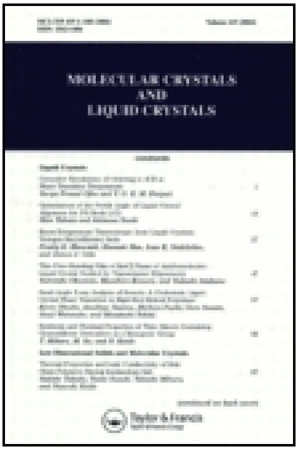

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Scaled Particle Theory of a System of Spherocylinders: Extension of Calculations to High Pressures

K. L. Savithramma [a] & N. Madhusudana [a]
[a] Raman Research Institute, Bangalore, 560080, India

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Scaled Particle Theory of a System of Spherocylinders: Extension of Calculations to High Pressures*

K. L. SAVITHRAMMA and N. V. MADHUSUDANA

Raman Research Institute, Bangalore 560080, India

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We have refined the scaled particle theory calculations on a system of spherocylinders by improving the evaluation of the angle dependent term in the expansion for the excluded volume. We present calculations on the nematic-isotropic transition properties for a hard rod system as well as a system superposed with an attractive potential of the Maier-Saupe type and subjected to different external pressures. The results are compared with the experimental data on para-azoxyanisole.

I. INTRODUCTION

The scaled particle theory (SPT) gives a reasonably good description of the nematic-isotropic (NI) transition.[1-3] Assuming the molecule to have a spherocylindrical shape and superposing an attractive potential of the Maier-Saupe type between such particles, Cotter has developed the most successful form of SPT as applied to nematic liquid crystals.[1-2] In an earlier paper[3] we have shown that her formulation leads to a good overall agreement with the experimental data on para-azoxyanisole (PAA) for spherocylinders of length to breadth ratio $x \simeq 1.75$. In the present paper we improve the model by a better evaluation of the angle dependent term in the expression for the excluded volume. Calculations based on the improved model are presented for (i) a hard rod system and (ii) a system superposed with an attractive potential of the Maier-Saupe type and at different pressures.

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II. THEORY

For a mathematical derivation of the theory, we refer to Cotter's paper.[1] The excluded volume between two spherocylinders has an angle dependent term which is proportional to $|\sin\ \theta_{ij}|$, where θ_{ij} is the angle between the long axes of the spherocylindrical molecules i and j. For the sake of simplicity Cotter assumed that

$$|\sin\ \theta_{ij}| \simeq \frac{\pi}{4} - \frac{5\pi}{32} P_2(\cos\ \theta_{ij})\,. \tag{1}$$

In the mean-field approximation, the ensemble average of $|\sin\ \theta_{ij}|$ over all possible orientations of the i and j molecules is then given by

$$\langle|\sin\ \theta_{ij}|\rangle \simeq \frac{\pi}{4} - \frac{5\pi}{32}\langle P_2\rangle^2.$$

However, as recognized by Cotter herself, this approximation leads to considerable errors, especially at lower values of θ_{ij} (see also Ref. 4). The discrepancy can be considerably reduced by including higher order terms in the expansion for $|\sin\ \theta_{ij}|$:

$$\langle|\sin\ \theta_{ij}|\rangle \simeq \frac{\pi}{4} - \frac{5\pi}{32}\langle P_2\rangle^2 - \left(\frac{3}{16}\right)^2 \pi\langle P_4\rangle^2 - \frac{65\pi}{(16)^3}\langle P_6\rangle^2 - \frac{595}{(16)^4}\pi\langle P_8\rangle^2 - \frac{617}{(16)^5}\pi\langle P_{10}\rangle^2 \tag{2}$$

