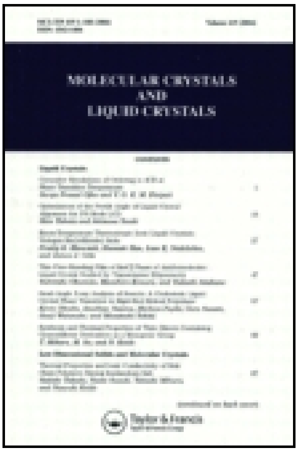

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A Theory of Melting of Molecular Crystals I. Theory and Evaluation of the Thermodynamic Properties of Melting

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A Theory of Melting of Molecular Crystals I. Theory and Evaluation of the Thermodynamic Properties of Melting

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The Pople and Karasz theory of melting of molecular crystals, which is based on the theory of melting of inert gas crystals by Lennard-Jones and Devonshire, is extended using a third energy parameter, W''. The extension is done as follows: the previous repulsive energy parameter W is divided into two parts. The first part is the interaction between molecules which are on different sites with the same orientations, called again W. The second is the interaction between molecules on different sites and also different orientations, namely W''. W'' is combined with the previous W' and the new W energy parameters by the arithmetic mean including an adjustable parameter. The thermodynamic properties are evaluated by the Bragg-Williams approximation. The theory is applied to plastic crystals and compared with the Pople and Karasz theory. By introducing a physical realistic coupling between orientational and positional order, v, the theory gives a solid state rotational transition and melting transition. For values of $v \leq 0.331$ the two transitions are separate, while for values of $v \geq 0.331$ they coalesce. 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. The agreement between our theory and the experimental data is better than the calculations of the Pople and Karasz theory, as result of the introduction of the parameter W'' in the present theory.

Keywords: Modified pople and Karasz theory, molecular crystals, order parameters, theoretical melting isotherms, thermodynamics of melting

1. INTRODUCTION

Physicists have been trying to develop an adequate theory of melting for a number of years, but in spite of these attempts, it would be fair to say no theory has yet been constructed that is able to give a satisfactory quantitative description of melting process. The main qualitative difference between a crystalline solid and a liquid phase has long been attributed to the disappearance of the long-range order of crystalline

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structure, though some degree of short-range order may still persist in the liquid and be lost gradually as the temperature rises and the volume increases. Review of the melting theories and a critical discussion of the problem are given by Ubbelohde.[1,2]

Probably, the most successful treatment of the melting of inert gas crystals is that due to Lennard-Jones and Devonshire (L-J and D) [3,4] based on the cell model. They had previously developed a theory of condensation [5] and considered only translational degrees of freedom. Therefore the theory has only one order parameter which is associated with the long range positional order. They describe a crystal of N spherical atoms (or molecules) in terms of two interpenetrating perfect lattices of N sites (A and B) each. At low temperatures the particles all occupy A-sites or all B-sites, corresponding to a state of perfect order (the solid at zero temperature). With the increasing temperature, the number of particles on the interstitial sites (e.g. B-sites in a crystal where mainly A-sites are occupied) increases, until a critical condition is reached where the long-range positional order is destroyed and two kinds of sites are equally populated, corresponding to a state of disorder (the liquid phase).

Pople and Karasz (P and K)[6,7] have extended the L-J and D theory by including orientational order as well as positional order and their theory gives a reasonably quantitative interpretation of the variations in the thermodynamic properties of melting of molecular crystals. Adding an orientational order parameter besides the positional order parameter, one can obtain phase transitions in either plastic or in liquid crystal systems depending on the choice of coupling-parameters. Pople and Karasz considered that molecules may take up one of two orientations on any site, so that it now has four possibilities A_1, A_2, B_1 and B_2. If all particles occupy sites and orientations of the same type, say A_1, the state is of perfect order. It is in a state of complete disorder if all four configurations are equally populated. Amzel and Becka[8] point out that restricting the number of permitted orientations to two is certainly artificial and they extended the P and K theory by taking into account the existence of more than two discrete possible positions of minimum orientational energy in the crystal. The quantitative predictions of the model are compared with experimental results for plastic crystals and they found that there is a good agreement between the theory and the experiment. Especially, the agreement is much better for solid-solid transition than with the calculation of P and K theory. Chandrasekhar *et al.*[9-12] have modified the P and K theory and applied it both plastic and liquid crystals. They suggest that the energy required for a molecule to be placed at an interstitial site varies as V^{-4}, as in P and K formulation, but that the orientational barrier varies as V^{-3}, in conformity with theoretical studies of the orientational potential energy of the molecules in nematic liquid crystals.[13] This modification is also applied to study the thermodynamics of solid-solid and melting transitions, as well as solid-nematic and nematic-liquid transitions. The results are in substantial agreement with the predictions of the theory in its original form given by P and K. The dynamic behaviour of the P and K theory was studied by Keskin[14] and Meijer and Keskin.[15] Recently, the P and K theory was used to study how to obtain metastable states by Keskin and Özgan.[16]

