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A Theory of Melting of Molecular Crystals. IV. The Complete Picture of Transition Temperatures

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The Pople and Karasz theory of melting of molecular crystals was modified using the third repulsive energy parameter and applied to study the thermodynamics of melting, solid-solid, solid-nematic and nematic-isotropic liquid transitions in our series of previous papers. In this study, we give the complete pictures of transition temperatures and compare with the original Pople and Karasz theory and as well as its volume dependence modification which was done by Chandrasekhar et al..

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

In this series of papers[1-3] (hereafter referred to as paper I, paper II and paper III) we have modified the Pople and Karasz (P and K) theory of melting of molecular crystals[4-7] using the third repulsive energy parameter. In paper I, the equilibrium behaviour of the modified theory and its thermodynamic properties of melting were studied. The quantitative predictions of the theory is compared with experimental results for plastic crystals by plotting entropy and volume changes versus melting/boiling temperature ratios and found that the agreement between the modified theory and experimental data is better than the calculation of the P and K theory. In paper II, the modified form of the P and K theory is applied to study the thermodynamic features of the solid-solid transitions and to obtain complete phase diagrams for transitions under pressure. The entropy of melting as a function of the ratio of the solid transition to boiling temperature, theoretical phase diagrams and the melting entropy versus the solid transition entropy obtained and are compared with available experimental data as well as the P and K theory. Finally, in paper III, the modified theory is used to examine thermodynamics of

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solid-nematic and nematic-isotropic liquid transitions. The results are compared with the predictions of the original P and K theory and its volume dependence modification, which was done by Chandrasekhar *et al.* (CST)[8,9] as well as some experimental data.

In the present work, we give and summarize the complete pictures of transition temperatures, namely solid-solid, solid-liquid, solid-nematic and nematic-isotropic liquid transitions, and compare with the original P and K and CST theories.

As explained in our previous papers[1-3], the transition temperatures depend on values of v, which is a measure of the relative energy barriers for the rotation of a molecule and for its diffusion to an interstitial site, and, r, which is an adjustable parameter including to obtain better agreement with experimental data. We took mostly $r = 1.6$ through the series of the work, because we have seen the agreement between our theory and the experimental data is better around $r = 1.6$. Therefore, in the present work we also take $r = 1.6$ for all the calculations and figures. The ranges of v defining the different types of transition are calculated and given in Table 1 along with P and K and CST theories.

In order to see the complete pictures of transition temperatures, first we plot the reduced transition temperatures of solid-solid (S-S), solid-liquid (S-L), solid-nematic (S-N) and nematic-isotropic liquid (N-I) transitions as a function of v, together with the values given by P and K, and CST theories, seen in Figure 1. Second, entropy changes of S-S, S-L, S-N and N-I transitions as a function of v are calculated and illustrated in Figure 2 along with P and K and CST theories. Finally, Figure 3 shows relative volume changes of S-S, S-L, S-N and N-I transitions as a function of v together with the values given by P and K and CST theories. It is worthwhile to

TABLE 1

The ranges of v defining the different types of transition for Present ($r = 1.6$), P and K and CST theories

Present theory	P and K theory	CST theory	Types of transitions
$v < 0.331$	$v < 0.325$	$v < 0.298$	Two transitions, solid -solid rotational transition preceding the melting transition
$v < 0.25$	$v < 0.17$	$v < 0.264$	Second-order solid-solid transition
$0.25 < v < 0.331$	$0.17 < v < 0.325$	$0.264 < v < 0.298$	First-order solid-solid transition
$0.331 < v < 1.115$	$0.325 < v < 1.925$	$0.298 < v < 0.975$	Single transition
$v > 1.115$	$v > 1.925$	$v > 0.975$	Two transitions, positional melting preceding the rotational melting
no second-order	no second-order	$0.975 < v < 1.047$	Second-order mesomorphic-isotropic transition
$v > 1.115$	$v > 1.925$	$v > 1.047$	First-order mesomorphic-isotropic transition

