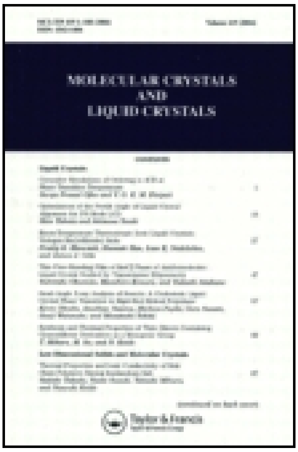

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A Theory of Melting of Molecular Crystals II. Phase Diagrams and Relations with Solid State Transitions

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A Theory of Melting of Molecular Crystals

II. Phase Diagrams and Relations with Solid State Transitions

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The Pople and Karasz theory of melting of molecular crystals is extended to include the third energy parameter mentioned in our previous paper.[1] The modified form of the Pople and Karasz theory is used to study solid-solid transitions and to obtain complete phase diagrams for transitions under pressure. It is found that solid-solid and melting transitions become second-order under certain conditions. The entropy of melting as a function of the ratio of the solid transition to boiling temperature, the theoretical phase diagrams as well as the melting entropy versus the solid transition entropy are compared with available experimental data and as well as the Pople and Karasz theory.

Keywords: Modified Pople and Karasz theory, molecular crystals, order parameters, theoretical isotherms, solid-solid and melting transitions.

1. INTRODUCTION

In paper I of this series,[1] we presented a modified form of the Pople and Karasz (P and K) theory of melting of molecular crystals,[2] taking into account of a third energy parameter W''. W'' is the interaction between molecules on different sites and also different orientations. W'' is combined with W (the interaction between molecules which are different sites with the same orientations) and W' (the interaction between molecules on the same sites and different orientations) by using the arithmetic mean multiplied by an adjustable parameter.

The P and K theory is based on the work of Lennard-Jones and Devonshire (L-J and D)[3] and it describes the melting of inert gas crystals. Inert gases all have f.c.c. lattice (except He) and since the molecules are spherical, the orientation plays no role. The P and K theory is a simple extension of the L-J and D theory by including an

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orientational order parameter S beside the positional order parameter Q. In this way, the theory could describe the phase transition in either plastic or in liquid crystal systems depending on the choice of coupling parameter. It is worthwhile to mention that the P and K theory has also been modified in different ways.[4] They were described extensively in paper I. The dynamic of the P and K theory was also studied by Keskin, and Meijer and Keskin.[5]

In paper I we introduced a modified form of P and K theory and studied its equlibrium behaviour. We also studied the thermodynamic properties of melting and compared with experimental data by plotting entropy changes versus the ratio of melting to boiling temperature for a number of substances.

In this paper, we will apply the modified P and K theory to the solid-solid transitions, establish the theoretical phase diagrams and compare it with the available experimental data. We will also study the predictions of the modified theory for the transition temperatures at higher pressure. This leads to a set of phase diagrams which can be compared directly with experimental data. Finally, we compare the modified theory with the P and K theory.

2. THE MODIFIED STATISTICAL MODEL

The modified model was described extensively in paper I, therefore we shall only give a brief summary here to indicate the additional features needed for calculations on solid-solid transitions. The modified model based on the P and K theory which is the extension of the work of the L-J and D theory by including orientational order beside positional order. It is assumed that each of the N molecules in the crystal is supposed to be placed on one of two interpenetrating lattice of N-sites, refered to as A-sites and B-sites. It is also assumed that the molecule can take up one of two orientations on any site, so that now we have namely four possibilities 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 perfect order (or the solid at zero temperature), and the state of complete disorder (or the liquid phase) as one in which all four configurations are equally populated. It should be mentioned that, there can also be states with a positional order and no orientational order and vice versa.

The complete partition function of the modified model is

$$\begin{aligned} Z &= f^{\mathrm{N}}\Omega \\ &= f^{\mathrm{N}}\Sigma \exp[-(\mathrm{N}_{\mathrm{A_1B_1}}+\mathrm{N}_{\mathrm{A_2B_2}})W-(\mathrm{N}_{\mathrm{A_1B_2}}+\mathrm{N}_{\mathrm{A_2B_1}})W''-(\mathrm{N}_{\mathrm{A_1A_2}}+\mathrm{N}_{\mathrm{B_1B_2}})W']/kT, \end{aligned} \tag{1}$$