In the P and K theory and its modifications, there are two energy parameters, one is associated with transition of molecules from A-sites to B-sites (or vice versa), W; and the other is associated with orientations, W', e.g. from A_1 to A_2 or B_1 to B_2 (or vice versa). There must be a third energy parameter W'' which should be associated with positions and orientations together, e.g. from A_1 to B_2 or A_2 to B_1 (or vice versa). In all above-mentioned theories, W'' is simply taken to be equal to W, because the simplest possible manner is assuming that $W$of A-B neighbours is independent of orientations. Our extension is done as follows: the previous repulsive energy parameter W is divided into two parts, the first part is the interaction between molecules which are on the same orientations and different sites, called again $W$and the second is the interaction between molecules which are on the different sites and also different orientations, namely W''. W'' is combined with the previous W', which is the interaction between molecules on the same sites and different orientations, and new W energy parameters by the arithmetic mean including an adjustable parameter.

Our purpose of the present series of papers is to extend the model of P and K by introducing the new energy parameters W'' in order to study more realistic picture of melting of molecular crystals as well as study of liquid crystalline phase. In this paper, we introduce first the modified form of the P and K theory and work out the equilibrium behaviour of the model by means of the Bragg-Williams approximation [17,18] and we also evaluate the thermodynamic properties of melting and make comparison of the modified theory with the experiment and also with the original P and K model by plotting entropy and volume changes versus melting/boiling temperature.

This paper is organized as follows: In section 2 details of the model are given. In section 3 the equilibrium solution of the model is presented. In section 4 the thermodynamic properties of the melting are evaluated. Finally, comparison with the experiments and the original theory are given in the last section.

Paper II of this series will give disordering solid-solid transitions and the complete phase diagrams for transitions under pressure. In paper III, the model will be applied to the liquid crystalline phase. In paper IV, we will describe the thermodynamics of solid-solid, solid-liquid, solid-nematic and nematic-liquid phase transitions using our modified model.

2. DESCRIPTION OF THE MODIFIED P AND K THEORY

The present statistical theory is a simple extension of the Pople and Karasz theory which is based on the L-J and D theory by including the orientational order as well as positional order. In the theory, molecules may occupy sites on one of two equivalent interpenetrating lattices 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 crystals. 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 perfect (periodic) order. If all four configurations are equally populated, the system is completely disordered and said to be in the liquid state. Clearly, there can also be states with a positional order and no orientational order and vice versa. 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'.

In the theory, there are three repulsive energies: The first one is W, the energy of an A_1B_1 or A_2B_2 interactions, the second one is W', the orientational energy of an A_1A_2 or B_1B_2 and the third one is W'', the energy of A_1B_2 or A_2B_1. It is worthwhile to mention that Pople and Karasz took into account in the simplest possible manner by assuming that the energy WA-B neighbours is independent of orientation, i.e. they took $W = W''$. Thus zW is the energy needed to transfer the molecule from one site to the other sites with 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 orientation 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 the positional and orientational energies, it should be combined with zW and $z'W'$. We use simply the arithmetic mean, including the adjustable parameter r. The reason including r factor is to obtain better agreement with experimental data.

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

Let $N_{A_1B_1}$ and $N_{A_2B_2}$ are the number of neighbouring AB pairs with the same orientation, $N_{A_1B_2}$ and $N_{A_2B_1}$ are the number of neighbouring AB pairs with the different orientation, $N_{A_1A_2}$ is the number of relative misorientations on neighbouring A-sites and $N_{B_1B_2}$ is defined similary, then the partition function for the whole assembly can be written

$$\begin{aligned} Z &= f^N\Omega \\ &= f^N\Sigma\exp[-(N_{A_1B_1} + N_{A_2B_2})W - (N_{A_1B_2} + N_{A_2B_1})W'' \\ &\quad -(N_{A_1A_2} + N_{B_1B_2})W']/kT, \end{aligned} \tag{2}$$

where the sum is over all orientations as well as over all arrangements of particles on A and B sites; f is the partition function per molecule in a state of perfect order which is treated as a function of volume per molecule and temperature only, and k is the Boltzmann constant.

