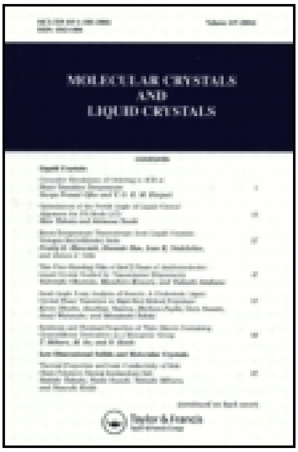

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A Theory of Melting of Molecular Crystals III. The Liquid Crystalline Phase

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A Theory of Melting of Molecular Crystals

III. The Liquid Crystalline Phase

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The Pople and Karasz theory of melting of molecular crystals was modified using the third repulsive energy parameter in our previous paper. The new modified model is applied to study thermodynamics of solid–nematic and nematic–isotropic liquid transitions. The thermodynamic properties are evaluated by the Bragg-Williams approximation. The results are compared with the predictions of the original Pople and Karasz theory and its volume dependence modification, as well as some experimental data.

Keywords: Modified Pople and Karasz theory, liquid crystals, solid–nematic and nematic–isotropic liquid transitions.

In this series of papers,[1,2] (hereafter referred to as paper I and paper II) we have modified the Pople and Karasz theory of melting of molecular crystals[3,4] and studied its equilibrium behaviour. Also, the thermodynamic properties of melting and solid–solid transitions were studied, and compared with the available experimental data. In the present letter, we shall extend the calculations on the melting transition (reported in paper I) and the solid–solid transition (reported in paper II) to the solid–nematic and nematic–isotropic liquid transitions.

Since the modified model was described extensively in paper I, we shall only give a brief summary here. The modified statistical theory is a simple extension of the Pople and Karasz theory which is based on the Lennard-Jones and Devonshire theory[5,6] by including the orientational order as well as positional order. In the theory, molecules may occupy sites on one of two equivalent interpenetrating lattices of N-sites, which we shall refer to as A-sites and B-sites, in order to allow for the possibility of increasing disorder in the positions of molecules in a crystal. It is also assumed that the molecule can take up one of two orientations on any site. This means that there are four possibilities for any molecule which can be denoted by A_1, A_2, B_1 and B_2. If all molecules occupy sites and orientations of the same type, say A_1-sites, the state is

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perfect (periodic) order. If all four configurations are equally populated, the system is a completely disordered system (or the liquid phase). It is assumed that each A-site is surrounded by z equivalent neighbouring B-sites and each B-site by z A-sites. Also the number of A-sites closest to any given A-site or the number of B-sites any given B-site is z'. There are three repulsive energies in the theory: The first one is, W, the interaction between molecules which are on different sites with the same orientations, the second one is W', the interaction between molecules on the same sites with different orientations, and the third one is, W'', the interaction between molecules on the different sites and also different orientations. Thus, zW is the energy needed to transfer the molecule from one site to the others with the same orientation, e.g., from A_1 to B_1. $z'W'$ is the energy required to turn out the molecule from one orientation to the other on the same site, e.g., from A_1 to A_2 when the remainder of the orientation is A_1. Interactions between more distant neighbours are neglected. Since W'' is associated with the positional and orientational energies, it should be combined with zW and $z'W'$. We simply use the arithmetic mean, including the adjustable parameter r. The reason including the r factor in papers I and II is to obtain better agreement with experimental data. Thus, W'' is defined as

$$W'' = r\left(\frac{zW + z'W'}{2}\right). \tag{1}$$

In order to solve the statistical problem, two long-range order parameters are introduced as follows: (1) the degree of positional order Q, which is the fraction of molecules occupying the A-sites, and (2) the orientational order S, defined as a fraction of molecules in one orientation. Using the Bragg-Williams approximation,[7] the two self-consistent equations in terms of Q and S are obtained as

$$\begin{aligned} \ln\frac{Q}{1-Q} &= \frac{zW}{2kT}(2Q-1)\{[1-2S+2S^2)+rS(1-S)] + vS(1-S)(r-2)\}, \\ \ln\frac{S}{1-S} &= \frac{zW}{kT}(2S-1)\{Q(1-Q)(r-2) + v[(1-2Q+2Q^2)+rQ(1-Q)]\}, \end{aligned} \tag{2}$$

where $v = (z'W'/zW)$ is a measure of the relative energy barriers for the rotation of a molecule and for its diffusion to an interstatial site.

