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Theory of Melting of Molecular Crystals
II: Solid-Solid and Melting Transitions

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Abstract—The modified form of the Pople-Karasz theory of melting of molecular crystals discussed in a previous paper is applied to study the thermodynamics of solid-solid and melting transitions. The results are in substantial agreement with the predictions of the theory in its original form.

In a previous paper[1] (hereafter referred to as (I)), we presented a modified form of the Pople–Karasz theory of melting of molecular crystals and discussed its applications to liquid crystalline transitions. In the present communication, we extend the calculations to solid–solid rotational transitions and melting transitions.

The thermodynamic properties were evaluated for various values of ν in the manner described in (I). (Here ν is a measure of the relative barriers for the rotation of a molecule and for its diffusion to an interstitial site.) The approximate ranges of ν defining the different types of transition are summarized below:

(a) $\nu < 0.298$: two transitions, solid–solid rotational transition preceding the melting transition
$\nu < 0.264$: second order solid–solid transition
$0.264 < \nu < 0.298$: first order solid–solid transition

(b) $0.298 < \nu < 0.975$: single transition (the upper limit of this range was inadvertently reported as 0.8 in (I))

(c) $\nu > 0.975$: two transitions, positional melting preceding the rotational melting

$0.975 < \nu < 1.047$: second order mesomorphic–isotropic transition

$\nu > 1.047$: first order mesomorphic–isotropic transition.

The reduced temperature, entropy and volume change of transition as functions of ν are shown in Figs. 1–3, together with the values

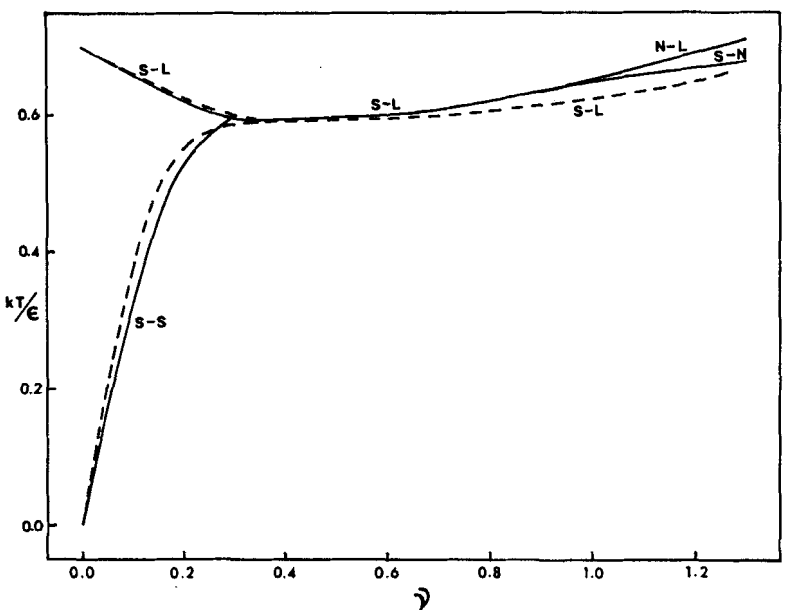

Figure 1. Reduced temperatures of solid-solid and melting transitions as functions of ν; —— Present theory; – – – Pople and Karasz.
S–S Solid–solid, S–L Solid–liquid, S–N Solid–nematic, N–L Nematic–liquid transitions.

given by the Pople–Karasz theory. It will be seen that the two theories give very nearly the same results for $\nu < 0.975$.

Figure 4 is a plot of the entropy of the solid–solid transition ΔS_s versus the entropy of the melting transition ΔS_m along with the experimental data for a few cases taken from Eucken.[2] The model in its present form gives rise to only a single solid transition, but as there are two solid transitions in a number of substances, both are shown in the diagram in those cases for which data are available.

