Solid–plastic and plastic–isotropic liquid phase transitions on molecular crystals

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Abstract

Crystalline solid–plastic solid and plastic solid–isotropic liquid phase transitions are studied using a modified Pople and Karasz model. The thermodynamic properties of the model are evaluated by the cluster variation method. The variation of positional and orientational order parameters with temperature is studied. We have also obtained theoretical isotherms, volume and entropy changes of transitions at zero pressure and theoretical phase diagrams at high pressures. The results are compared with the original Pople and Karasz theory and the other by a modified Pople and Karasz theory which was done by Chandrasekhar et al.

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1. Introduction

The fundamental question to be faced with when discussing the mesomorphs, plastic solids (PSs) and liquid crystals, and their relationship to one another and to melting in molecular crystals is essentially this: what is the difference between a crystalline solid (CS) and a liquid? A number of considerations must be taken into account to describe the crystalline and liquid state, order, molecular dynamics, mechanical properties, thermal properties, crystal structure and molecular structure. A CS has both three-dimensional long-range positional order and orientational order; an isotropic liquid (IL) has neither. A PS has long-range positional order but orientationally it is completely disordered; a liquid crystal has both orientational order and zero (or reduced) positional order.

PSs, orientationally disordered solids, have been studied in several theoretical and experimental works [1–7]. The most useful concept in discussing
the mesophases is the theory of fusion of molecular crystals of Pople and Karasz [8,9], which is an extension of the Lennard–Jones and Devonshire [10,11] theory.

Amzel and Becka [12] point out that restricting the number of permitted orientations to two is certainly artificial and they extended the Pople and Karasz theory by taking into account the existence of more than two discrete possible positions of minimum orientational energy in the crystal.

Chandrasekhar et al. [13–15] have modified the Pople and Karasz theory by taking the energy required for a molecule to diffuse to an interstitial site that varies as $V^{-4}$, as in Pople and Karasz formulation, but the orientational barrier varies as $V^{-3}$, in conformity with theoretical studies of the orientational potential energy of the molecules in nematic liquid crystals.

The dynamic behavior of the Pople and Karasz theory was studied by Meijer and Keskin [16] and the Pople and Karasz theory was used by Keskin and Özgan [17] to study how to obtain metastable states. Keskin and Özgan [18–22] extended the Pople and Karasz theory and evaluated the thermodynamic properties by the Bragg–Williams approximation. The modified Pople and Karasz theory was applied to the solid–solid, solid–nematic and nematic–IL phase transitions.

Our purpose in this work is to modify the Pople and Karasz theory using a new energy parameter $W''$ which is the required energy for simultaneously changing both the position and the orientation of a molecule. The cluster variation method (CVM) [23–25] is used to study the equilibrium properties of the modified Pople and Karasz model. We applied the modified theory to crystalline solid–plastic solid (CS–PS) and plastic solid–isotropic liquid (PS–IL) phase transition. We obtained the changing positional and orientational order parameters with relative to temperature, theoretical isotherms, volume and entropy changes of phase transitions at zero pressure, and the theoretical phase diagrams.

The organization of the paper is as follows: In Section 2, details of the model and the solutions of equilibrium of the model are given. In Section 3, evaluation of the thermodynamic properties, isotherms for transition temperatures, changing of volume and entropy of transitions and theoretical phase diagrams are studied. Finally, a comparison with other theoretical results and conclusions are given in Section 4.

2. Model description

The present statistical theory is a simple extension of the Pople and Karasz theory. The model has two long-range order parameters; positional and orientational. The molecules may occupy sites on one of the two equivalent interpenetrating lattice N-sites to allow phase transitions, which is referred to as A- and B-sites. It is also assumed that the molecules can take up one of the two orientations at 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 $A_1$-site, this state corresponds to the equilibrium configuration of the solid. If all four configurations are equally populated, the system is completely disordered at both the position and orientation and said to be in the IL state. It is assumed that the A-site is surrounded by $z$ equivalent neighboring 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 closest to any given B-sites is $z'$.