In the calculation, we use two interpenetrating face-centred cubic lattices, hence $z = 6$, $z' = 12$. These two non-linear algebraic equations are solved by using the Newton-Raphson method and were discussed extensively in paper I. Calculations are obtained for $r = 1.6$, because we have seen that the agreement between our theory and the experimental data is better around $r = 1.6$ in papers I and II. As a summary: For small values of $v (v < 0.579)$ first S disappears as the reduced temperature, kT/zW, increases then Q disappears (see Fig. 1a in ref. 1). This is the case for a compact, globular molecular characteristic of plastic crystals.[8] For $v = 0.579$, orientational and positional disorder occur at the same reduced temperature corresponds to oridinary melting (see Fig. 1b in ref. 1). For $v > 0.579$, this case looks like the case of $v < 0.579$, except that the behaviour of S and Q are interchanged, i.e., first Q disappears as the reduced temperatures increase then S disappears, see Figure 1. It corresponds to a high orientational barrier (or low translational barrier), behaviour which at first glance appears similar to that of a nematic liquid crystal is obtained. It is worthwhile to mention that one cannot obtain a complete picture of the transitions from plots like Figure 1, therefore it is necessary to examine the theoretical isotherms.

The isotherms are obtained by evaluating the pressure as a function of volume, temperature, v and r. The pressure can be conveniently split in two parts

$$P = P_o + P_d, \tag{3}$$

where $P_o = -(\partial F_o/\partial V)_T$ and $P_d = -(\partial F_d/\partial V)_T$. The first part, P_o, gives the contribution due to the completely ordered solid, and the second, P_d, gives the contribution

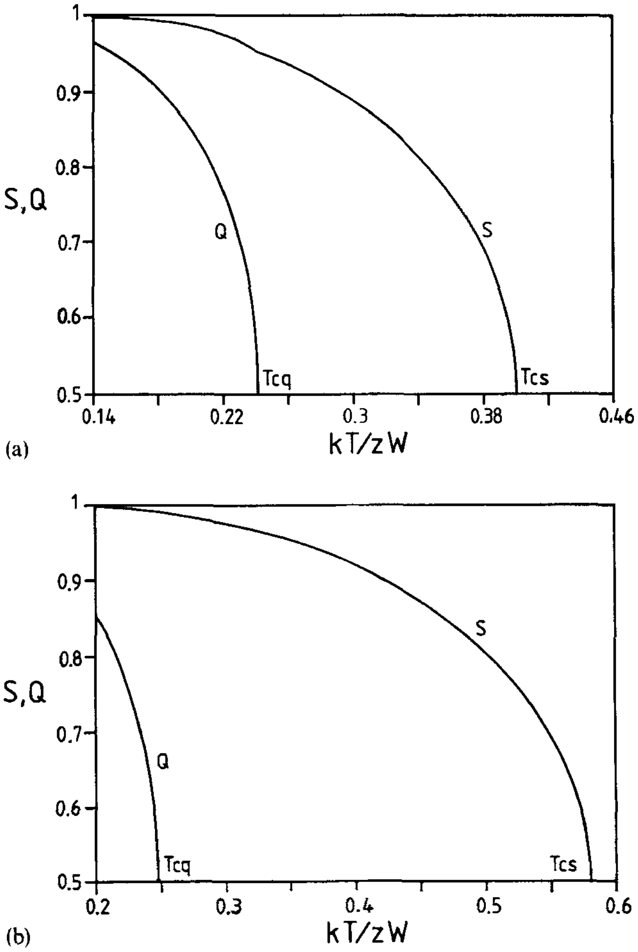

FIGURE 1 Variation of the positional order Q and the orientational order S with the reduced temperatue kT/zW. Tcq and Tcs are the critical reduced temperatures for Q and S respectively ($r = 1.6$). a) $v = 1.0$; b) $v = 1.4$.