The pressure P and the Gibbs energy G_c of the nematic phase are given by (see Ref. 1)

$$\frac{Pv_0}{kT} \simeq \frac{d\left[1 + d + \frac{2}{3}d^2(1 + Q - Q^2/2) + 2Rd\{1 + (1 + 2Q)d/3\}\langle|\sin\ \theta_{ij}|\rangle\right]}{(1 - d)^3} - \frac{1}{2}\frac{d^2}{v_0 kT}(\vartheta_0 + \vartheta_2\langle P_2\rangle^2) \tag{3}$$

$$\frac{G_c}{NkT} = \langle\ln f(\cos\ \theta)\rangle + \ln\left(\frac{p}{1 - d}\right) + 6d\left[1 + \frac{2R}{3}\langle|\sin\ \theta_{ij}|\rangle\right] + \frac{4d^2(1 + Q/2)(1 - Q/4 + R\langle|\sin\ \theta_{ij}|\rangle)}{(1 - d)^2}$$

$$+\frac{d\left[1 + d + \frac{2}{3}d^2(1 + Q - Q^2/2) + 2Rd\{1 + (1 + 2Q)d/3\}\langle|\sin\theta_{ij}|\rangle\right]}{(1-d)^3}$$

$$-\frac{d}{v_0 kT}(\vartheta_0 + \vartheta_2\langle P_2\rangle^2) \quad (4)$$

where $d = v_0\rho$; $v_0 = \pi r^2 l + 4\pi r^3/3$ is the volume of a spherocylinder of radius r and cylindrical height l; $Q = 2/(3x - 1)$, $R = 6(x - 1)^2/\pi(3x - 1)$, where $x = 1 + l/2R$ and ϑ_0 and ϑ_2 are the strengths of the isotropic and anisotropic interactions respectively. Further

$$f(\cos\theta_i) = \frac{\exp\left\{\frac{\vartheta_2\rho}{kT}\langle P_2\rangle P_2(\cos\theta_i) + \frac{4Rd\left[1 - (1 - Q)\frac{d}{3}\right]}{(1-d)^2}\chi(\cos\theta_i)\right\}}{\int_0^1 \exp\left\{\frac{\vartheta 2\rho}{kT}\langle P_2\rangle P_2(\cos\theta_i) + \frac{4Rd\left[1 - (1 - Q)\frac{d}{3}\right]}{(1-d)^2}\chi(\cos\theta_i)\right\}d(\cos\theta_i)} \quad (5)$$

where

$$\chi(\cos\theta_i) = \frac{5\pi}{32}\langle P_2\rangle P_2(\cos\theta_i) + \left(\frac{3}{16}\right)^2\pi\langle P_4\rangle P_4(\cos\theta_i)$$
$$+ \frac{65\pi}{(16)^3}\langle P_6\rangle P_6(\cos\theta_i) + \frac{595\pi}{(16)^4}\langle P_8\rangle P_8(\cos\theta_i)$$
$$+ \frac{617\pi}{(16)^5}\langle P_{10}\rangle P_{10}(\cos\theta_i),$$

and

$$\langle P_{2n}\rangle = \int_0^1 P_{2n}(\cos\theta) f(\cos\theta)\, d(\cos\theta) \quad (6)$$

III. RESULTS AND DISCUSSION

(a) *Hard rod system:* Results of the calculations made by retaining terms only up to $P_2(\cos\theta_{ij})$ as in the original theory due to Cotter,[1] are given in our earlier paper[3] (see also Ref. 2). Results obtained by including higher order terms up to $P_{10}(\cos\theta_{ij})$ in the expansion of $|\sin\theta_{ij}|$ (Eq. (2)) are given in Table I for x ranging from 1.25 to 6.0. We have not listed $\langle P_6\rangle$, $\langle P_8\rangle$ and $\langle P_{10}\rangle$ in the table since they are not experimentally accessible. Comparing the results with the corresponding results obtained from the two-terms expansion of $|\sin\theta_{ij}|$ given in Ref. 3, we find that the long range order parameter $\langle P_2\rangle$ increases by ~30% for x lying between 1.5 and 3. Indeed, Cotter herself noted that excluding higher order terms in the expansion of $|\sin\theta_{ij}|$ would underestimate the value of $\langle P_2\rangle$. Further d_{nem} decreases slightly whereas $\Delta\rho/\bar{\rho}$ [where $\bar{\rho} = (\rho_{\mathrm{nem}} + \rho_{\mathrm{iso}})/2$] increases by a factor of two. Correspondingly the entropy change at T_{NI} given by