In the theory, there are three repulsive energies. The first one is $W$ which is the required energy for a molecule moving from one site to another, the energy of an $A_1 B_1$ or $A_2 B_2$ interactions. The second one is $W'$ which is the required energy for a molecule turning from $A_1$ to $A_2$ or $B_1$ to $B_2$, the orientational energy of an $A_1 A_2$ or $B_1 B_2$. Finally, the third one is $W''$, the energy of $A_1 B_2$ or $A_2 B_1$. If a molecule changes both position and orientation, e.g. from $A_1$ to $B_2$ or $A_2$ to $B_1$, the required energy is $W''$. The Pople and Karasz theory was modified using a third energy parameter $W''$. The $W''$ is a new energy parameter added by using the geometric mean of $W$ and $W'$ energies and is written as

$$W'' = (WW')^{1/2}.$$  (1)
The variation of the energies $W$ and $W'$ with volume is given by

$$W = W_0(V_0/V)^4, \quad W' = W'_0(V_0/V)^4,$$

$$W_0/\varepsilon_0 = 0.977,$$ (2)

where $W_0$ and $W'_0$ are constants about the characteristic of the material, $\varepsilon_0$ is the minimum energy of the intermolecular potential, and $V/V_0$ is the reduced volume.

Each sublattice-site can be either vacant or occupied with molecules that may have two orientations. There are six probabilities which they show: $X_1$ up orientation, $X_2$ down orientation and $X_3$ vacant site on one of the A-sites as the spin system. Similarly, $X_4$ up orientation, $X_5$ down orientation and $X_6$ vacant site on one of the B-sites are probabilities. The six probabilities, which we will call internal variables, are associated with two long-order parameters $Q$ and $S$ as follows:

$$X_1 = QS; \quad X_2 = Q(1 - S);$$
$$X_3 = 1 - Q; \quad X_4 = (1 - Q)S;$$
$$X_5 = (1 - Q)(1 - S); \quad X_6 = Q$$ (3)

The first three variables refer to the first sublattice and the second set of three variables refers to the second sublattice. Each set is normalized separately as

$$\sum_{i=1}^{3} X_i = 1 \quad \text{and} \quad \sum_{i=4}^{6} X_i = 1.$$ (4)

The internal energy, $E$, of the model is

$$E = N[zW(X_1X_4 + X_2X_5) + z'W'(X_1X_2 + X_4X_3)$$
$$+ z''W''(X_1X_5 + X_2X_4)],$$ (5)

where $N$ is the number of lattice points in each sublattice site.

2.1. Solution for the model at equilibrium

The equilibrium properties of the theory are investigated by the lowest approximation of the CVM. The weight factor $\Omega$ is written in terms of the internal variables as

$$\Omega = \frac{(N!)^2}{\prod_{i=1}^{3}(X_iN)! \prod_{i=4}^{6}(X_iN)!}.$$ (6)

Both entropy $S_e'$ and free energy $F''$ are contributions due to the disordering of the positions and orientations of the molecules and are given by

$$S_e'' = k \ln \Omega; \quad F'' = E - TS_e''$$ (7)

where $k$ is the Boltzmann constant and $T$ is the absolute temperature.

Using Eqs. (5)–(7) and making use of the Stirling approximation, the free energy per molecule is found to be

$$\phi = \frac{\beta F''}{N} = \beta E + \sum_{i=1}^{6} X_i \ln X_i.$$ (8)

The quantity $\beta = 1/kT$. Using Eqs. (3) and (8), the free energy per molecule is written in term of the order parameters as

$$\phi = \frac{\beta F''}{N} = [S \ln S + 2Q \ln Q + (1 - S)\ln(1 - S)$$
$$+ 2(1 - Q)\ln(1 - Q)] + (zW/kT)$$
$$\times [Q(1 - Q)(1 - 2S + 2S^2) + S(1 - S)$$
$$\times (1 - 2Q + 2Q^2)v$$
$$+ 2QS(1 - S)(1 - Q)^{\sqrt{v}}]],$$ (9)

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. It is a physical realistic coupling constant between orientational and positional order and a key parameter in the present theory. The thermodynamic properties of the system investigated depends on values of $v$.

The minimization of Eq. (9) with respect to $Q$ and $S$ gives

$$\frac{\partial \phi}{\partial Q} = 0, \quad \frac{\partial \phi}{\partial S} = 0.$$ (10)

Using Eqs. (9) and (10) the two self-consistent equations in terms of the long-range order
parameters are obtained:
\[
\ln \frac{Q}{1 - Q} = \frac{zW}{kT} (2Q - 1) \\
\times [(1 - 2S + 2S^2) + 2S(1 - S)(\sqrt{v} - v)].
\]
\[
\ln \frac{S}{1 - S} = \frac{zW}{kT} (2S - 1) \\
\times [(1 - 2Q + 2Q^2)v \\
+ 2Q(1 - Q)(\sqrt{v} - 1)].
\] (11)

Eq. (11) gives Eqs. (3.5) and (3.6) in the Pople and Karasz theory if \( W' = W \) and Eq. (9A) in Lennard–Jones and Devonshire theory if \( W'' = W' \) and \( W'' = 0 \).