where the sum is over all orientations as well as over all arrangements of particles on A and B sites. f^{N} is the partition function of the totally ordered system and f is the partition function of a molecule in this state and is treated as function of volume per molecule and temperature only. $\mathrm{N}_{\mathrm{A_1B_1}}$ and $\mathrm{N}_{\mathrm{A_2B_2}}$ are the number of neighbouring AB pairs with the same orientation, $\mathrm{N}_{\mathrm{A_1B_2}}$ and $\mathrm{N}_{\mathrm{A_2B_1}}$ are the number of neighbouring AB pairs with different orientation, $\mathrm{N}_{\mathrm{A_1A_2}}$ is the number of relative misorientations on neighbouring A-sites and $\mathrm{N}_{\mathrm{B_1B_2}}$ is defined similarly. Again W is the interaction between molecules which are different sites with the same orientations, W'' is the interaction between molecules on different sites and also different orientations and W' is the interaction between molecules on the same sites and different orientations.

Since two long-range order parameters Q and S are introduced, the partition function Ω is written in the form

$$\Omega = \sum_{Q,S} \Omega(Q,S) \tag{2}$$

Applying the Bragg-Williams approximation,[6] the two self-consistent equations in terms of Q and S are obtained

$$\ln\frac{Q}{1-Q} = (zW/2kT)(2Q-1)\{[1-2S+2S^2)+rS(1-S)]+vS(1-S)(r-2)\} \tag{3}$$

$$\ln\frac{S}{1-S} = (zW/2kT)(2S-1)\{Q(1-Q)(r-2)+v[(1-2Q+2Q^2)+rQ(1-Q)]\},$$

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 and r is the adjustable parameter. v and r is the key parameters in the modified theory. z is the number of B-sites immediately surrounding any A-site and z' is the coordination number of the A-lattice itself, i.e. the number of A-sites is closest to any one of A-site. For the purpose of numerical calculations, we assume the model to be two interpenetrating face centered cubic lattice, so that $z = 6$ and $z' = 12$.

It should be mentioned that W'' is combined with W and W' by the arithmetic mean including the adjustable parameter r as

$$W'' = r\left(\frac{zW + z'W'}{2}\right). \tag{4}$$

The solution of Equation (3) was given in paper I for $r = 1.6$ and three different values of v. However a number of additional solutions were obtained by Özgan[7] for different values of v and r. As a summary: for a small values of v, first S disappears ($S = 0.5$) as the reduced temperature increases then Q becomes 0.5. For larger values of v ($v < 0.579$ and $r = 1.6$), disappearing of S and Q ($S = 0.5$ and $Q = 0.5$) occurs in the closed temperatures as the reduced temperature increases. This is the case for a compact, globular molecule characteristic of a plastic crystals.[8] For $v = 0.579$ and $r = 1.6$, orientational and positional disorder occur at the same reduced temperature and corresponding to ordinary melting. For $v > 0.579$ ($r = 1.6$), this case looks like the case of $v < 0.579$, except that the behaviour of S and Q are interchanged and this is anologous to the properties of liquid crystals[8] which will be reported in the papers III and IV.

In order to investigate how these transitions show up thermodynamically, one needs to examine the isotherms associated with the total free energy

$$F = F_o + F_d, \tag{5}$$

where

$$F_o = -NkT\ln f \quad \text{and} \quad F_d = -kT\ln\Omega(Q,S),$$

as described in paper I. The pressure associated with the partition function f have been tabulated by Wentorf *et al.*[9] We should mention that in order to study the solid-solid transition completely, it is necessary to know the thermodynamic function for lower temperatures than those tabulated by Wentorf *et al.*[9] These were found by interpolating between the values actually tabulated and the known behaviour in the limit of the zero temperature. W'/W is taken independent of volume and

$$\begin{aligned} W &= W_o(v_o/v)^4, \\ W_o/\varepsilon &= 0.977, \end{aligned} \tag{6}$$

where v_o is the standard volume if the molecules are placed on a f.c.c. lattice with a nearest neighbouring 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 thermodynamic behaviour predicted by the theory depends on the values of v and r. We have already reported[1] that there is a critical value of v ($v = 0.331$ for $r = 1.6$ below which two separate transitions occur, namely the solid-solid (S-S) and solid-liquid (S-L) transitions. If $v > 0.331$ ($r = 1.6$), two transitions meet into one first-order transition with correspondingly larger entropy and volume changes. For $v > 1.115$ ($r = 1.6$), again two separate transitions occur, namely the solid-nematic (S-N) and nematic-isotropic liquid (N-L) transition about which we will report in paper IV.