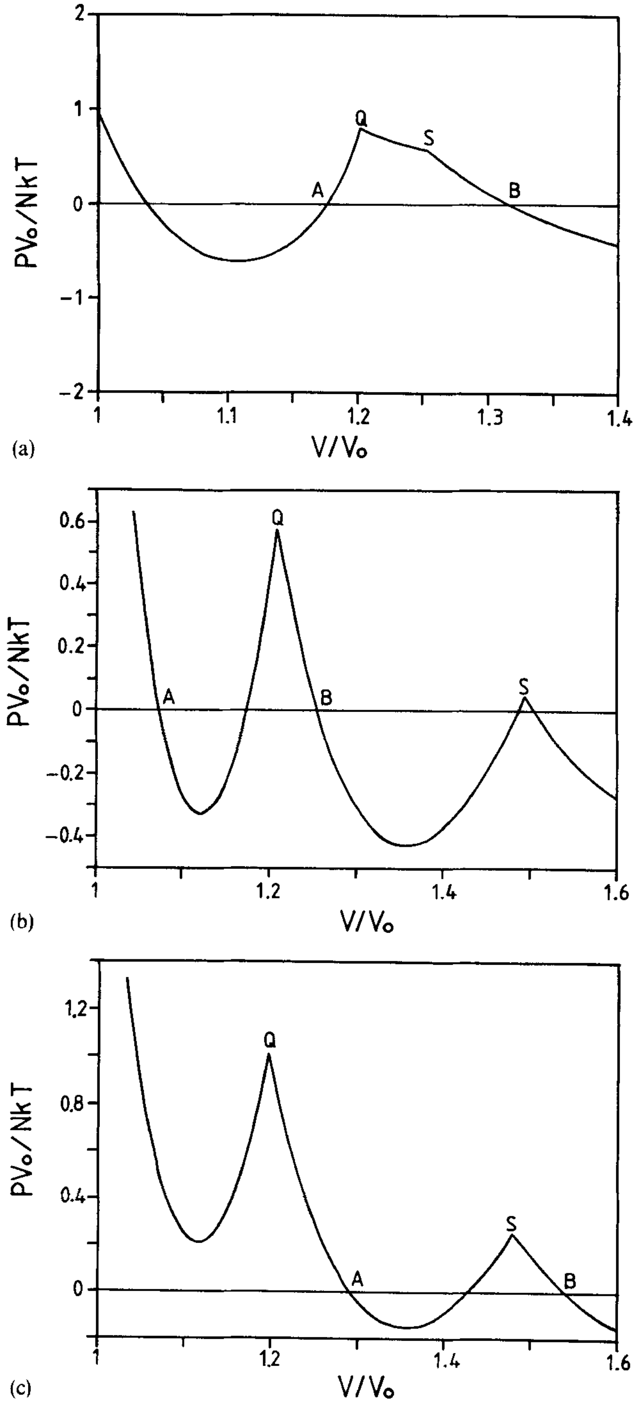

FIGURE 2 Theoretical isotherms ($r = 1.6$). a) $v = 0.7$ and the melting temperature, kT/ε, is 0.632; b) $v = 1.4$ and the solid–nematic transition, kT/ε, is 0.683; c) $v = 1.4$ and the nematic–isotropic liquid transition, kT/ε, is 0.711.