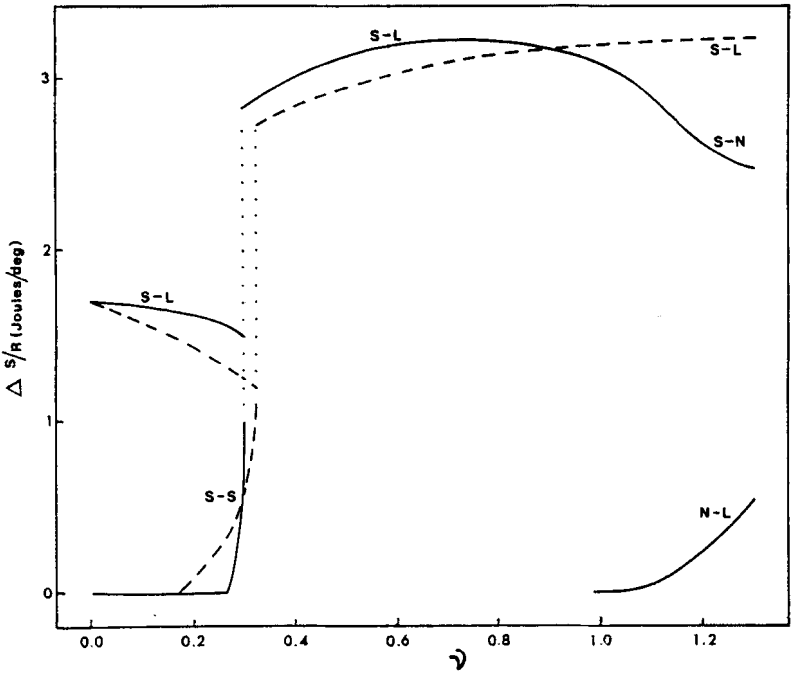

Figure 2. Entropy changes of solid–solid and melting transitions as functions of ν.

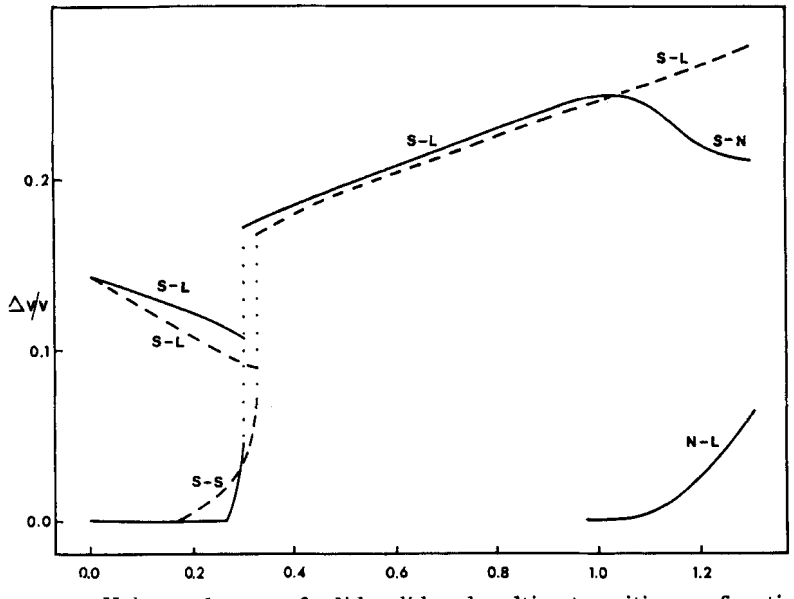

Figure 3. Volume changes of solid–solid and melting transitions as functions of ν.