3. EVALUATION OF THE SOLID-SOLID TRANSITION

In this section we establish the solid-solid (S-S) transition at zero pressure for $v < 0.331$ and $r = 1.6$, because in this region S-S transition occur which was also stated in paper I. If v is between 0.25 and 0.331 for the lower values of kT/ε, the S-S transition is found to be first-order, but $v < 0.25$ the solid-solid transition is the second order. In order to see whether the transitions the first-order or second-order, one should obtain isotherm.

Figure 1a illustrates a typical isotherm for the S-S transition temperature for $v = 0.3$, $r = 1.6$. The transition occurs $kT_s/\varepsilon = 0.5785$. The points indicated S and Q denote volumes at which orientational and positional order disappear. The two phases denoted by the points A and B exist in equilibrium at a given pressure, since the areas enclosed above and below the pressure line are equal. The point A corresponds to the solid ($S = 0.829$ and $Q = 0.975$) with long-range order both in positions and orientations and B to the different phase of solid ($S = 0.5$ and $Q = 0.937$) with long-range disorder in orientations. For small values of v the shape of the isotherm are different than Figure 1a as well as the isotherms in paper I, because isotherms lose their sigmoid shapes. v less than about 0.25, there is only one kink in the isotherms, namely the kink

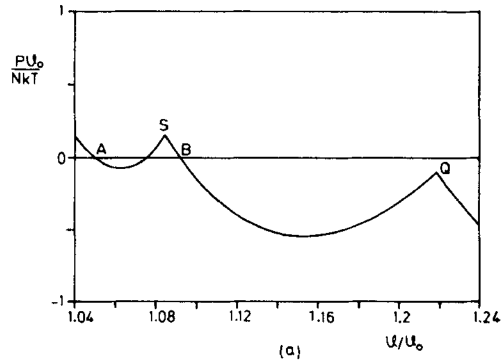

FIGURE 1a Theoretical isotherm for the solid-solid transition temperature, $\nu = 0.3$, $r = 1.6$ and the solid-solid transition temperature, kT_s/ε, is 0.5785.

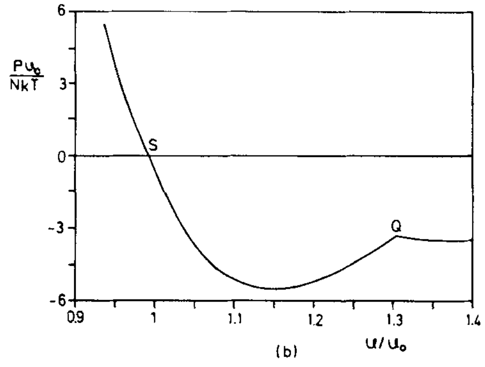

FIGURE 1b Theoretical isotherm showing the second-order solid-solid transition. $\nu = 0.15$, $r = 1.6$ and the solid-solid transition temperature, kT_s/ε, is 0.451.

which the positional order parameter Q disappears but there is no kink for orientational order parameter S. However, there is a discontinuity in slope to mark the loss of orientational order parameter S. Thermodynamically, this means that the transition changes from the first to second-order for these small values of ν. Figure 1b illustrates a typical transition isotherm in this range for $\nu = 0.15$, $r = 1.6$. The transition reduced temperature is found $kT_s/\varepsilon = 0.451$.

By investigating various isotherms in this way, we can find reduced transition temperatues kT_s/ε and kT_m/ε for each value of ν parameter, shown in Figure 2 ($r = 1.6$). Here small s and m indicate the solid-solid and the solid-liquid transitions, respectively. In the figure the solid lines represent the present theory and the dashed lines indicate the P and K theory.

Relative volume changes of solid-solid and solid-liquid transition functions of ν can be obtained easily from the isotherms at transition temperatures. Figure 3 shows $\Delta v/v^*$ versus ν for $r = 1.6$, where Δv is the increase in volume and v^* is the volume

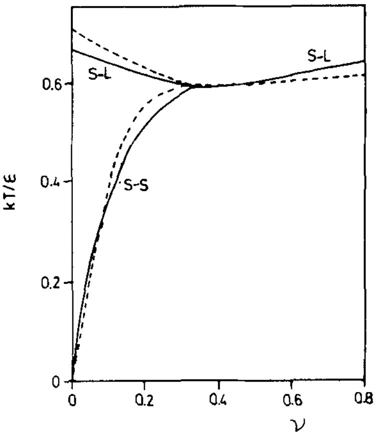

FIGURE 2 Reduced transition temperatures of solid-solid (S-S) and melting (solid-liquid) (S-L) transitions as functions of ν ($r = 1.6$) – – – – – –represents the P and K theory and ——— the present theory.

of the phase immediately below the transition. From the figure one can easily see, that for $\nu < 0.25$, solid transition becomes second-order and the volume change is then zero.