due to disordering. The pressure and other therodynamic functions associated with the partition function for a completely ordered system have been tabulated by Wentorf *et al.*[9] on the basis of a 6–12 intermolecular potential and three shell spherically smoothed cell fields. These tabulated values were used, and when necessary were extrapolated to lower temperatures. To calculate the "disordered" part of the thermodynamic fuction, the volume dependence of W and W' are specified. Following paper I we take W/W' independent of volume and

$$\begin{aligned} W &= W_o\left(\frac{V_o}{V}\right)^4 \\ W_o/\varepsilon &= 0.977 \end{aligned} \tag{4}$$

where V_o is the standard volume if the molecules are placed on a f.c.c. lattice with a nearest distance of $2^{1/6}\,r_o$, r_o is the separation for zero interaction and ε is the energy minimum of the intermolecular potential. The pressure P_d can be found as[1]

$$\begin{aligned} \frac{P_d V_o}{NkT} = -4\left(\frac{V_o}{V}\right)\left(\frac{zW}{kT}\right)\{&[(1-2S+2S^2)+rS(1-S)Q(1-Q) \\ &+\nu[(1-2Q+2Q^2)+rQ(1-Q)]S(1-S)\} \end{aligned} \tag{5}$$

This equation gives $P_d V_o/NkT$ as a function of (V/V_o), (kT/ε) and r, so that by adding to $P_o V_o/NkT$, the complete isotherm is obtained at zero pressure as is done in papers I and II, see Figure 2. In the figure, the sigmoid portions of the curve correspond to phase transition, i.e. two phase will be in equilibrium at a given pressure when the areas enclosed by the curve above and below the pressure line are equal.

Figure 2a illustrates the isotherm for melting (solid–liquid, S–L) transition temperature for $\nu = 0.7$, $r = 1.6$. The transition occurs $kT/\varepsilon = 0.63\,2$, the point A corresponds to

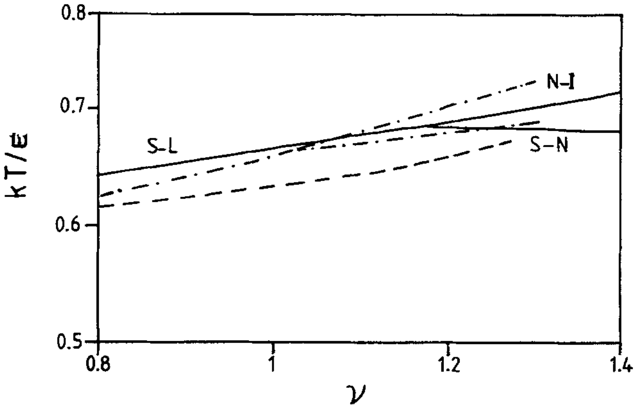

FIGURE 3 Reduced transition temperatures of solid–nematic (S–N) and nematic–isotropic liquid (N–I) transitions as functions of $\nu(r = 1.6)$; ———— Present theory; – – – – – Pople and Karasz; –·–·– Chandrasekhar, Shashidhar and Tara

the solid ($Q = 0.978$, $S = 0.995$) with the long-range order both in positions and orientations and B to the liquid ($Q = 0.5, S = 0.5$). Figure 2b illustrates solid–nematic (S–N) transition isotherm for $v = 1.4$ and $r = 1.6$. The transition temperature is found $kT/\varepsilon = 0.683$. The point A corresponds to solid ($Q = 0.948, S = 0.999$) and B to the nematic liquid crystal ($Q = 0.5, S = 0.979$). Finally, keeping v values constant, namely $v = 1.4$ and increasing the temperature, nematic–isotropic liquid (N–I) transition is found at $kT/\varepsilon = 0.711$, see Figure 2c. In the Figure, A corresponding to a nematic phase ($Q = 0.5, S = 0.959$) and B to isotropic liquid with $Q = 0.5$, $S = 0.5$.

By investigating various isotherms in this way, the reduced temperature, entropy and volume change of transition as functions of v are shown in Figure 3–5, together with the values given by the Pople-Karasz theory and its volume dependence modification studied by Chandrasekhar, Shashidhar and Tara[10,11]. It is seen that the three theories give very nearly the same results for $v < 0.975$. Moreover the present and the Chandrasekhar, Shashidhar and Tara theories give nearly the same results for $v > 0.975$. It should be noted that the reduced temperature, entropy and volume change of S–L transitions for lower values of v are given in paper I and S–S transitions are extensively studied in paper II.