3. SOLUTION FOR THE THEORY AT EQUILIBRIUM

The equilibrium properties of the theory are determined by the Bragg-Williams (or zeroth order) approximation[17, 18] of the co-operative order-disorder problem. First, we define the degree of a positional order Q which is the fraction of the molecules in the A-sites, and the degree of orientational order S, where S is the fraction of molecules in one orientation. Then the total Ω function may be written as a sum of partition functions for given Q and S

$$\Omega = \sum_{Q,S} \Omega(Q,S) \equiv \Omega(Q,S). \tag{3}$$

$$\Omega(Q,S) = \sum^{(Q,S)} \exp[-(N_{A_1B_1} + N_{A_2B_2})W - (N_{A_1B_2} + N_{A_2B_1})W'' - (N_{A_1A_2} + N_{B_1B_2})W']/kT, \tag{4}$$

where $\Sigma^{(Q,S)}$ is sum over all configurations taking into account all possible arrangements in positions and orientations. If N is the total number of molecules in the system, there evidently,

NQS molecules in A_1 positions,
$N(1-S)$ molecules in A_2 positions,
$N(1-Q)S$ molecules in B_1 positions,
$N(1-Q)(1-S)$ molecules in B_2 positions.

If $Q = S = 1/2$, both positions and orientations are completely disordered and if $Q = S = 1$, both of them are perfect order.

Applying the Bragg-Williams aproximation, the configuration partition function can be expressed

$$\Omega(Q,S) = \gamma(Q,S)\exp[-(N_{A_1B_1} + N_{A_2B_2})W - (N_{A_1B_2} + N_{A_2B_1})W'' - (N_{A_1A_2} + N_{B_1B_2})W']/kT, \tag{5}$$

where $\gamma(Q,S)$ is the number of ways of distributing the molecules among the sites for given Q and S and can be written

$$\gamma(Q,S) = \left\{\frac{N!}{[NQ]!\,[N(1-Q)]!}\right\}^2 \cdot \frac{[NQ]!}{[NQS]!\,[NQ(1-S)]!} \cdot \frac{[N(1-Q)]!}{[N(1-Q)S]!\,[N(1-Q)(1-S)]!}, \tag{6}$$

After using Equations (5) and (6) with free energy, $F = -kT\ln\Omega(Q,S)$, and the Stirling approximation, the free energy F_d is found to be

$$\Phi = F_d/N = -zW/kT\{[(1-2S+2S^2) + rS(1-S)]Q(1-Q) + v[(1-2Q+2Q^2) + rQ(1-Q)]S(1-S)\} - [S\ln S + 2Q\ln Q + (1-S)\ln(1-S) + 2(1-Q)\ln(1-Q)], \tag{7}$$

where d indicates the free energy contribution due to the disordering of Q and S.

In Equation (7) the free energy is given in terms of S and Q, at equilibrium

$$\frac{\partial\Phi}{\partial Q}=0, \quad \frac{\partial\Phi}{\partial S}=0. \tag{8}$$

Using Equations (7) and (8), the two self-consistent equations in terms of Q and S are obtained.

$$\ln\frac{Q}{1-Q}=(zW/2kT)(2Q-1)\{[(1-2S+2S^2)+rS(1-S)+vS(1-S)(r-2)\}, \tag{9}$$

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

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 interstitial site, and it is one of the key parameters in the theory. The other one is r. Equation (9) reduces to Equations (3.5) and (3.6) in P and K theory[6] if $W''=W$ and Equation (9A) in L-J and D theory[4] if $W''=W$ and $W'=0$. It is very easy to see that the point $Q=S=1/2$ is always a solution of Equation (9), this corresponds for high zW/kT and for lower zW/kT, $Q=S=1$. The behaviour of intermediate zW/kT depends on the strength of v critically, as well as on r. For the purpose of numerical calculations, we assume the model to be two interpenetrating face-centered cubic lattice, so that $z=6$ and $z'=12$.

The variations of the equilibrium values of S and Q as a function of the reduced temperature kT/zW are shown for several values of v in Figure 1. Figures are obtained for $r=1.6$, because we have seen the agreement between our theory and the experimental data is better around $r=1.6$ through the series of the work. The behaviour of these figures is similar to Figure 1 of the P and K theory, but disappearance of the S and Q are different. This is very important for transition temperatures as well as in good agreement with experimental works. From the behaviour of these figures one can find the following results:

a) $v<0.579$, $S=Q=1$ for the low reduced temperature kT/zW, as kT/zW is increased first S becomes $1/2$, shown in Figure 1a ($v=0.5$). Therefore the orientation order parameter is disordered ($S=1/2$) but the position is ordered ($Q\neq 1/2$). The low value of v corresponds to molecular system with a relatively low barrier to reorientation. This would be the case for a compact, globular molecular characteristic of a plastic crystal. Also S becomes disorder continuously, but Q has a discontinuity at the certain kT/zW (e.g. $kT/zW=0.1935$ for $v=0.5$).