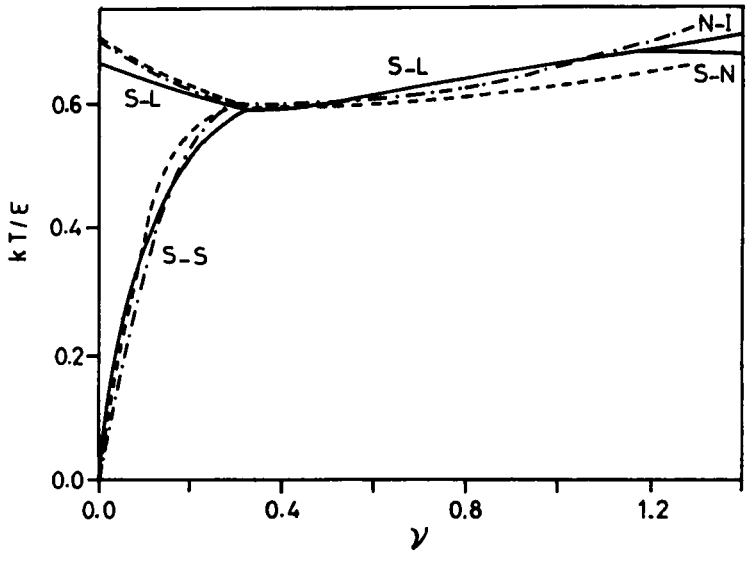

FIGURE 1 The reduced transition temperatures of solid-solid (S-S), solid-liquid (S-L), solid-nematic (S-N) and nematic-isotropic liquid (N-I) transitions as a function of v; ——— present theory ($r = 1.6$); ---- P and K theory; ····· CST theory.

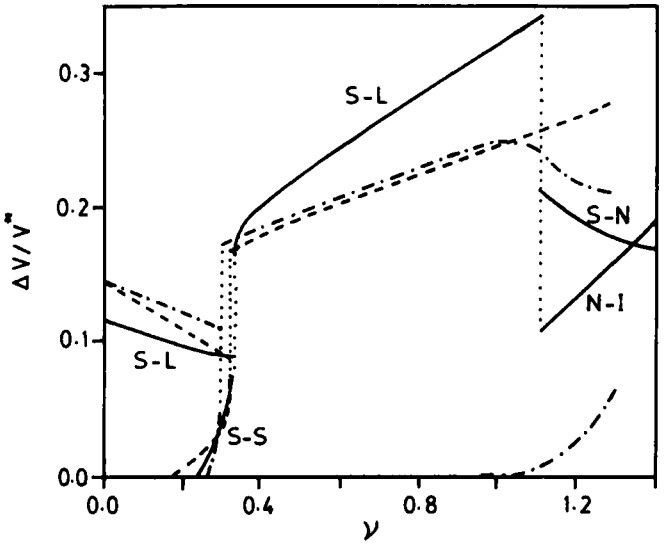

FIGURE 2 Entropy changes of solid-solid (S-S), solid-liquid (S-L), solid-nematic (S-N) and nematic-isotropic liquid (N-I) transitions as a function of v: ——— Present theory ($r = 1.6$);—— P and K theory; ····· CST theory.

mention that all these figures are obtained with the help of the isotherms which were explained in the previous papers extensively[1-3]. It is seen that the three theories give nearly the same results for $v < 0.975$. Moreover the present and CST theories also give nearly the same results for $v < 0.975$.

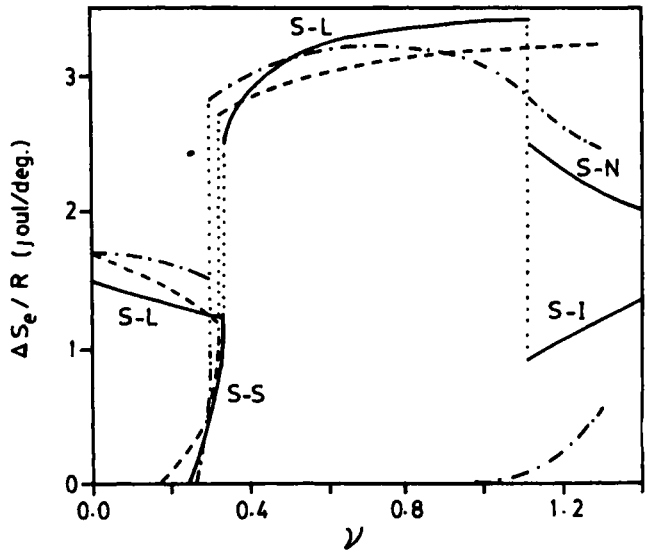

FIGURE 3 Relative volume changes of solid-solid (S-S), solid-liquid (S-L), solid-nematic (S-N) and nematic-isotropic liquid (N-I) transitions as a function of v; ——— Present theory ($r = 1.6$); - - - - P and k theory; ····· CST theory.

Finally, it should be noticed that the largest difference between the P and K theory and the present theory (as well as CST theory) occurs during the first-order mesomorphic-isotropic transition. This transition comes forth at $v = 1.925$ in the P and K theory, at $v = 1.047$ in the CST theory and at $v = 1.115$ in the present theory. Due to the this fact: 1) the present and CST theories give nearly the same $\Delta S/R$ and $\nabla V/V^*$ for the nematic-isotropic transition and these results are also close to the observed data, 2) for the s(nematic) at the transition temperature T_1, the present and CST theories give very nearly the same results and the agreement with the experimental data is reasonably good, as seen in Table 1 of paper III.

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