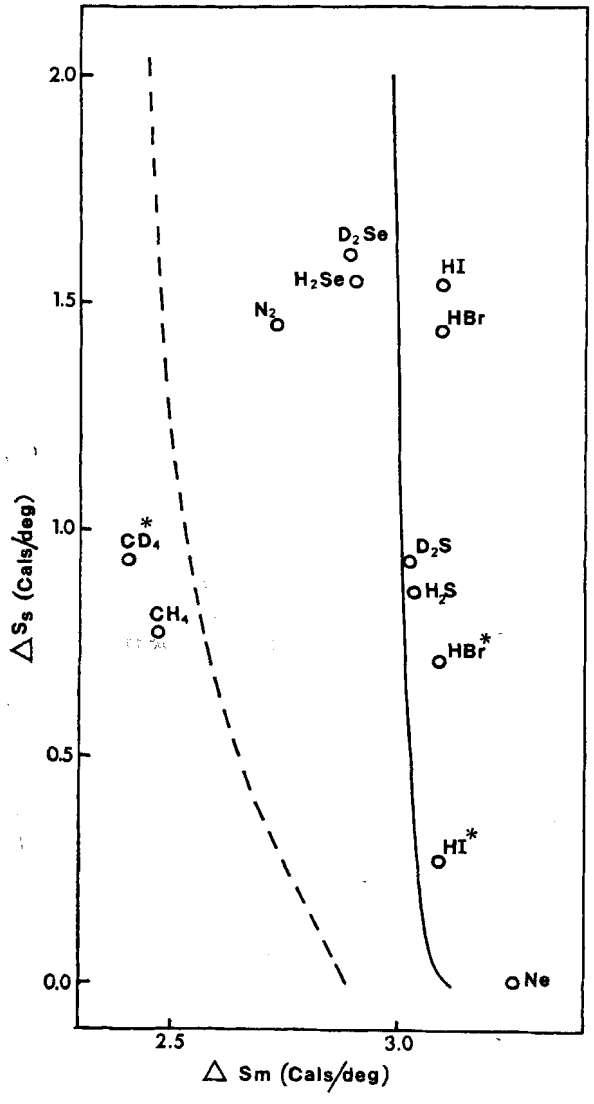

Figure 4. Comparison of solid–solid transition entropy ΔS_s with melting entropy ΔS_m. —— Present theory; – – – Pople and Karasz; for substances showing two solid transitions, a star denotes the lower transition.

The present theory appears to give a slightly better fit with the observed data than that of Pople and Karasz.

Theoretical phase diagrams were drawn by the method outlined in (I) and it was verified that they reproduce all the features described by Pople and Karasz. We present in Fig. 5 one such phase diagram and compare it with the experimental data on the solid–solid and melting transitions of nitrogen. The data on the solid transitions (α–β phase) are taken from Swenson[3] and the melting point data from Robinson.[4] The Lennard–Jones and

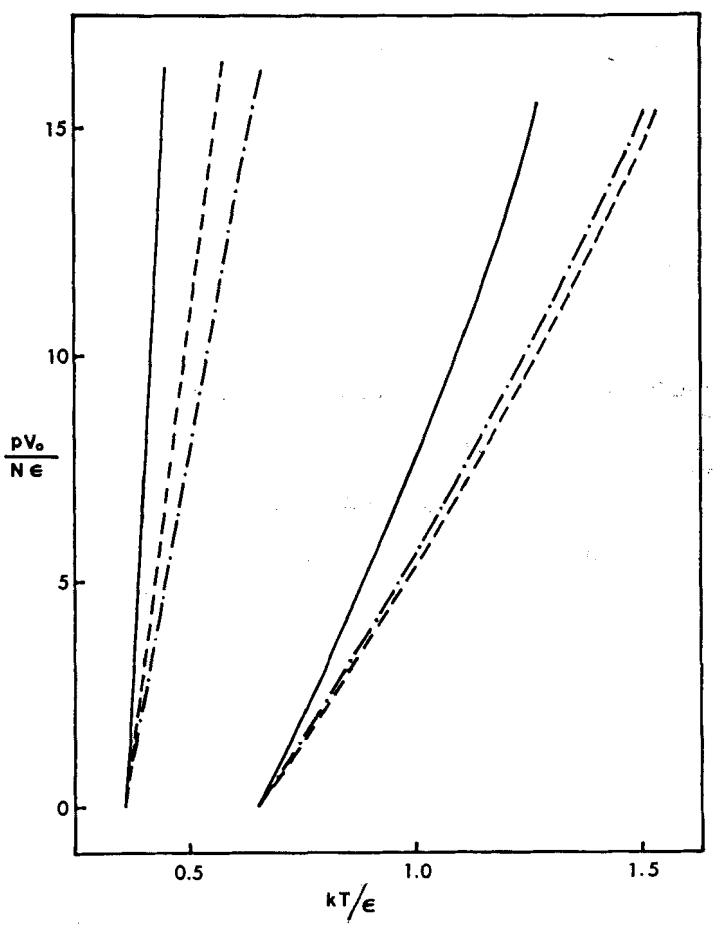

Figure 5. Comparison of experimental (——) and theoretical phase diagrams for nitrogen; – – – Present theory; – · – · – Pople and Karasz theory.

Devonshire interaction parameters ϵ and r_0 were obtained from Hirschfelder *et al.*[5] and the experimental values converted to the reduced temperature kT/ϵ and reduced pressure $pV_0/N\epsilon$. It was also necessary to choose a particular value of ν, and this was done by reading off from Fig. 1 the appropriate ν corresponding to kT/ϵ for nitrogen at zero pressure. The value of ν assigned was 0.115. It can be seen from Fig. 5 that both theories are in reasonably good agreement with the data.

Thus, although the two theories diverge considerably for large orientational barriers (as was shown in (I)), they are in substantial agreement for low and moderate barriers. The conclusions of Pople and Karasz regarding solid–solid and melting transitions are therefore essentially unaltered.

Acknowledgements

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