b) $v=0.579$, orientational and positional disorder occur continuously at the same temperature and corresponding to ordinary melting, see Figure 1b.

c) $v>0.579$, this case looks like the case of $v<0.579$, except that the behaviour of S and Q is interchanged, see Figure 1c ($v=0.7$). It corresponds to high orientational barrier (or low translational barrier), behaviour which at first glance appears similar to that

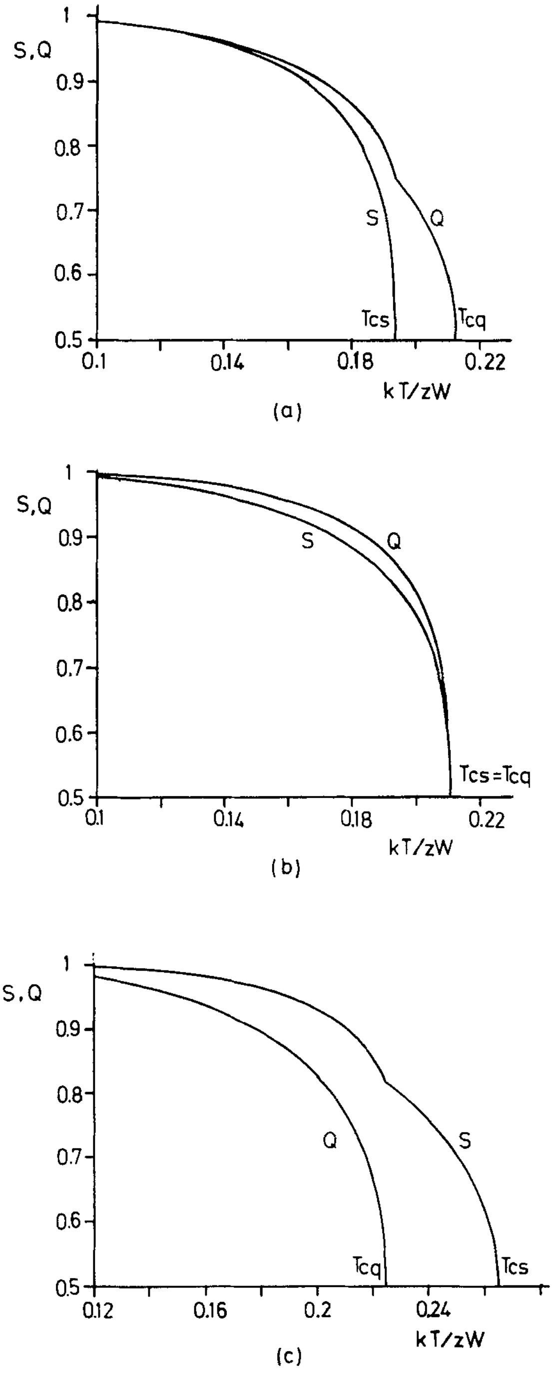

FIGURE 1 Variation of the positional order Q and the orientational order S with the reduced temperature kT/zW. T_{cq} and T_{cs} are the critical reduced temperatures for Q and S respectively ($r = 1.6$). a) $v = 0.5$ b) $v = 0.579$ c) $v = 0.7$

obtained of a nematic liquid crystal. Positional order disappears at lower temperature than does orientational order. Furthermore we should point out that, one cannot obtain a complete picture of the transition from plots like that in Figure 1; it is necessary to examine the theoretical transition isotherms. In the next section and in the series of our papers, we will work out theoretical isotherms for the melting, solid-solid transition, solid-nematic transition, nematic-isotropic transition and also obtain phase diagrams and compare with experimental data.

It should be mentioned that more detailed figures of the variation of Q and S as a function of the reduced temperature for different values of ν and r were studied by Özgan.[19]

4. EVALUATION OF THERMODYNAMIC PROPERTIES OF MELTING

In order to study the conditions under which the theory predicts phase changes, extensively and precisely, we need first to examine the free energy, F. The partition function consists of two parts, the first part gives the contribution due to completely ordered solid, and the second one gives the contribution due to the disordering. We can split F into two parts accordingly:

$$F = F_0 + F_d, \tag{10}$$

where

$$F_0 = -NkT \ln f,$$

$$F_d = -kT \ln \Omega(Q,S).$$

Again F_0 gives the partition function for the completely ordered system and F_d gives the contribution due to the disordering of Q and S. Other thermodynamic functions can be derived from the free energy and also expressed as a sum of two parts in this way. In order to study the equation of state and to obtain the isotherms, we need to find the pressure which also can be conveniently split into two parts

$$P = P_0 + P_d, \tag{11}$$

where

$$P_0 = -\left(\frac{\partial F_0}{\partial v}\right)_T \quad \text{and} \quad P_d = -\left(\frac{\partial F_d}{\partial v}\right)_T.$$

