PVT Measurements on 4′-*n*-Hexyl-Biphenyl-4-Carbonitrile (6CB) and 4′-*n*-Heptyl-Biphenyl-4-Carbonitrile (7CB) up to 300 MPa

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P, V_m, T data were established for 4′-*n*-hexyl-biphenyl-4-carbonitrile (6CB) and 4′-*n*-heptyl-biphenyl-4-carbonitrile (7CB) between 300 and 370 K up to 300 MPa, and specific volumes were determined for the liquid crystalline, isotropic, and also partly for the crystal phases. Volume and enthalpy changes at the phase transitions are also presented. In the case of 6CB, a new crystal phase has been detected, corresponding to a triple point at 338 K and 196 MPa. The p, V_m, T data enabled us to separate the entropy change into a volume-dependent part and configurational part. From the molar volumes along the nematic-isotropic phase transition $T_{\mathrm{NI}}(p)$, the molecular field parameter $\gamma = \partial \ln T_{\mathrm{NI}} / \partial \ln V_{\mathrm{NI}}$ was determined.

Key words: 6CB, 7CB, High Pressure, pVT, Phase transitions, Thermodynamics.

1. Introduction

Recently we reported p, V_m, T data for 5CB and 8PCH [1]. In this work we extend the measurements to 6CB and 7CB, which have also been studied dielectrically [2, 3,]. Thus we can test the influence of the alkyl chain length on the thermodynamic properties. Several homologous series have been studied at atmospheric pressure with respect to odd – even effects and the influence of different molecular cores. In particular alkylcyanobiphenyls (*n*CB) have been extensively studied in the past, due to their broad nematic range and chemical stability [4–14].

2. Experimental

The high-pressure dilatometric cell has been described in [1, 15]. Volume changes are recorded by a moving piston, whose displacement is measured inductively. The data are collected after pressurizing the vessel and thermal equilibration. Usually the measurements start with the highest pressure, which is then released step by step. The densities at normal pressure were determined with a commercial vibrating-tube densimeter Anton Paar DMA58.

The 6CB ($M = 263.4$ g mol^{-1}) and 7CB ($M = 277.4$ g mol^{-1}) samples were obtained from Merck and used without further purification. The nematic phases were not oriented in the dilatometer.

3. Results

3.1 *4′-n-hexyl-biphenyl-4-carbonitrile (6CB)*

Figure 1 shows the specific volume of 6CB as a function of pressure and temperature. The large step represents the volume change on melting. Above 200 MPa the isotherms exhibit an additional step, corresponding to the phase transitions of a pressure-induced crystal form (cr$_{\mathrm{II}}$). Densities at ambient pressure are reported by Dunmur and Miller [5], Łabno et al. [6], and Shirakawa et al. [7]. Figure 2 shows that there is good agreement with the data of Miller and Łabno. The relative volume change at the NI transition is 0.0013, somewhat larger than reported by Dunmur and Miller (0.00096), but still significantly smaller than found for 5CB and 7CB.

The pressure dependence of the phase transition temperatures is displayed in Figure 3. The phase diagram shows a new triple point at 338 K and 196 MPa that has so far not been reported in literature. The high-pressure form cr$_{\mathrm{II}}$ has not been observed in previous high-pressure measurements [2, 11, 12]. The melting line of cr$_{\mathrm{I}}$ agrees well with results from Shashidhar et al. [12], but the NI transition line agrees better with Wallis *et al.* [11] and Brückert [2]. The pressure dependences of the phase transition temperatures have been fitted to polynomials and are collected in Table 1. Below 200 MPa there is good agreement with data reported in [14].

With the use of the Clausius-Clapeyron equation we have evaluated the enthalpy and entropy changes accompanying the phase transitions. The thermodynamic results are presented in Table 2. Figure 1 shows that the

