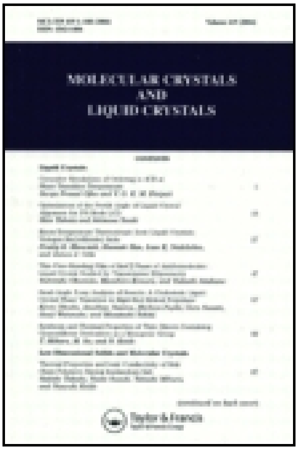

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Determination of the Parameters in the Pseudo-Potential for Nematic Liquid Crystals

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The Maier-Saupe theory[1] of the order-disorder transition in nematogens has been extended to allow for a rigorously correct form of the anisotropic intermolecular potential.[2] The potential energy of one rod-like molecule in the field generated *via* the interaction with its neighbours is found to be

$$U(\cos\theta) = \sum_{L(\text{even})} \bar{u}_L \bar{P}_L P_L(\cos\theta)\,, \tag{1}$$

where θ is the angle made by the rod axis with the director. $P_L(\cos\theta)$ denotes the Lth Legendre polynomial and its ensemble average $\bar{P}_L$ is a measure of the orientational order in the mesophase. The expansion coefficients $\bar{u}_L$ are defined by.

$$\bar{u}_L = \rho\int \Sigma u_{LL:n}(r) g(r)\,\mathrm{dr}, \tag{2}$$

where ρ is the number density, $g(r)$ is the radial distribution function and the $u_{LL:n}(r)$ determine the distance dependence of the intermolecular potential.[2] Measurements[3] of the orientational order $\bar{P}_2$ for 4,4′-dimethoxyazoxybenzene, at constant volume, reveal that the volume dependence of the coefficients $\bar{u}_L$ is given by[4]

$$\bar{u}_L = \bar{u}_L^0\ V^{-4}. \tag{3}$$

In addition the temperature dependence of $\bar{P}_2$ at constant pressure, for the same nematogen, is found to be accurately predicted when the potential, or pseudo-potential, in Eq. (1) is restricted to just the first two terms.[2] However the parameters $\bar{u}_2^0$ and $\bar{u}_4^0$ were determined by assuming that the volume did not change at the nematic-isotropic transition point. Consequently the transition temperature was identified by finding when the molar orientational Helmholtz free energy

$$A_m = -\frac{N}{2}\left\{\bar{u}_2\bar{P}_2^2 + \bar{u}_4\bar{P}_4^2\right\} - RT\ln Z, \qquad (4)$$

vanishes. In this expression N is the Avagadro number, R is the gas constant and Z is the orientational partition function.[2] The parameter $\bar{u}_4$ or more precisely the ratio $\bar{u}_4/\bar{u}_2$ was then varied until the predicted orientational order $\bar{P}_2$, calculated from the consistency condition

$$\bar{P}_2 = \int P_2(\cos\theta)\exp\left\{-U(\cos\theta)/kT\right\}\sin\theta\,d\theta/Z, \qquad (5)$$

agreed with the experimental value.[2] This procedure is not entirely satisfactory since the volume of real nematogens does increase slightly at the nematic-isotropic transition. This Research Note examines the effect of allowing for the volume change on the agreement between theory and experiment as well as on the magnitude of the parameters $\bar{u}_2^0$ and $\bar{u}_4^0$.

Since the measurements of the orientational order $\bar{P}_2$ are invariably made at constant pressure the transition point must be identified by determining when the orientational Gibbs free energy vanishes. According to the derivation of the pseudo-potentional in Eq. (1) the contributions of the scalar and anisotropic intermolecular interactions to the free energy are independent. The total molar Gibbs free energy at the nematic-isotropic transition is therefore

$$G_m = A_m^0(V_1, T_K) + A_m(V_1, T_K) + P_K V_1, \qquad (6)$$

where P_K is the pressure, V_1 is the volume of the mesophase and A_m^0 is the contribution of the scalar interactions to the molar Helmholtz free energy. Similarly the molar Gibbs free energy of the isotropic phase, at the same temperature and pressure, is

$$G_m = A_m^0(V_2, T_K) + P_K V_2, \qquad (7)$$

where V_2 is the molar volume of the isotropic liquid. At the phase transition these two Gibbs functions are equal and so the orientational Helmholtz free energy is given by

$$A_m(V_1, T_K) = A_m^0(V_2, T_K) - A_m^0(V_1, T_K) + P_K\Delta V, \qquad (8)$$

where ΔV is $(V_2 - V_1)$. Application of thermodynamic arguments[1] shows that the orientational Helmholtz free energy does not vanish at the transition but is given by

$$A_m(V_1, T_K) = -\,\Delta V(\partial A_m/\partial V)_{T=T_K}/2, \tag{9}$$

and in terms of the two parameter pseudo-potential this reduces to

$$A_m(V_1, T_K) = \frac{\Delta V}{V_K}\,\frac{N}{RT_K} + \left\{\bar{u}_2\bar{P}_2{}^{(K)2} + \bar{u}_4\bar{P}_4{}^{(K)2}\right\}. \tag{10}$$

The determination of the parameters $\overline{u}_2^0$ and $\overline{u}_4^0$ now demands a knowledge of $\Delta V/V_K$ but proceeds in an exactly analogous manner to the previous calculation.