The pressure and other thermodynamic functions associated with the single partition function f have been tabulated by Wentorf *et al.*[20] on the basis of the Lennard-Jones 6–12 intermolecular potential and the three-shell spherically smoothed cell fields. We used these tabulated values and we extrapolated to lower temperatures when necessary. In order to determine the contribution due to the disordering part of the thermodynamic function we need to specify the volume dependence of W and W'. Following Pople and Karasz [6,7] we take W/W' independent of volume and

$$W = W_0(v_0/v)^4,$$

$$W_0/\varepsilon = 0.977, \tag{12}$$

where v_0 is the standard volume if the molecules are placed on f.c.c. lattice with a nearest neighbouring distance of $2^{1/6}\, r_0$, r_0 is the separation for zero interaction, i.e., balance between attractive and repulsive energies and ε is the energy minimum of the intermolecular potential.

The pressure P_d can be found using Equations (7), (11) and (12)

$$\begin{aligned}\frac{P_d v_0}{NkT} &= \frac{v_0}{N}\left[\frac{\partial}{\partial v}\Omega(Q,S)\right] \\ &= -4(v_0/v)(zW/kT)\{[(1-2S+2S^2)+rS(1-S)]Q(1-Q) \\ &\quad + \nu[(1-2Q+2Q^2)+rQ(1-Q)]S(1-S)\}.\end{aligned} \tag{13}$$

This equation gives $P_d v_0/NkT$ as a function of (v/v_0), kT/ε, ν and r, so that by adding to $P_0 v/\mathrm{NkT}$ one can obtain a complete isotherm. In this paper we have only looked for transitions at zero pressure as done by Pople and Karasz.

Three typical isotherms are shown in Figure 2 where one can see one or two kinks when the two kinds of long-range order disappear. In the isotherms, points marked S and Q, in other words kinks, indicate volumes at which orientational and positional orders disappear. The two phases represented 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. Figure 2a shows the isotherm for $\nu = 0.3$, $kT_m/\varepsilon = 0.5965$ and $r = 1.6$. The point A corresponds to the solid ($S = 0.5$ and $Q = 0.89$) and B to the liquid ($S = Q = 0.5$). Since $S = 0.5$ at the point A, the solid at the melting point has its molecules orientationally disordered and the phase transition is the first order transition. It is worthwhile to mention that for $kT_s/\varepsilon = 0.5785$, the other isotherm was obtained for which it could be possible to have two solid phases in equilibrium corresponding to a solid-transition temperature. Since paper II of this series will give disordering solid-solid transitions and complete phase diagrams for transition under pressure, we will not study the description of solid transitions any further in this paper.

For larger values of ν, the two kinks in the curve where Q and S disappear become closer together as shown in Figure 2b ($\nu = 0.5$, $kT_m/\varepsilon = 0.6075$ and $r = 1.6$). In this case the melting isotherm is such that the Q and S both occur together in the first-order transition at point A, $S = 0.982$; $Q = 0.983$ and at B, $S = Q = 0.5$. Figure 2c the isotherm for $\nu = 0.579$, $kT_m/\varepsilon = 0.617$ and $r = 1.6$. Since the positional and the orientational order parameters disappear together, we found only one kink as is shown in the figure. This exactly coincides with Figure 1b. Again the point A corresponds to the solid A ($S = 0.990$ $Q = 0.982$) and B to the liquid ($S = Q = 0.5$). For $v > 0.579$, the behaviour of Q and S is interchanged in isotherms where the point at which S becomes 0.5 is at higher volume than the corresponding point for Q. The same behaviour has been also seen in Figure 1. Eventually for further larger values of v, the theory predicts a separation again into two thermodynamic transitions, namely nematic-liquid and solid-nematic. This is analogous to the properties of liquid crystals [21] and will be reported in paper III and IV.

We should also mention that the last two values of v, i.e. $v = 0.5$ and $v = 0.579$ there will be no solid state transition below the melting point. The critical values of $v = 0.331$