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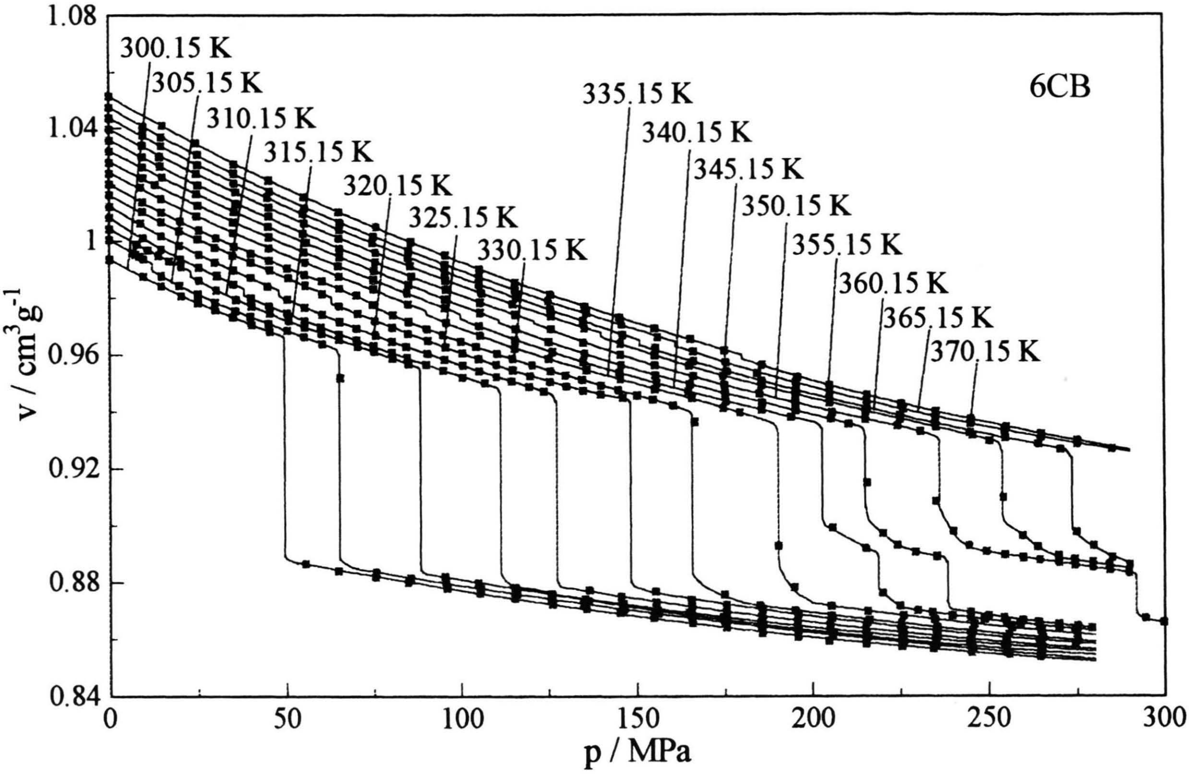

Fig. 1. Specific volumes of 6 CB as functions of pressure; the steps in the isotherms refer to the transitions $cr_{II} \rightarrow cr_I \rightarrow$ nematic $\rightarrow$ isotropic. The numerical data can be obtained from the authors.

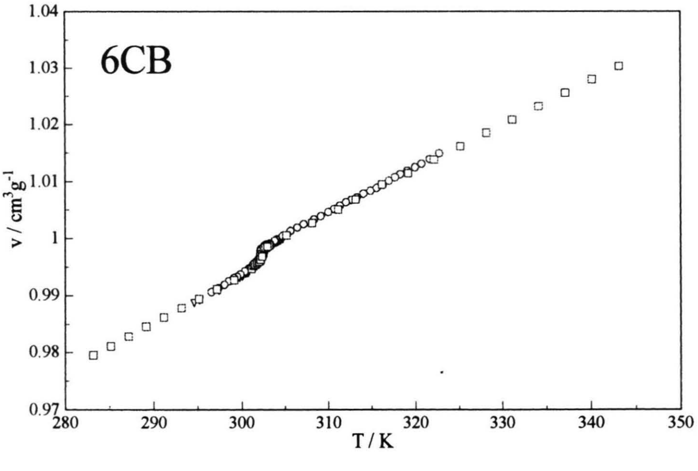

Fig. 2. Specific volumes of 6CB at atmospheric pressure, (□ this work, ▽ Dunmur *et al.* [5], ○ Łabno *et al.* [6]).

volume change due to the NI transition is rather small, but detectable at all pressures. The volume, enthalpy, and entropy changes, ΔV_{NI}, ΔH_{NI}, ΔS_{NI}, do not exhibit a significant pressure dependence. One has to take into account a larger relative error for these small quantities. For the crystal I – and crystal II – nematic transition the thermodynamic changes are considerably larger, but only for crystal I – nematic ΔV, ΔH, ΔS, display a significant pressure dependence. At atmospheric pressure the following ΔH values are reported: for the melting: 24.267 kJ/mol