$$\frac{\Delta S}{Nk} = -\frac{Pv_0}{kT}\left(\frac{d_{\mathrm{nem}} - d_{\mathrm{iso}}}{d_{\mathrm{nem}}d_{\mathrm{iso}}}\right)$$

also increases by the same factor. dT/dP (calculated by using the Clausius-Clapeyron equation) increases slightly whereas the compressibility factor Pv_0/kT decreases. The variations of all the properties as functions of x are similar to those obtained by using the two terms expansion for $|\sin\theta_{ij}|$.

(b) *System superposed with an attractive potential:* In this case, the theory has two adjustable parameters, viz., ϑ_0 and ϑ_2. We select the values of ϑ_0 and ϑ_2 such that T_{NI} and the packing fraction of the nematic phase (d_{nem}) at T_{NI} are equal to 409 K and 0.62 respectively, corresponding to the experimental values for para-azoxyanisole (PAA). The method of calculation is given in detail in Ref. 3. The change in internal energy ΔU and entropy change ΔS at T_{NI} are obtained by using the relations

$$\frac{\Delta U}{NkT} = -\frac{\vartheta_0}{2v_0kT}[d_{\mathrm{nem}} - d_{\mathrm{iso}}] - \frac{\vartheta_2}{2v_0kT}d_{\mathrm{nem}}\langle P_2\rangle^2$$

$$\frac{\Delta S}{Nk} = \frac{\Delta U}{NkT} + \frac{Pv_0}{kT}\left[\frac{d_{\mathrm{iso}} - d_{\mathrm{nem}}}{d_{\mathrm{iso}}d_{\mathrm{nem}}}\right].$$

TABLE I

Results for hard spherocylinders

Properites at T_{NI}	x							
	1.25	1.50	2.00	2.50	3.00	4.00	5.00	6.00
$\langle P_2\rangle$	0.5532	0.5700	0.6009	0.6256	0.6448	0.6722	0.6905	0.7039
$\langle P_4\rangle$	0.2304	0.2449	0.2740	0.2986	0.3136	0.3489	0.3705	0.3867
d_{nem}	0.8756	0.7943	0.6861	0.6127	0.5575	0.4776	0.4207	0.3774
d_{iso}	0.8753	0.7930	0.6817	0.6050	0.5467	0.4618	0.4014	0.3558
$\Delta\rho/\bar{\rho}$	0.0003	0.0016	0.0063	0.0126	0.0196	0.0336	0.0468	0.0588
$\Delta S/Nk$	0.4587	0.4785	0.5217	0.5589	0.5895	0.6359	0.6695	0.6950
dT/dP K/kbar	1.36	7.04	29.55	61.84	100.16	187.68	283.86	385.24
Pv_0/kT	1228.94	236.83	56.40	26.95	16.64	8.88	5.87	4.33

Various transition properties for a range of values of x calculated by using the $|\sin \theta_{ij}|$ expansion as given in Eq. (2) are given in Table II. (Again $\langle P_6 \rangle$, $\langle P_8 \rangle$ and $\langle P_{10} \rangle$ are not tabulated.) The experimental data on PAA[5-7] are also given in the table for comparison.