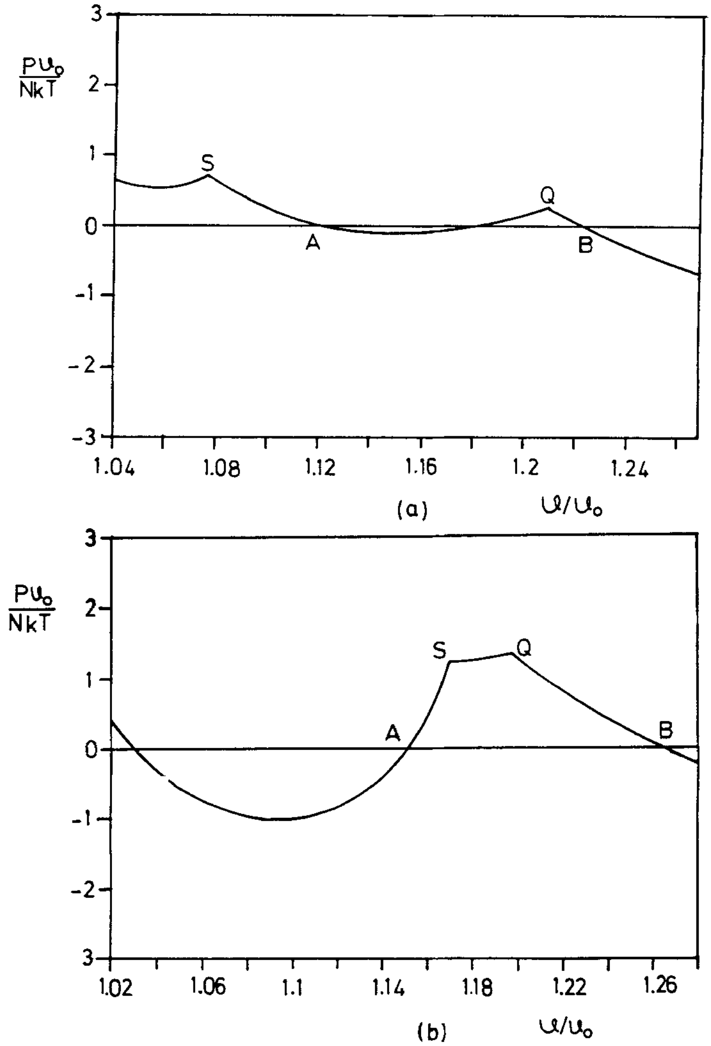

FIGURE 2 Theoretical melting isotherms ($r = 1.6$). a) $v = 0.3$ and the melting temperature, kT_m/ε, is 0.5965. b) $v = 0.5$ and the melting temperautre, kT_m/ε, is 0.6075. c) $v = 0.579$ and the melting temperature, kT_m/ε, is 0.617.

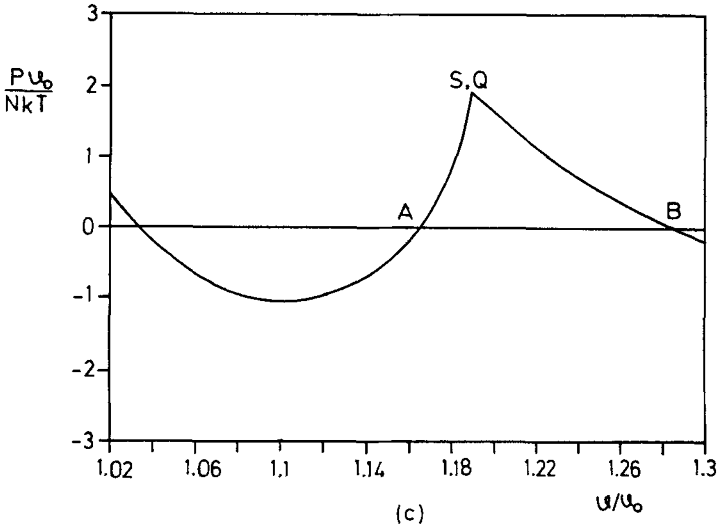

FIGURE 2 *(Continued)*

which the solid rotational transition temperature and the melting temperature first coincide as illustrated in Figure 3. Since we have found the melting isotherms at zero pressure for a number of values of ν, the theory can now be used to predict other thermodynamic properties. For example the relative volume change $\Delta v/v^*$, where v^* is the solid volume at the melting temperature, as a function of ν values can be obtained immediately as shown in Figure 4. From Figure 4, one can see directly that the second

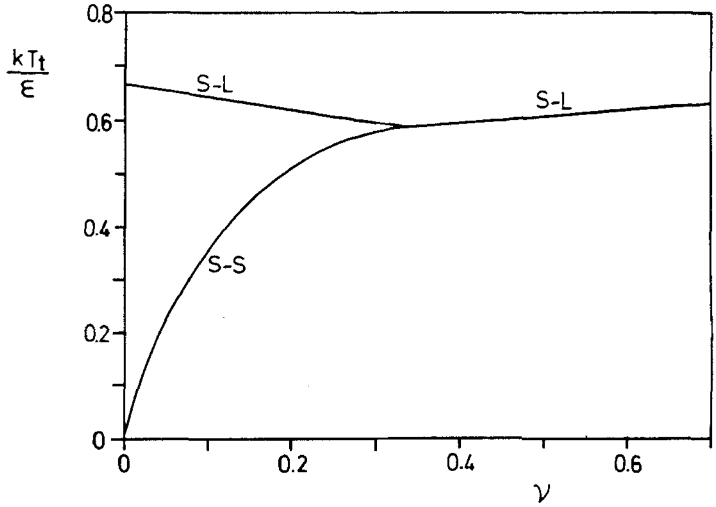

FIGURE 3 Reduced transition temperatures of solid-solid ($S-S$) and melting (solid-liquid) ($S-L$) transitions as functions of ν ($r = 1.6$).