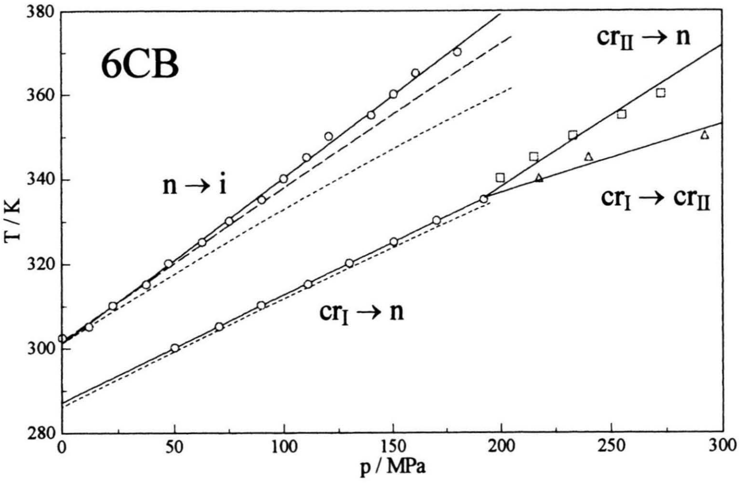

Fig. 3. Phase diagram of 6CB, —— this work, - - - - Wallis *et al.* [11], · · · · · · Shashidhar *et al.* [12].

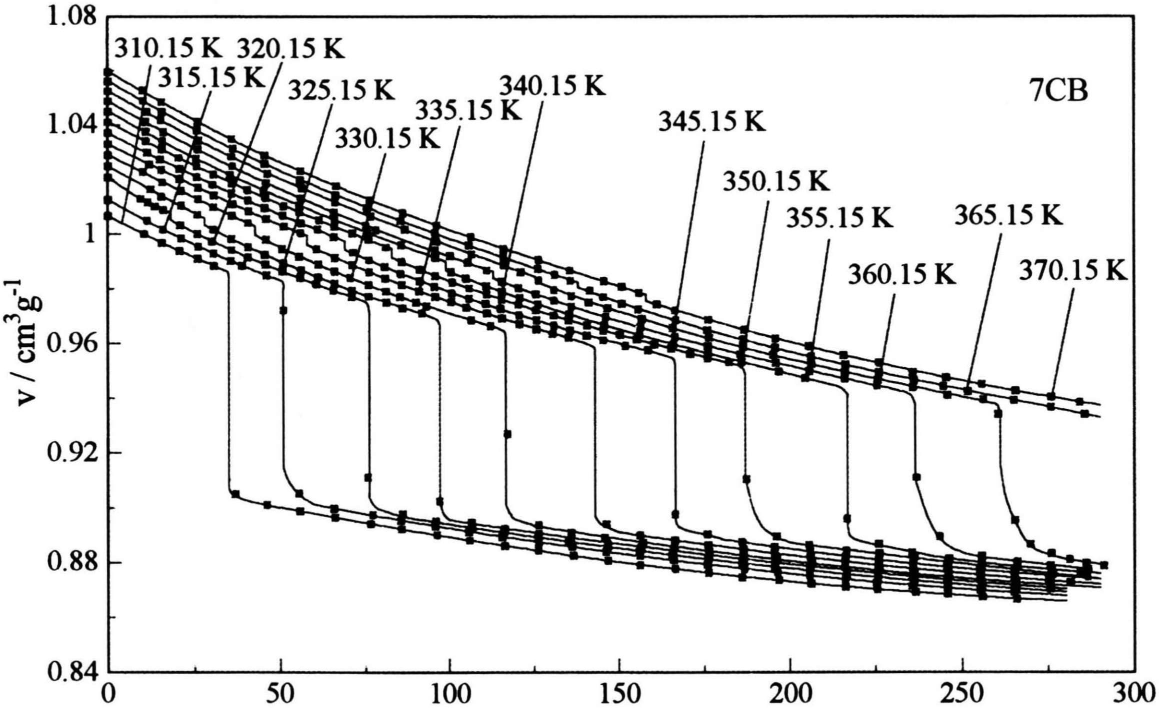

Fig. 4. Specific volumes of 7CB as functions of pressure; the steps in the isotherms refer to the transitions cr → nematic → isotropic. The numerical data can be obtained from the authors.