Comparing the results with those obtained by restricting $|\sin \theta_{ij}|$ to first two terms only,[1,3] as in the original theory due to Cotter,[1] we notice the following differences. For spherical molecules ($x = 1$) with an angle independent excluded volume, obviously there is no change in the calculated values. As x is increased, the inclusion of higher order terms leads to an increase in the strength of the transition: the values of $\langle P_2 \rangle$, $\Delta\rho/\bar{\rho}$ and $\Delta U/NkT$ go up, the relative increase being higher for larger values of x. Further, we also see that the internal energy change increases considerably as x is increased which is a trend to be expected. We can note here that if the expansion of $|\sin \theta_{ij}|$ is confined to the $P_2(\cos \theta_{ij})$ term, a reverse trend, though quite weak, is observed (see Ref. 3), bringing out the importance of including the higher order terms in the expansion. Comparing the calculated values of $\langle P_2 \rangle$, $\Delta\rho/\bar{\rho}$ and $\Delta U/NkT$ with the experimental data on PAA, a value of x lying between 1.2 and 1.5 would appear to give reasonable agreement, even though the calculated values of both $\langle P_2 \rangle$ and $\Delta U/NkT$ would still be considerably higher than the experimental data. However, we know from our earlier calculations that

$$\gamma = (\partial \ln T/\partial \ln V)_{\langle P_2 \rangle}$$

would agree with the experimental value on PAA for $x \simeq 1.75$. Further, the (dT/dP) value calculated using the Clausius-Clapeyron equation would also be in better agreement with the data on PAA for $x \simeq 1.75$ than for $x \simeq 1.2$–1.5. Hence $x = 1.75$ is the value which gives the best *overall* agreement with experimental results. Consequently we have chosen $x = 1.75$ for our calculations on the phase transition properties at high pressures. The results are presented in the next section.

(c) *Results at high pressures:* The theory enables us to study the properties such as T_{NI}, molar volume of nematic (V_n) and isotropic (V_i) phases, entropy change (ΔS), internal energy change (ΔU) at the NI transition, etc., as functions of pressure. We have studied these properties as the pressure is changed from one bar to 6.5 *k*bar for $x = 1.75$. To calculate the phase transition properties at a pressure of say n bar, we proceed as follows. For $x = 1.75$, fixing ϑ_0 and ϑ_2 to the appropriate values listed in Table II and starting from some value of T and d, the consistency conditions for the long range order parameters (Eq. (6)) are satisfied. The pressure of the nematic phase is calculated from Eq. (3). The assumed value of d is adjusted by an iterative procedure to make the pressure equal to n bar. The pressure of the isotropic phase calculated by setting $\langle P_{2n} \rangle = 0$

TABLE II

Results at 1 atmosphere for spherocylinders with an attractive potential

Properties at T_{NI}	x								
	2.45	2.20	2.0	1.80	1.75	1.50	1.20	1.0	expt.
ϑ_0/ϑ_2	1571.86	90.38	49.61	33.48	30.88	22.17	17.02	15.68	
ϑ_2/v_0k	38.704	649.78	1142.08	1625.69	1743.80	2303.96	2842.88	2999.81	
T_{NI} K	409	409	409	409	409	409	409	409	409
$\langle P_2 \rangle$	0.6574	0.5895	0.5440	0.5070	0.4990	0.4659	0.4407	0.4345	0.36
$\langle P_4 \rangle$	0.3319	0.2562	0.2119	0.1792	0.1725	0.1461	0.1275	0.1230	0.07
d_{nem}	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
d_{iso}	0.6080	0.6117	0.6138	0.6154	0.6157	0.6170	0.6181	0.6184	
$\Delta\rho/\bar{\rho}$	0.0195	0.0135	0.0100	0.0075	0.0070	0.0048	0.0031	0.0026	0.0035
$\Delta U/NkT$	0.9017	0.7658	0.6853	0.6253	0.6130	0.5645	0.5305	0.5227	0.17
dT/dP K/kbar	58.60	47.53	39.59	32.40	30.71	22.91	15.52	13.32	47

in Eq. (3) is also equated to n bar and d_{iso} is calculated. Then the Gibbs energies of both the nematic and isotropic phases are calculated by using Eq. (4). The assumed value of T is adjusted by an iterative procedure to equalize the Gibbs energy of both the phases. This procedure has been repeated for n ranging from 1 to 6500. The different properties calculated as functions of pressure are tabulated in Table III.