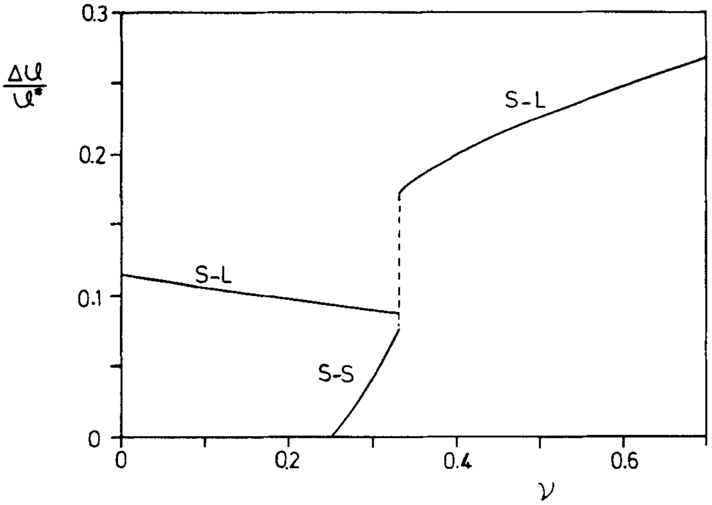

FIGURE 4 Relative volume changes of solid-solid ($S - S$) and solid-liquid ($S - L$) transitions as functions of ν ($r = 1.6$).

order solid-solid transition occur for $\nu < 0.25$ because the change of volume is zero and $\nu > 0.25$ the transition is the first order phase transition. Similarly the entropy change of melting ΔS_e can be found by calculating the entropies of two phases in the equilibrium from

$$S_e = S_{e0} + S_{ed} = -\left(\frac{\partial F_0}{\partial T}\right)_v - \left(\frac{\partial F_d}{\partial T}\right)_v . \tag{14}$$

Using Equations (10) and (14), S_e can be found,

$$\frac{S_e}{R} = -[S \ln S + 2Q \ln Q + (1-S)\ln(1-S) + 2(1-Q)\ln(1-Q)]. \tag{15}$$

where R is the gas constant. $\Delta S_e/R$ as a function of ν is plotted in Figure 5. Again from Figure 5 one can easily see that for $\nu < 0.25$ the second-order phase transition and for $\nu > 0.25$ the first-order phase transition occur. Also from Figures 4 and 5, we can immediately find that the solid-solid and solid-liquid transition temperatures first coincide at $\nu = 0.331$ which can be also seen in Figure 3. We should notice that in this paper we have only drawn the solid-solid transitions in Figures 3–5 for completeness of figures. However we will study the solid-solid transitions extensively in paper II.

5. COMPARISONS WITH EXPERIMENTAL DATA

Since we have modified the P and K theory, behaviour of the figures are similar to the figures in the P and K theory.[6] However, the melting transition temperatures are different. This makes our theory crucial and important for a comparison with experi-

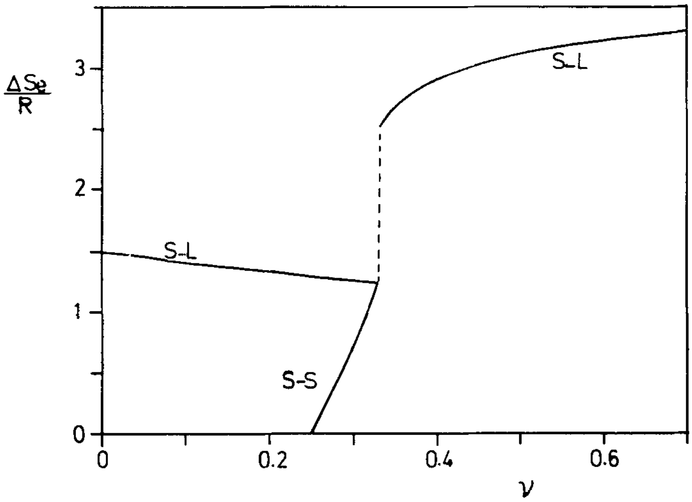

FIGURE 5 Entropy changes of solid-solid ($S-S$) and solid-liquid ($S-L$) transitions as functions of ν ($r = 1.6$).

mental data. Also some general feature of figures, especially Figures 3-5, is given by Pople and Karasz,[6] therefore we will only compare our theory with P and K and the experimental data.