The temperature dependence of $\bar{P}_2$ together with the change in the relative volume $\Delta V/V_K$ at the transition point are available for the five nematogens listed in the table. We have therefore determined the two parameters in the pseudo-potentials for these nematogens using Eq. (10) together with the observed order $\bar{P}_2$ and obtained the results given in the table. The temperature dependence of $\bar{P}_2$ calculated with these parameters is found to be in good agreement with the experiment for all of the nematogens and this is shown for 2,4-nonadienic acid in the figure. Two points concerning the magnitude of the parameters merit

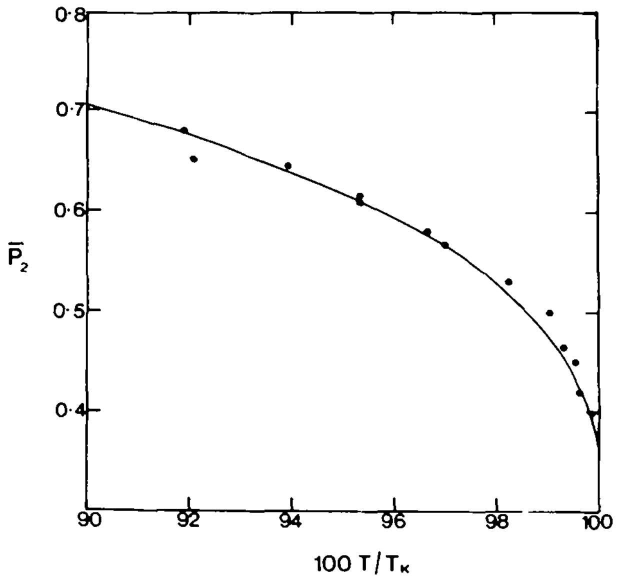

FIGURE 1 The orientational order $\bar{P}_2$ for 2,4-nonadienic acid plotted as a function of the reduced temperature T/T_K.

TABLE I

The parameters in the pseudo-potentials

Nematogen	Transition temperature (T_K/K)	$\Delta V/V_K$ ($\times 10^4$)	$\Delta V \neq 0$		$\Delta V \neq 0$		References	
			$\bar{u}_2^0/kT_K V_K^4$	$\bar{u}_4^0/\bar{u}_2^0$	$\bar{u}_2^0/kT_K V_K^4$	$\bar{u}_4^0/\bar{u}_2^0$	$\Delta V/V_K$	$\bar{P}_2$
2,4-nonadienic acid	326.5	47	4.534	−0.075	4.568	−0.083	5	5
2,4-undecadienic acid	335.5	39	4.532	−0.067	4.573	−0.099	5	5
4,4′-dimethoxyazoxybenzene	408.0	35	4.567	−0.195	4.593	−0.187	1	6
4,4′-diethoxyazoxybenzene	438.0	60	4.430	0.150	4.493	0.116	7	6
anisaldazine	454.0	54	4.532	−0.100	4.583	−0.140	8	9

some comment. The first is that the parameter $\bar{u}_2$ is directly proportional to the product $T_K V_K^2$ to within a few percent and so accurately reflects the thermal stability of the mesophase. Secondly the ratio $|\bar{u}_4^0/\bar{u}_2^0|$ is always much less one which demonstrates the rapid convergence of this expansion of the pseudo-potential. Such convergence is in accord with model calculations of the un-averaged coefficients $u_{LL:n}(r)$ provided the intermolecular separation r is greater than about 1.3 times the molecular dimensions. However we must await the results of similar analyses for many nematogens before the relationship between molecular structure and $\bar{u}_4^0$ becomes apparent.

The temperature dependence of $\bar{P}_2$ was also analysed with the assumption of zero volume change at the phase transition and the derived parameters are shown in the table. The agreement between the calculated and experimental temperature dependence of the orientational order was again found to be rather good. In addition the values for the approximate parameter $\bar{u}_2$ are within 1 or 2% of the correct result. However, as we might have expected, the discrepancies in the ratio $\bar{u}_4^0/\bar{u}_2^0$ are much greater and can be as high as 40%. We can conclude therefore that when the relative volume change at the transition point is available it should be used in conjunction with the orientational order to determine the parameters in the pseudo-potential. However if the volume change is not known then the assumption that it is zero will not lead to any serious error in $\bar{u}_2^0$ although the error in $\bar{u}_4^0$ may be considerable.

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References

1. Maier, W. and Saupe, A., *Z.Naturforsch.* **13a**, 564 (1958); **14a**, 882 (1959); **15a**, 287 (1960).
2. Humphries, R. L., James, P. G. and Luckhurst, G. R., *J.C.S.Faraday II*, 68, 1031 (1972).
3. McColl, J. R. and Shih, C. S., *Phys.Rev.Letters* 29, 85 (1972).
4. Humphries, R. L. and Luckhurst, G. R., *Chem.Phys.Letters* 17, 514 (1972).
5. Maier, W. and Markau, K., *Z. Physik. Chem.* 28, 190 (1961).
6. Rowell, J. C., Phillips, W. D., Melby, L. R. and Panar, M., *J.Chem.Phys.* 43, 3442 (1965).
7. Bauer, E. and Bernamont, J., *J.Phys.Radium* 7, 19 (1936).
8. Conrat, F., *Z.Physik.* 10, 202 (1909).
9. Madhusudana, N. V., Shashidhar, R. and Chandrasekhar, S., *Mol.Cryst. and Liq.Cryst.* 13, 61 (1971).