TABLE III

Results at various pressures

P_n bar	$V_n \frac{\text{cm}^3}{\text{mol}}$	$\frac{\Delta V}{V_n} \times 10^{-3}$	$\frac{\Delta S}{Nk}$	$\Delta U \frac{kJ}{\text{mol}}$	$\langle P_2 \rangle$	$\langle P_4 \rangle$
1	223.43	7.00	0.613	2.085	0.4990	0.1725
250	222.45	6.75	0.606	2.061	0.4993	0.1729
500	221.53	6.54	0.600	2.041	0.4997	0.1733
750	220.68	6.35	0.594	2.025	0.5001	0.1738
1000	219.89	6.18	0.589	2.011	0.5005	0.1742
1250	219.14	6.03	0.585	1.999	0.5010	0.1747
1500	218.45	5.90	0.581	1.990	0.5015	0.1752
1750	217.79	5.80	0.578	1.981	0.5019	0.1757
2000	217.17	5.68	0.574	1.974	0.5026	0.1764
2500	216.03	5.49	0.569	1.962	0.5034	0.1772
3000	215.00	5.33	0.564	1.954	0.5044	0.1781
3500	214.07	5.20	0.560	1.948	0.5054	0.1791
4000	213.21	5.08	0.556	1.944	0.5064	0.1800
4500	212.42	4.98	0.553	1.941	0.5074	0.1810
5000	211.69	4.89	0.550	1.939	0.5083	0.1819
5500	211.01	4.81	0.548	1.938	0.5092	0.1827
6000	210.38	4.74	0.545	1.938	0.5102	0.1836
6500	209.79	4.68	0.543	1.938	0.5110	0.1845

We have plotted the pressure P and dT/dP as functions of T_{NI} in Figure 1. Experimental data on PAA for the variation of T_{NI} with P are also shown for the sake of comparison. As we can see from Figure 1, the calculated value of $dT/dP \simeq 30\ K/k$bar up to 1 $k$bar, whereas the experimental value is $\simeq$ 47 for PAA.[8-12] The ratio dT/dP decreases as T increases which is in qualitative agreement with the experimental data on PAA,[8-10] N-p-methoxybenzylidene-p'-butylaniline (MBBA),[13,14] p-n-pentyl-p'-cyanobiphenyl (5CB)[13] and N-p-ethoxybenzylidene-p'-butylaniline (EBBA).[10,14] Variation of the molar volume of the nematic phase V_n as a function of pressure is in good agreement with the experimental result.[9,10] The theoretical values of $\Delta V/V_n$ ($\Delta V = V_n - V_i$), $\Delta U/NkT$ and $\Delta S/Nk$ are much larger than the experimental values, but their variations with P are in qualitative agreement with the experimental trends.

Experiments on PAA[12] from 1 to 2 $k$bar shows that $\langle P_2 \rangle$ is constant along the NI transition line. The theoretical value of $\langle P_2 \rangle$ is almost constant, increasing very slightly from 0.499 to 0.503 over the same range of pressures (see Table III). For 5CB and MBBA, Horn and Faber[16] observed that $\langle P_2 \rangle$ is not constant along the NI transition line. Indeed in these cases $\langle P_2 \rangle$ decreases as the pressure is increased, which is a trend opposite to that given by the theory.