Finally, entropy changes of solid-solid and solid-liquid transition functions of ν are also easily determined from the isotherms at the transition temperatures. $\Delta S_e/R$ is plotted as function of ν ($r = 1.6$) in Figure 4. ΔS_e is found by calculating the entropies of two phases in the equilibrium and S_e can be calculated from Equation (19) in paper I. Again there is no entropy change associated with the second-order transition below $\nu > 0.25$. Also in Figures 3 and 4, the solid lines represent the present theory and dashed lines denote the P and K theory.

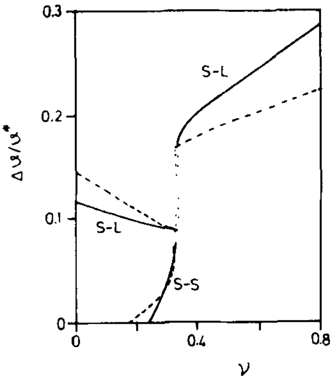

FIGURE 3 Relative volume changes of solid-solid (S-S) and solid-liquid (S-L) transitions as functions of ν ($r = 1.6$). – – – – – – represents the P and K theory and ——— the present theory.

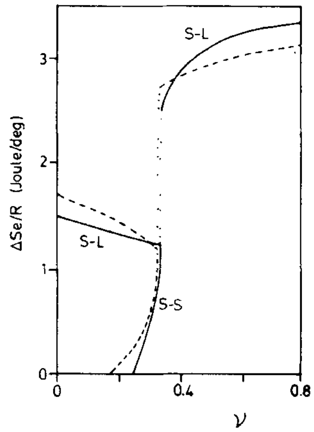

FIGURE 4 Entropy changes of solid-solid (S-S) and solid-liquid (S-L) transitions as functions of ν ($r = 1.6$). ------ represents the P and K theory and ——— the present theory.

4. THEORETICAL PHASE DIAGRAMS

In order to predict phase diagrams for the condensed system we use the "equal area principle" to the sigmoid portions of the isotherms to determine the equilibrium pressure for the solid-liquid and solid-solid transitions. Several phase diagrams were constructed by using the reduced pressure and temperature coordinates as shown in Figure 5. It should be mentioned that all phase diagrams are obtained for $r = 1.6$. The changing of r values does not change the behaviour of phase boundaries, namely solid-solid and solid-liquid, it only shifts the boundary to higher values of the reduced temperature, as was investigated by Özgan.[7]

Figure 5a shows the phase diagram for $\nu = 0$. Of course there is no solid-solid transition and a single solid-liquid transition is obtained. For $\nu > 0$ and up to $\nu = 0.331$ we find two solid phases, namely solid I and solid II, in equilibrium and as well as solid-liquid phase boundary at all pressure, e.g. see in Figure 5b ($\nu = 0.2$). Figure 5c illustrates the phase diagram for $\nu = 0.331$ which is the critical value where the two transitions meet at zero pressure. For all pressure greater than zero the transitions are separated and we obtain a phase diagram that is essentially similar to Figure 5b. For $\nu > 0.331$, the solid-solid and the solid-liquid transition merge at zero pressure as well as lower pressure. However, at higher pressures the solid-solid transition is again separated, therefore we have the solid-solid and solid-liquid boundaries, i.e. we have solid I, solid II and liquid phases in the phase diagrams at higher pressure, as shown in Figure 5d, $\nu = 0.4$. Finally, Figure 5e shows the behaviour for $\nu = 0.579$ which is the special case in the present theory, where the two kinks in the isotherms coincide (see paper I, Fig. 2c) and we find just one combined transition for all pressure.