In order to compare the theoretical predictions of our model with experimental data we need to allocate values of ν and r. The parameter ν cannot be found directly from experiments nor estimated theoretically in our best of present knowledge of intermolecular forces. Therefore, we will relate the thermodynamic properties of different compounds with the ratio of melting to boiling temperatures which this ratio is derived directly from the experiments.

Figure 6 illustrates the entropy of melting as a function of the ratio of melting to boiling temperatures for a number of substances as well as the theoretical prediction of the P and K and the present modified theories. Since the P and K theory contains no adjustable parameter, the agreement is reasonably good only for certain kind of substances. However, since our theory includes an adjustable parameter and it gives a good agreement not only for certain kind of substances but also gives reasonably satisfactory agreement for different kind of substances if one changes the adjustable parameter, as shown in Figure 6. Unfortunately, we cannot also reach the points on the left half of Figure 6. while changing r values and taking series of ν values. Figure 7 shows the entropy of melting as a function of volume changes for a number of substances as well as the theoretical prediction of the P and K and the present theory. As seen from the figure, the P and K theory gives a good agreement only for Xe, Ar and CH_4. However the present theory gives a good agreement not only for these substances but also predicts a reasonably satisfactory agreement for different kind of substances if one changes the adjustable parameter r. For example, taking $r = 2$ a good agreement obtains for Xe and Ar, $r = 1.6$ for CH_4 and $r = 1.3$ for PH_3.

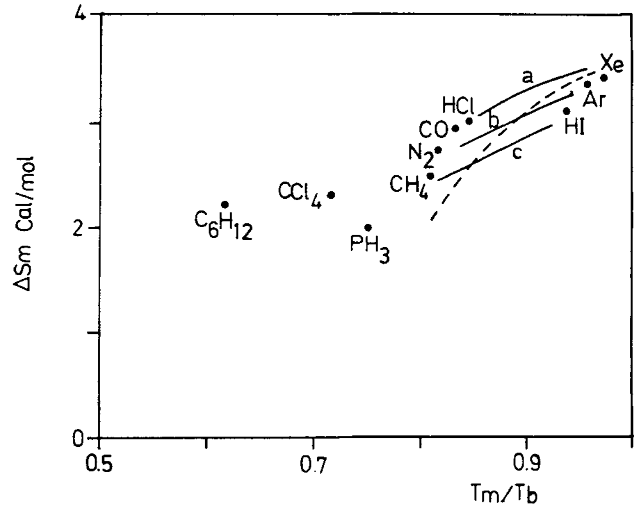

FIGURE 6 Entropy of melting as a function of the ratio of melting to boiling temperatures for a number of substances. ---- the P and K theory and —— the present theory for the different values of an adjustable parameter. (a) $r = 2$, (b) $r = 1.8$ and (c) $r = 1.6$.

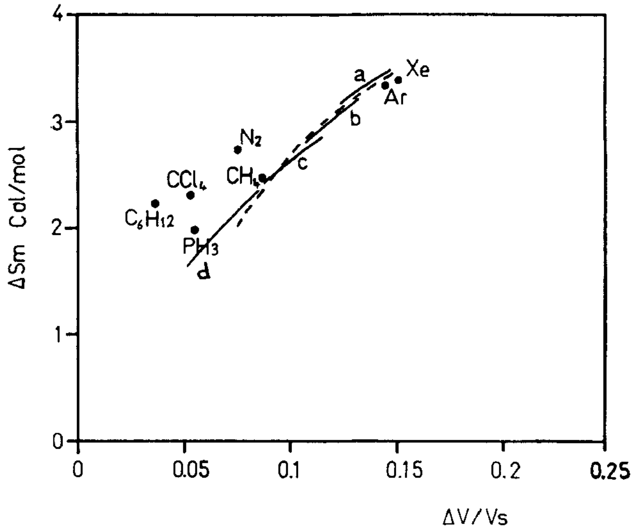

FIGURE 7 Entropy of melting as a function of volume changes for a number of substances. ---- the P and K theory and —— the present theory for the different values of an adjustable parameter. (a) $r = 2$, (b) $r = 1.8$, (c) $r = 1.6$ and (d) $r = 1.3$.

Therefore, changing the r, one can obtain a good agreement if one wants to fit certain experimental data.

Finally, we should point out that the present theory gives much better agreement with experimental data for the comparison of melting entropy ΔSm with the solid transition to boiling temperature ratio for a number of substances, will be seen in paper II.

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