[14], 20.9 kJ/mol [16], and for the NI transition: 290 J/mol [14, 16, 17], which agree well with this work ($\Delta H = 25.4$ kJ/mol and $\Delta H = 260$ J/mol, respectively).

3.2 4′-n-heptyl-biphenyl-4-carbonitrile (7CB)

Figure 4 shows the specific volumes as a function of pressure of different isotherms. As for 6CB, the nematic – isotropic transition is clearly discernable. At atmospheric pressure we can compare our results with literature data from Sen *et al.* [4], Dunmur *et al.* [5], Łabno *et al.* [6], Orwoll *et al.* [8], Ibrahim et al. [18], and Oweimreen *et al.* [19], see Figure 5. There is good agreement within the limits of experimental error (except [4]). The relative volume change at the NI transition amounts to 0.0022, in agreement with Dunmur *et al.* [5] and Oweimreen *et al.* [19]. Orwoll *et al.* found a relative volume change of 0.0024 [8]. Data from Shirakawa *et al.* [7] deviate by more than 0.5%. The thermodynamic quantities are collected in Table 3. As was found for 6CB, the ΔV_{NI} and ΔH_{NI} values do not exhibit a significant pressure dependence, whereas ΔV_{cr-N}, and ΔH_{cr-N} decrease. The enthalpy of melting at atmospheric pressure ($\Delta H = 28.7$ kJ/mol) is considerably larger than reported in [14] (25.94 kJ/mol) and [16] (25.5 kJ/mol). For the NI transition we find $\Delta H = 530$ J/mol, being smaller than literature data (578 [14], 630 [16], 560 [17]). The phase diagram is shown in Figure 6. As for 6CB the melting line

Table 1. Transition temperatures as a function of pressure for 6CB and 7CB. $T/\mathrm{K} = a + b \cdot p/\mathrm{MPa} + c \cdot (p/\mathrm{MPa})^2$.

Transition		a	b	$10^5\, c$
6CB	$cr_I \rightarrow n$	287.21	0.258	−4.39
	$cr_{II} \rightarrow n$	259.01	0.509	−50.9
	$cr_I \rightarrow cr_{II}$	313:35	0.127	
	$n \rightarrow i$	301.23	0.390	−0.189
7CB	$cr \rightarrow n$	302.10	0.250	−10.9
	$n \rightarrow i$	314.61	0.370	−8.4

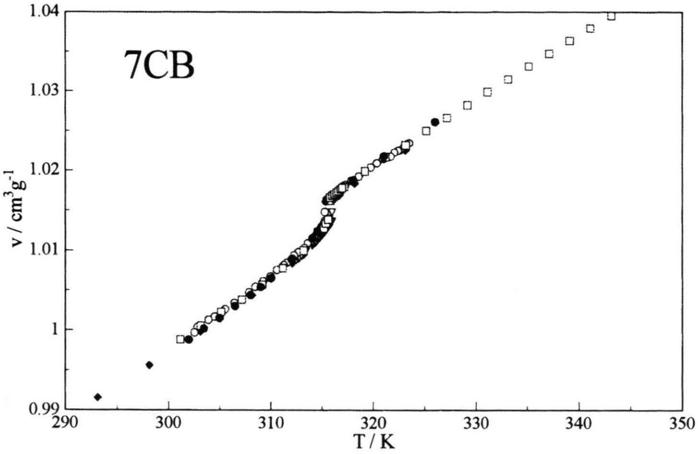

Fig. 5. Specific volumes of 7CB at atmospheric pressure, (□ this work, ● Ibrahim *et al.* [18], ▽ Dunmur *et al.* [5], ○ Łabno *et al.* [6], ◆ Orwoll *et al.* [8], △ Oweimreen *et al.* [19]).