The theoretical results of entropy and volume change of transitions for a few v are given along with available data for some compounds[10] in Table 1. From Table 1, one can see that as far as the solid–nematic transition is concerned, three theories give

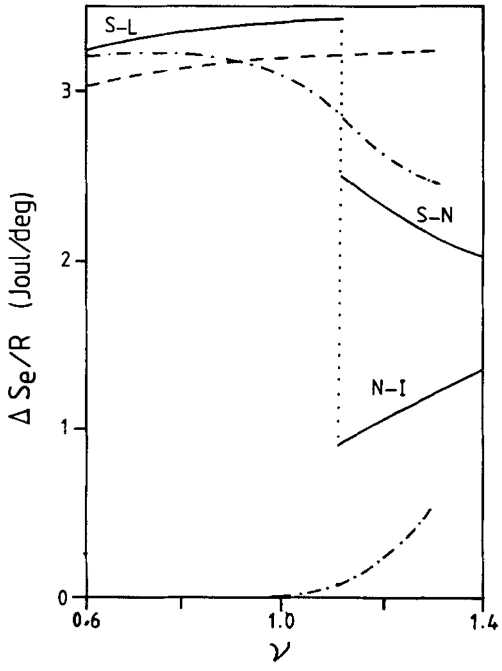

FIGURE 4 Entropy changes of solid–nematic (S–N) and nematic–isotropic-liquid (N–I) transitions as functions of $v(r = 1.6)$; ——— Present theory; - - - - - Pople and Karasz; –·–·– Chandrasekhar, Shashidhar and Tara.

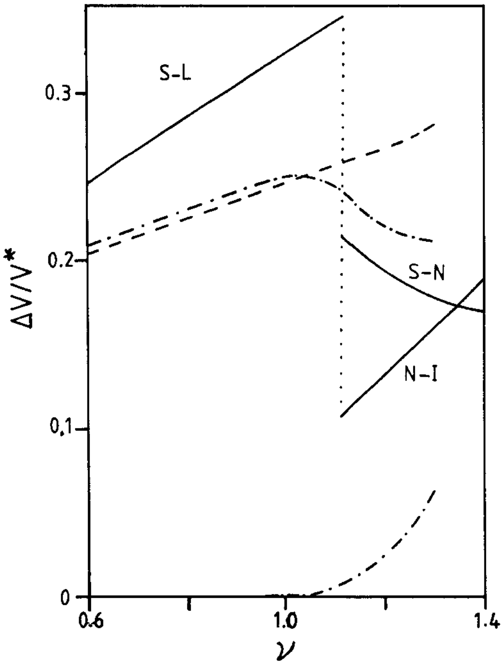

FIGURE 5 Relative volume changes of solid nematic (S–N) and nematic isotropic–liquid (N–I) transitions as functions of $\nu(r = 1.6)$; ———— Present theory; – – – – – Pople and Karasz; –·–·– Chandrasekhar, Shashidhar and Tara.

nearly the same $\Delta S/R$ (R is the universal gas constant) and $\Delta V/V^*$ (V^* is the volume of the phase immediately below the transition), but values are significantly lower than the experimental data. For the nematic–isotropic liquid transition and s nematic ($s = 2S - 1$) at the transition temperature T_1 (solid–nematic) and T_c (nematic–isotropic liquid), the Chandrasekhar, Shashidhar and Tara theory gives better agreement than the other two theories. However, the consistency between the present theory and the experimental data is better than the calculations of the Pople and Karasz theory. Moreover, if one includes the volume dependence modification in the present theory, one can improve the theory very much.