It is worthwhile to mention that for $1.115 > \nu > 0.579$ for the lower pressure the theory predicts only the solid-liquid boundaries but the higher pressures the theory predicts the solid-nematic and the nematic-liquid boundaries. For $\nu = 1.115$ is the second critical values where all the phases merge at zero pressure. For $\nu > 1.115$ the

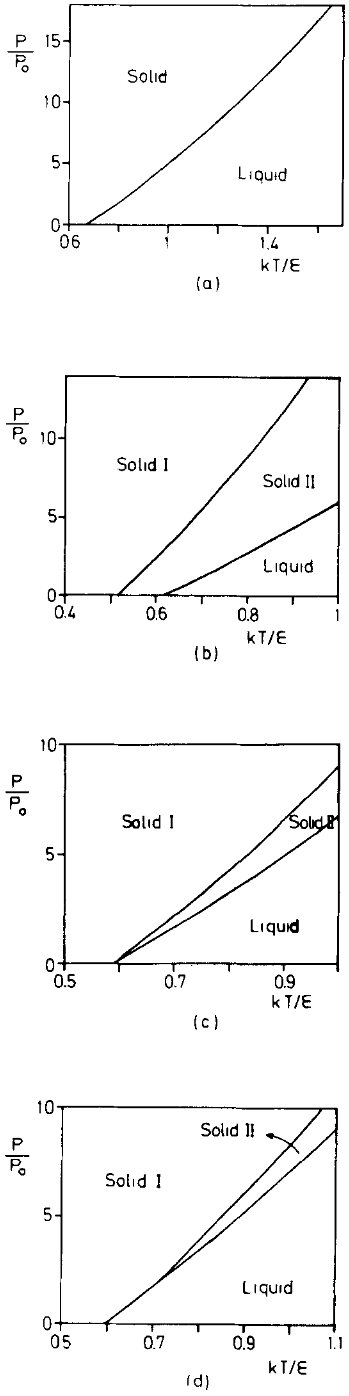

FIGURE 5 Theoretical phase diagrams for various of values of v. P_o is defined $N\varepsilon/v_o$ and $r = 1.6$. a) $v = 0.0$, b) $v = 0.2$, c) $v = 0.331$, d) $v = 0.4$, e) $v = 0.579$.

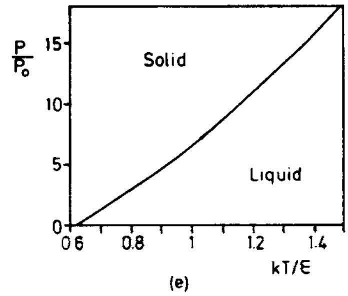

FIGURE 5 *(Continued)*

theory predicts the solid-nematic and nematic-liquid boundaries even at zero pressure. Therefore, for $v > 1.115$ corresponds to the liquid crystal and will be reported extensively in papers III and IV.

5. COMPARISON WITH EXPERIMENTAL DATA

In order to compare the theoretical predictions of our model with experimental data we need to establish values for v and r. The parameter v cannot be found directly from experiments nor estimated theoretically from the present knowledge of intermolecular forces. Therefore, we will relate the thermodynamic properties of different compounds with the ratio of the solid transition temperatures to boiling temperatures since this ratio can be derived directly from the experiments.

Figure 6 shows the entropy of melting as a function of the solid transition to boiling temperatures for a number of substances as well as the theoretical prediction of the P and K and also the present modified theory (for three different values of r). From Figure 6, one can see the P and K theory gives a reasonable good agreement only for certain kind of substances, namely, Ar, HI_{τ}^{*}, HBr* and H_2S*. However the present

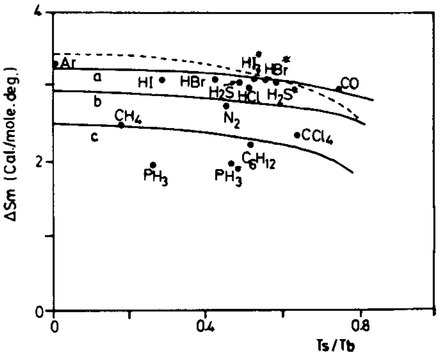

FIGURE 6 The entropy of melting as a function of the ratio of solid transition to boiling temperatures for a number of substances. ------ the P and K theory and ——— the present theory for the different values of an adjustable parameter. a) $r = 1.8$, b) $r = 1.6$ and c) $r = 1.3$. For substances showing two solid transitions, a star denotes the upper transitions.