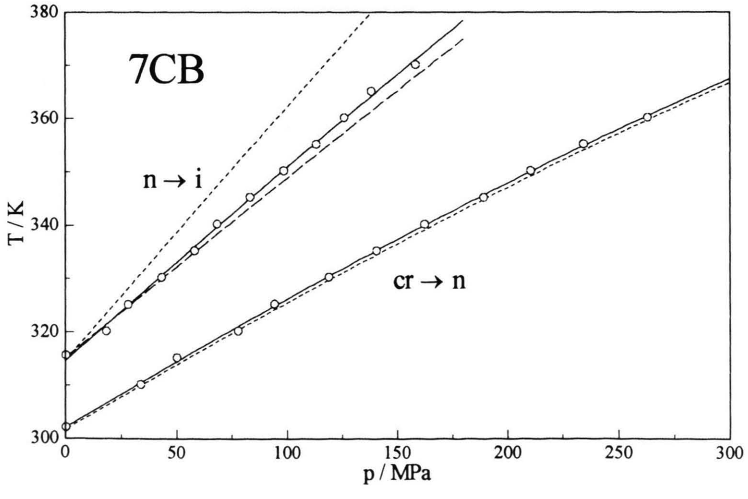

Fig. 6. Phase diagram of 7CB, —— this work, - - - - Wallis *et al.* [11], · · · · · · Shashidhar *et al.* [12].

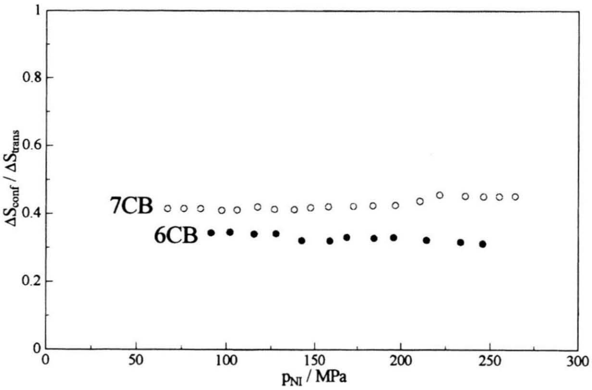

Fig. 7. Entropy separation for the nematic → isotropic transition for 6CB, and 7CB.

Table 2. Thermodynamic properties of 6CB.

Phase transition	T (K)	p (MPa)	ΔV_m (cm^3 mol^{-1})	ΔH_m (kJ mol^{-1})	ΔS_m (J mol^{-1} K^{-1})
$cr_I \rightarrow n$	287.20	0.1	22.8	25.4	88.4
	300.15	50.3	20.4	24.1	80.4
	305.15	70.6	19.4	23.5	77.0
	310.15	89.9	18.9	23.4	75.6
	315.15	111.1	17.6	22.3	70.9
	320.15	130.0	17.5	22.7	71.0
	325.15	150.6	17.1	22.7	69.9
	330.15	170.6	16.0	21.7	65.8
	335.15	192.2	13.0	18.1	53.9
$cr_{II} \rightarrow n$	340.15	199.7	8.9	9.9	29.0
	345.15	215.1	8.0	9.5	27.4
	350.15	232.9	7.6	9.8	28.1
	355.15	255.0	7.5	10.7	30.0
	360.15	272.6	7.2	11.1	30.9
$cr_I \rightarrow cr_{II}$	340.15	217.5	4.6	12.3	36.3
	345.15	240.1	4.6	12.4	36.1
	350.15	292.2	3.6	10.0	28.6
$n \rightarrow i$	302.45	0.1	0.34	0.26	0.9
	305.15	12.0	0.66	0.52	1.7
	310.15	22.6	0.54	0.43	1.4
	315.15	37.5	0.59	0.48	1.5
	320.15	47.5	0.46	0.38	1.2
	325.15	62.8	0.59	0.49	1.5
	330.15	75.3	0.28	0.24	0.7
	335.15	90.2	0.29	0.25	0.7
	340.15	100.2	0.46	0.40	1.2
	345.15	110.6	0.23	0.20	0.6
	350.15	120.6	0.19	0.17	0.5
	355.15	140.2	0.38	0.35	1.0
	360.15	150.6	0.46	0.43	1.2
	365.15	160.9	0.43	0.40	1.1
	370.15	180.4	0.35	0.33	0.9

agrees well with that reported by Shashidhar *et al.* [12], whereas the NI phase boundary agrees better with results of Wallis *et al.* [11] and Brückert *et al.* [3].