In order to investigate the effect of pressure on the temperature transitions, the theoretical phase diagrams are plotted for two values of ν in Figure 6. These are constructed by drawing the summed $P_o + P_d$ isotherms for given ν and for a range of temperatures and applying the principle of equal areas to the sigmoid portions to find the equilibrium pressures for the transition temperatures. Figure 6a represents the case where the nematic phase occurs above the zero pressure. At the low pressure, there is only a single transition, namely the solid–isotropic melting transition, but at higher pressures branching takes place and two transitions occur, *viz*, the solid–nematic and nematic–isotropic liquid. The branching point indicates the solid–nematic–isotropic liquid triple point. In Figure 6b, ν is large enough for the nematic phase to occur at zero pressure. As the pressure increases, the solid–nematic and the nematic–isotropic liquid

TABLE 1

Theoretical results of entropy and volume change of transitions for a few v along with the available data for some compounds

Present Theory			Chandrasekhar, Shashidhar and Tara			Pople and Karasz			Experimental $(CH_2)_xHOC_6H_4NONC_6H_4OH(CH_2)_x$		
v	$\Delta S/R$	$\Delta V/V$	v	$\Delta S/R$	$\Delta V/V$	v	$\Delta S/R$	$\Delta V/V$	x	$\Delta S/R$	$\Delta V/V$
						Solid–Nematic Transition					
1.073	2.77	0.24	1.15	2.74	0.22	< 1.925	no mesophase		1	9.29	
1.09	2.61	0.23	1.18	2.67	0.21	1.95	2.24	0.19	2	8.02	0.084
1.13	2.45	0.21	1.20	2.62	0.21	2.10	2.15	0.18	3	8.45	
1.20	2.28	0.19	1.30	2.48	0.20	2.30	2.10	0.18	4	6.72	
									5	5.04	
						Nematic– isotropic transition					
1.073	0.849	0.096	< 1.1	2^{nd} ord. trans		< 1.925	no mesophase		1	0.203	0.0035
1.09	0.878	0.101	1.15	0.12	0.01	1.95	1.17	0.15	2	0.410	0.0060
1.13	0.949	0.112	1.18	0.19	0.02	2.10	1.40	0.20	3	0.285	
1.20	1.066	0.132	1.20	0.24	0.03	2.30	1.57	0.23	4	0.385	
			1.30	0.53	0.06				5	0.328	

s(nematic) at the transition temperatures T_1 and T_c

s(Present Theory)			s(Chandrasekhar, Shashidhar) and Tara			s(People and Karasz)				s(experimental)	
v	T_1	T_c	v	T_1	T_c	v	T_1	T_c		T_1	T_c
1.073	0.700	0.800	1.15	0.643	0.308	1.95	0.892	0.879	P-azoxyanisole	0.51	0.34
1.09	0.776	0.810	1.18	0.648	0.403	2.10	0.922	0.912	P-azoxyphenetole	0.69	0.47
1.13	0.840	0.830	1.20	0.719	0.450	2.30	0.956	0.940	2, 4 nonadienic acid	0.68	0.38
									2, 4 decadienic acid	0.70	0.3
									2, 4 undecadienic acid	0.67	0.35

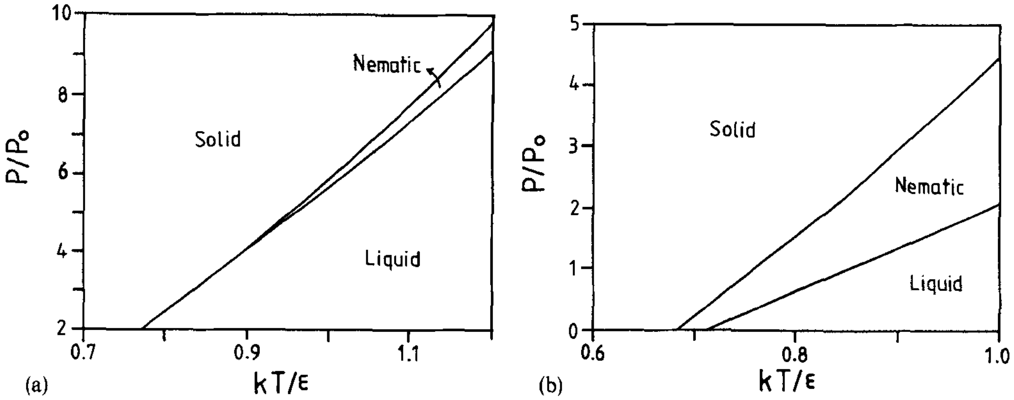

FIGURE 6 Theoretical phase diagram for values of v, P_o is defined $N\varepsilon/V_o$ and $r = 1.6$. a) $v = 1.115$; b) $v = 1.4$.

