ is from the exact relation

$$\left(\frac{\partial n}{\partial T}\right)_V = \left(\frac{\partial n}{\partial T}\right)_p + \left(\frac{\partial n}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V, \quad (1)$$

where $(\partial p/\partial T)_V = \alpha_p/\beta_T$. Measurements made in the Koninklijke Shell Laboratorium in Amsterdam by Coumou and co-workers² for Eq. (1), give $(\partial n/\partial T)_V > 0$ (Table I). It would be of interest to know $(\partial n/\partial p)_T$ from the exact Eq. (1) for α_p and β_T used by Terazima, unfortunately he did not specify them (nor β_S , c_p , c_V) although he used them in calculating the *TG* signal.

A more complicated way to obtain $(\partial n/\partial T)_V$ is from the isotropic Rayleigh light scattering (Smoluchowski, Einstein) by the approximate formula

$$\left(\frac{\partial n}{\partial T}\right)_V = \left(\frac{\partial n}{\partial T}\right)_p + \frac{\lambda^2}{\pi} \left(\frac{R_{is}}{2kT\beta_T}\right)^{0.5} \frac{\alpha_p}{n}, \quad (2)$$

where $R_{is} = [(1 - 7D/6)/(1 + D)]R$, D is the depolarization degree, R the absolute Rayleigh ratio. The absolute isotropic Rayleigh ratio values of Coumou's *et al.*² are well accepted and used to calibrate the scattering apparatus.³ Also for these data Eq. (2) gives $(\partial n/\partial T)_V > 0$ (Table I). Certainly, even good accuracy of R_{is} cannot guarantee Eq. (2) to be as accurate as Eq. (1) with $(\partial n/\partial T)_p$ and $(\partial n/\partial p)_T$, nevertheless satisfactory agreement of these equations for liquids listed in Table I is obtained except of slight negative value for *n*-octane.

From a new optical equation of a nonpolar liquid proposed by Niedrich⁴

$$(\epsilon - 1) \frac{2\epsilon + 1}{9\epsilon} = c_\lambda r \exp \frac{r^2}{1 - T/T_1}, \quad (3)$$

where $\epsilon \equiv n^2$, $c_\lambda \geq 1$ is the liquid constant at wavelength λ , $r \equiv (4/3)\pi p\alpha$, α the mean molecular polarizability, $T_1 = ap/NR$ the internal temperature, a the Van der Waals constant, comes

$$\left(\frac{\partial n}{\partial T}\right)_V = (\epsilon - 1) \frac{2\epsilon + 1}{2\epsilon + 1/\epsilon} \left(\frac{r}{1 - T/T_1}\right)^2 \frac{1}{2nT_1}, \quad (4)$$

therefore $(\partial n/\partial T)_V > 0$. Comparison of Eq. (4) with Eq. (1) in Table I needs no comment. There is no such equation in the literature to give similar numerical agreement for negative experimental values of $(\partial n/\partial T)_V$. The physical interpretation of Eq. (4) involves the structure of a liquid via the equation

$$\left(\frac{\partial n}{\partial T}\right)_V = (\epsilon - 1) \frac{2\epsilon + 1}{2\epsilon + 1/\epsilon} \left(\frac{\partial}{\partial T} \langle x^{-6} \rangle\right)_V \frac{\alpha^2}{n}, \quad (5)$$

where $\langle x^{-6} \rangle$ is the binary radial correlation parameter, and which means that $(\partial \langle x^{-6} \rangle / \partial T)_V > 0$.

Until now we have taken into consideration the experimental results by Coumou *et al.* because (i) they were obtained for the same samples of liquids at identical conditions for both derivatives $(\partial n/\partial T)_p$ and $(\partial n/\partial p)_T$, as well as for R and D , simultaneously, (ii) the pressure while determining $(\partial n/\partial p)_T$ was not higher than 2 atm being in the range of strict linearity of $n(p)$. However, there are in the literature other experimental results which due to Eq. (3) are in support of $(\partial n/\partial T)_V > 0$. As an example let us take the high pressure increase of n of carbon disulfide, with the largest $(\partial n/\partial T)_V$ in Table I, which has been measured by Chen and Vedam.⁵ This increase, calculated by the formula resulting from Eq. (3)

$$\Delta n = [z + (z^2 + 0.5)^{0.5}]^{0.5} - n_0, \quad (6)$$

where $z \equiv 0.25\{1 + 9c_\lambda r \exp[r^2/(1 - T/T_1)]\}$, $\alpha = 8.74 \cdot 10^{-24}$ cc, $a = 1.11 \cdot 10^{13}$ cm⁴ dyne/mole², and $c_\lambda = 1.04$ to fit n_0 at 1

TABLE I. $(\partial n/\partial T)_V \times 10^5$ K⁻¹ for nonpolar liquids.