The value of γ evaluated by taking the slope of the curve obtained by plotting ln T vs ln V_n is found to be $\simeq$ 4 (see Figure 2) for pressures

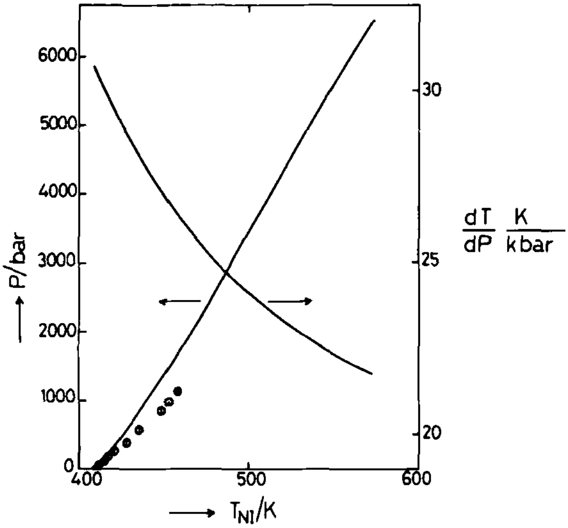

FIGURE 1 Variation of P and dT/dP as functions of T_{NI}.

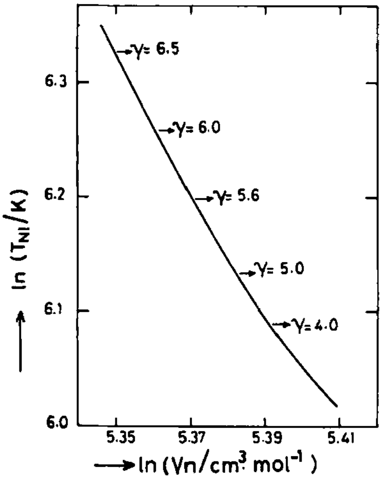

FIGURE 2 Variation of ln T_{NI} as a function of ln V_n.

ranging from 1 to 2 *k*bar, which is in very good agreement with the experimental result on PAA.[12] However, as the pressure is increased, say to 6 *k*bar, the theoretical value of γ increases to $\simeq$ 6.5 (see Figure 2). Experimental values of γ has been obtained for MBBA also, but the values quoted by different authors vary from 2.6 to 5.3.[13–15]

In conclusion, the SPT calculations are in broad agreement with the experimental results on PAA at high pressures.

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References

1. M. A. Cotter, *J. Chem. Phys.*, **66**, 1098 (1977).
2. M. A. Cotter, in 'The Molecular Physics of Liquid Crystals', Ed. G. R. Luckhurst and G. W. Gray, 1979, p. 169.
3. K. L. Savithramma and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **62**, 63 (1980).
4. K. L. Savithramma and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **74**, 243 (1981).
5. H. Arnold, *Z. Phys. Chem.*, **226**, 146 (1964).
6. A. P. Kapustin and N. T. Bykova, *Soviet Phys. Crystallogr.*, **11**, 297 (1966).
7. W. Maier and A. Saupe, *Z. Naturforsch.*, **159**, 287 (1960).
8. S. Chandrasekhar, S. Ramaseshan, A. S. Reshamwala, B. K. Sadashiva, R. Shashidhar, and V. Surendranath, *Proc. Int. Liq. Cryst.*, Conf., Bangalore, 1973, Pramana Suppl. 1, p. 117.

9. S. M. Stishov, V. A. Ivanov, and V. N. Kachinskii, *JETP Lett.*, **24,** 297 (1976).
10. V. N. Kachinskii, V. A. Ivanov, A. N. Zisman, and S. M. Stishov, *JETP,* **48,** 273 (1979).
11. S. Chandrasekhar and R. Shashidhar, *Advances in Liquid Crystals,* **4,** 83 (1979).
12. J. R. McColl, *Phys. Lett.,* **38A,** 55 (1972).
13. R. G. Horn, *J. de Physique,* **39,** 167 (1978).
14. E. Kuss, *Mol. Cryst. Liq. Cryst.,* **47,** 71 (1978).
15. P. H. Keyes and W. B. Daniels, *J. de Physique,* **40,** C3-380 (1979).
16. R. G. Horn and T. E. Faber, *Proc. Roy. Soc.,* London, **A368,** 199 (1979).