transition temperatures increase. The slope dT/dP for the nematic–isotropic is greater than the solid–nematic. This behaviour can also be seen at the experimental phase diagram for PAA.[12,13]

Finally, we should also give the influence of the adjustable parameter r to the thermal variations of order parameters, theoretical isotherms and theoretical phase diagrams. Figure 7 shows the positional and the orientational order parameters as a function of the reduced temperature for three different values of r. It can be seen from Figure 7 that, as the r values increase, Tcs and Tcq values increase, also values of Tcs and Tcq demerge each other. Figure 8 illustrates theoretical isotherms for the nematic–isotropic liquid transition on account of three different values of r. As r values increase,

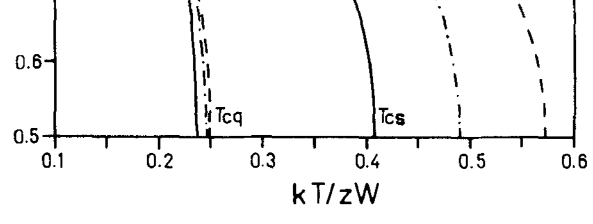

FIGURE 7 Thermal variations of order parameters S and Q as a function of the reduced temperature for three different values of $r(v = 1.2)$. ———— $r = 1.3$; –·–·– $r = 1.6$ and ----- $r = 1.9$.

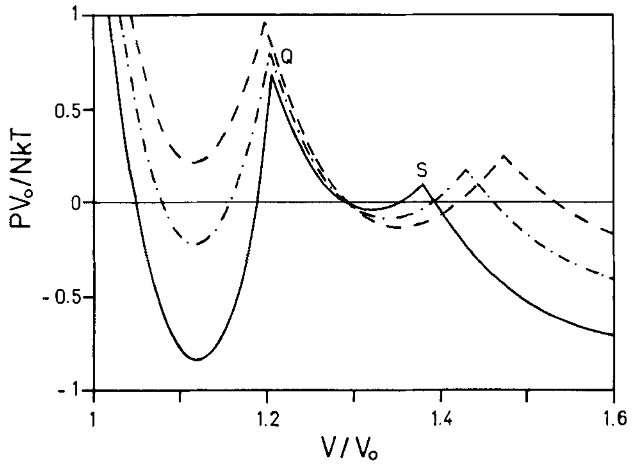

FIGURE 8 Thermal isotherms for the nematic-isotropic liquid transition, kT/ε, ($v = 1.2$). ——— $r = 1.3$; and $kT/\varepsilon = 0.655$; –·–·– $r = 1.6$ and $kT/\varepsilon = 0.686$; ----- $r = 1.9$ and $kT/\varepsilon = 0.710$.

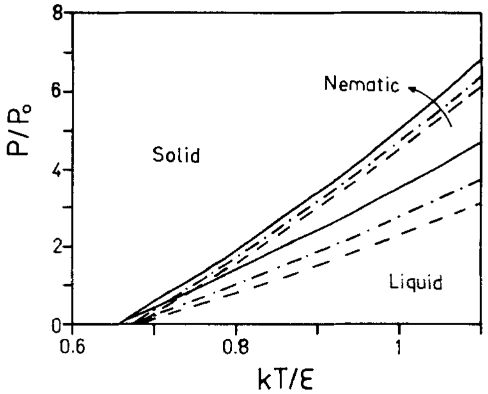

FIGURE 9 Theoretical phase diagrams for three different values of $r(v = 1.2)$. ——— $r = 1.3$; –·–·– $r = 1.6$ and ----- $r = 1.9$.

transition temperatures, namely the nematic–isotropic liquid transitions, increase and the height of the kinks also raises. Figure 9 again gives theoretical phase diagrams for three different values of r. For big values of r, the nematic regions are large and transition temperatures are also high, as seen in Figure 9.

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