Liquid	Experiment			Theory Niedrich Eq. (4)
	Terazima (Ref. 1)	Coumou <i>et al.</i> (Ref. 2)		
		Eq. (1)	Eq. (2)	
CS ₂	−2.5	+4.7	+5.8	+4.4
benzene	−2.1	+3.1	+1.8	+2.1
CCl ₄	−2.9	+1.7	+0.6	+1.6
C ₆ H ₁₂ ^a	−2.6	+1.1	+0.1	+1.4
<i>n</i> -decane	−2.1	+1.7	+0.1	+1.0
<i>n</i> -octane	−2.3	+1.0	−0.5	+1.1
<i>n</i> -hexane	−2.1	+1.2	+1.7	+1.1

^aCyclohexane.

TABLE II. $\Delta n(p)$ for liquid carbon disulfide.

Pressure p/kbar	Experiment	Theory
	Chen, Vedam (Ref. 5) $\Delta n \times 10^2$	Niedrich (Ref. 4) $\Delta n \times 10^2$
0.54	3.12	3.15
2.18	9.40	9.50
4.26	14.80	14.88
6.19	18.72	18.76
8.22	22.25	22.13
10.86	26.18	25.84
12.46	28.32	27.85

atm and 20 °C, gives excellent agreement with experiment (Table II). As an another example we present in Table III $\sim 1\%$ agreement for *n*-hexane and toluene of our calculation by the formula coming from Eq. (3)

$$\left(\frac{\partial n}{\partial T}\right)_p = (\epsilon - 1) \frac{2\epsilon + 1}{2\epsilon + 1/\epsilon} \left[1 + \left(2 - \frac{3T + 1/\alpha_p}{T_1} \right) \times \left(\frac{r}{1 - T/T_1} \right)^2 \right] \frac{\alpha_p}{n}, \quad (7)$$

with data from Ref. 4, with the experimental results obtained by Li, Segre, Gammon, Sengers, and Lamvik.⁶

It comes from Table I that only systematic error in Ref. 2, a little larger than the estimated, could be the reason for $(\partial n/\partial T)_V < 0$ obtained by Terazima, and vice versa. To resolve this controversy we propose to determine $(\partial n/\partial T)_p$, $(\partial n/\partial p)_T$, α_p and β_T for carbon diselenide, for which Eq. (4) gives $(\partial n/\partial T)_V = 6 \cdot 10^{-5} \text{ K}^{-1}$, the larger value than that for CS₂ and therefore the error being smaller part of it than for the liquids investigated previously.

TABLE III. $(-\partial n/\partial T)_p \times 10^4 \text{ K}^{-1}$ -temperature dependence.

	<i>n</i> -hexane		toluene	
	Niedrich Eq. (7)	exp- <i>t</i> Ref. 6	Niedrich Eq. (7)	exp- <i>t</i> Ref. 6
15 °C	5.298	5.356	5.615	5.634
20 °C	5.341	5.394	5.636	5.638
25 °C	5.384	5.433	5.646	5.648
30 °C	5.423	5.475	5.653	5.656
35 °C	5.469	5.520	5.662	5.667
40 °C	5.508	5.564	5.669	5.681
45 °C	5.551	5.611	5.677	5.700

Despite the small numerical value of $(\partial n/\partial T)_V$ it is of importance in our understanding the role of molecular interactions in liquids. From Terazima's data it comes that only dispersion interaction is important for $(\partial n/\partial T)_V$ while *H*-bonding interaction (water) is negligible. From Coumou *et al.* data and experimental $(\partial n/\partial T)_V^{\text{water}} = -1.5 \cdot 10^{-5} \text{ K}^{-1}$ it comes that the influence of *H*-bonding interaction is nearly twice as large as that from dispersion interaction and has the opposite sign. We must know the exact value of $(\partial n/\partial T)_V$ to answer what is the case.

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