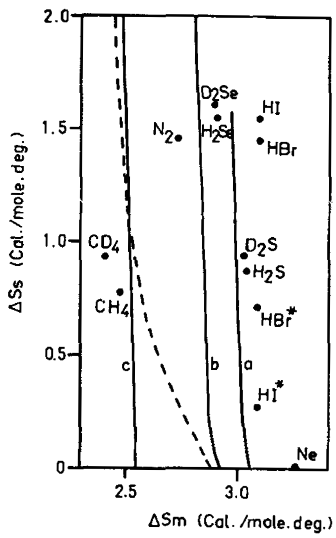

FIGURE 7 Comparison of melting entropy ΔS_m with solid transition entropy ΔS_s. ------ the P and K theory and ——— the present theory. For substances showing two solid transitions, a star denotes the upper transitions a) $r = 1.9$, b) $r = 1.8$ and c) $r = 1.6$.

theory gives a good agreement not only for certain substances but also predicts a reasonably satisfactory agreement for different kind of substances if one changes the adjustable parameter r. For example, taking $r = 1.8$ a good agreement obtains for Ar, HI_{r}^{*}, HBr^* and H_2S^*, $r = 1.6$ for N_2 and $r = 1.3$ for CH_4 and C_6H_{12}, seen in Figure 6.

Figure 7 illustrates a similar plot of ΔS_m versus ΔS_s. The agreement between the P and K theory and experimental data is less satisfactory in this plot. However the present theory gives a reasonable good agreement. Also by changing the adjustable

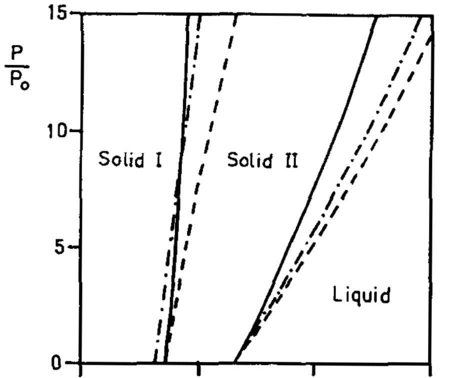

FIGURE 8 Comparison of experimental (------) and Theoreticals phase diagrams for nitrogen. ------ the P and K theory and —·—·— the present theory ($v = 0.085$ and $r = 1.3$).

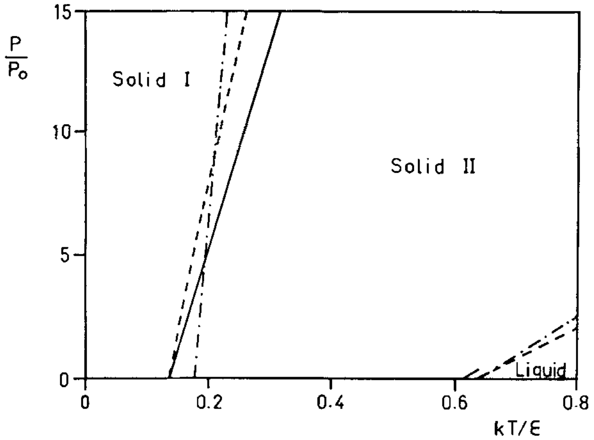

FIGURE 9 Comparison of experimental (------) and Theoreticals phase diagrams for methane. ------ the P and K theory and —·—·— the present theory ($\nu = 0.034$ and $r = 1.3$).

parameter r, one can obtain a very good agreement if one wants to fit certain experimental data. For instances, taking $r = 1.8$ a good agreement obtains for O_2S and H_2S and $r = 1.6$ for CH_4.

Figure 8 shows the values predicted (by the P and K and the present theories) and experimental orientational (solid-solid) and melting (solid-liquid) transitions for nitrogen. From Figure 8, one can see that the present theory gives better agreement than the P and K theory for the experimental solid-liquid transitions and as well as the solid-solid transitions. It should be noted that, a good agreement also obtains for the entropy of melting as a function of the ratio of solid transition to boiling temperatures for nitrogen around $r = 1.6$ (actually less than 1.6), seen in Figure 6. Therefore these two figures coincide each other for $r = 1.55$. Finally, Figure 9 shows a similar comparison for the methane ($\nu = 0.034$ and $r = 1.3$). Again, the agreement with the present theory is better than the P and K theory for P/Po is around 5 in the solid-solid transitions but the present theory is not good for higher values of P/Po, seen in Figure 9. It is worthwhile to mention that for $r = 1.3$, a good agreement also finds for the entropy of melting as a function of the ratio of solid transition to boiling temperatures for methane, as seen in Figure 6. Consequently, Figure 6 for methane and Figure 9 agree each other for $r = 1.3$.

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