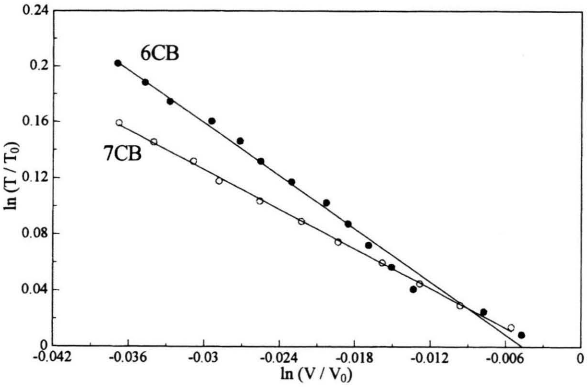

Fig. 8. Logarithm of the clearing temperature against the logarithm of the molar volume as a function of pressure for 6CB and 7CB, T_0 and V_0 refer to atmospheric pressure.

Table 3. Thermodynamic properties of 7CB.

Phase transition	T (K)	p (MPa)	ΔV_m (cm^3 mol^{-1})	ΔH_m (kJ mol^{-1})	ΔS_m (J mol^{-1} K^{-1})
$cr \rightarrow n$	302.12	0.1	23.7	28.7	94.9
	310.15	33.8	22.1	28.3	91.2
	315.15	50.2	20.9	27.5	87.4
	320.15	78	20.5	28.2	88.0
	325.15	94.4	18.3	26.0	79.9
	330.15	119.1	18.2	26.8	81.1
	335.15	140.6	18.1	27.6	82.3
	340.15	162.4	15.0	23.7	69.8
	345.15	189.1	12.3	20.4	59.1
	350.15	210.5	12.3	21.0	60.1
	355.15	234.4	12.4	22.1	62.3
	360.15	262.9	11.4	21.3	59.3
$n \rightarrow i$	315.65	0.1	0.62	0.53	1.7
	320.15	18.3	0.75	0.65	2.0
	325.15	28.1	0.72	0.64	2.0
	330.15	43.3	0.93	0.85	2.6
	335.15	58.3	0.93	0.87	2.6
	340.15	68.5	0.85	0.81	2.4
	345.15	83.4	0.89	0.86	2.5
	350.15	98.5	0.87	0.86	2.5
	355.15	113.2	0.69	0.70	2.0
	360.15	125.9	0.49	0.51	1.4
	365.15	138.2	0.51	0.54	1.5
	370.15	158.4	0.67	0.72	2.0

4. Discussion

The p, V_m, T data enable us to split the entropy change, ΔS_{tr}, into a constant-volume (or configurational) part, and a volume-dependent part [1, 8]:

$$\Delta S_{tr} = \Delta S_{conf} + (\partial S / \partial V)_T \Delta V_{tr} = \Delta S_{conf} + (\partial p / \partial T)_V \Delta V_{tr} .$$

Combining the slope of the first-order transition line ($(\partial p / \partial T)_{tr} = \Delta S_{tr} / \Delta V_{tr}$) with the slope of an isochoric line

$(\partial p/\partial T)_V$, we obtain [1]:

$$\Delta S_{\mathrm{conf}}/\Delta S_{\mathrm{tr}} = [(\partial p/\partial T)_{\mathrm{tr}} - (\partial p/\partial T)_V]/(\partial p/\partial T)_{\mathrm{tr}}.$$

This ratio is plotted in Fig. 7 for 6CB and 7CB. It is only one third for 6CB and 40-45% for 7CB; in any case, only less than half of the total entropy change ΔS_{NI} can be considered as a configurational part. In previous studies on related liquid crystals a ratio of approximately 50% was found [1, 8, 20].

Another important quantity can be derived from the pressure dependence of the nematic → isotropic phase transition. The slope $\gamma = \partial \ln T_{\mathrm{NI}}/\partial \ln V_{\mathrm{NI}}$ describes the volume dependence of the interaction coefficient: $\upsilon = \upsilon_0 V^{-\gamma}$ (υ can be derived from dielectric measurements: $\upsilon = q/S$, q = nematic potential, S = order parameter [14, 21]. A corresponding plot (Fig. 8) yields $\gamma = 6.3$ for 6CB and $\gamma = 4.7$ for 7 CB. In agreement with previous findings [1, 14], γ is significantly larger than 2, showing the inadequacy of the Maier-Saupe theory.

Acknowledgement

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