\( Q = S = \frac{1}{2} \) is always a solution of Eq. (11) that corresponds to the complete disorder state of the system in both position and orientation. Order parameters change from \( \frac{1}{2} \) to 1 in the Pople and Karasz theory where 1 corresponds to the ordered system and \( \frac{1}{2} \) to the disordered system. In order to change the order parameters from 0 to 1, we define \( q = 2Q - 1 \) and \( s = 2S - 1 \).

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 Fig. 1. The low value of \( v(v = 0.25) \) corresponds to a molecular system with a relatively low barrier to reorientation. This would be the case for a compact, globular molecule characteristic of a PS. The values \( q \) and \( s \) decrease from 1 to 0 continuously; as \( kT/zW \) increases first, \( s \) becomes 0 then \( q \). In this case, molecules have positional order and disorder in orientation in which there is CS–PS phase transition. If \( kT/zW \) increases, \( q \) will be zero too and PS–IL phase transition is shown in Fig. 1(a).

For higher values of \( v, v = 0.4 \) in Fig. 1(b), there are similar behaviors of \( s \) and \( q \) with a decreasing interval of temperature which becomes 0 of \( s \) and \( q \). In special values of \( v, v = 0.7176 \) in Fig. 1(c), \( s \) and \( q \) becomes 0 at the same reduced temperature. Although \( s \) becomes 0, \( q \neq 0 \), so that values of \( v \) corresponds to PSs. Because, the molecules of PSs have order positional but disorder orientation. For the values of \( v > 0.7176 \), the \( s \) orientation and \( q \) position order parameters have different roles and corresponds to liquid crystals. We won’t investigate the liquid crystals in this paper.

3. Evaluation of the thermodynamic properties

In order to study the thermodynamic properties, we can write down the Helmholtz free energy \( F \) from the partition function and conveniently split
it into two parts:

\[ F = F' + F'', \quad F'/NkT = -\ln f, \]
\[ F''/NkT = -N^{-1} \ln \Omega. \quad (12) \]

The first part \( F' \) gives the partition function for the completely order system and the second part \( F'' \) gives the contribution due to the disordered positions and orientations of the molecules. \( f \) is the partition function per molecule in a state of perfect order where all molecules occupy A-sites. \( \Omega \) is the complete order system and the second part gives the contribution due to the disordering of pressure into two parts: \( P = P' + P'' \), \( P' = -(\partial F'/\partial V)_T, \)
\[ P'' = -(\partial F''/\partial V)_T. \quad (13) \]

The contribution of the order to free energy \( F' \), pressure \( P' \) and entropy \( S'_e \) have been tabulated by Wentorf et al. [26] and we shall use their values (extrapolated to lower temperature where necessary).

The pressure \( P' \) which is the contribution of the disorder of the molecules both at the position and the orientation can be found using Eqs. (8), (10) and (11):

\[ \frac{P''V_0}{NkT} = \frac{V_0}{N} \left( \frac{\partial \Omega}{\partial V} \right)_T \]
\[ = 4 \frac{V_0^3 W}{V} \frac{zW}{kT} \{ s(1 - S) \}
\[ \times \left[ (1 - 2Q + 2Q^2)v + 2Q(1 - Q)\sqrt{v} \right] \]
\[ + Q(1 - Q)(1 - 2S + 2S^2) \}. \quad (14) \]

This equation gives \( P''V_0/NkT \) as a function \( V/V_0, kT/u_0 \) and \( v \), so that by adding to \( P'V_0/NkT \) we obtain a complete isotherm.

The thermodynamic behavior depends on the value of the parameter \( v \). There is a critical value of \( v = 0.315 \) below which two separate transitions, the CS–PS transition for low temperature and PS–IL (melting) transition for the higher temperature are obtained. If \( v \) is greater than 0.315, the two transitions coalesce and there occurs a single CS–IL (ordinary melting) phase transition with much greater entropy and volume changes.

Three isotherms are shown in Fig. 2 and the points marked \( s \) and \( q \) on the kinks indicate pressures and volumes at which orientational and positional order disappear. Two phases in equilibrium represented by the points A and B could be obtained and for this the temperature \( kT/u_0 \) has to be adjusted to give equal areas above and below the zero-pressure line. Fig. 2(a) shows a theoretical isotherm for the CS–PS transition temperature for \( v = 0.3 \) and \( kT/u_0 = 0.523 \). The phases corresponding to the points A and B may exist in equilibrium with each other. The phase at the A point is a CS which has both the position and orientation order and phase B is a PS of which molecules have positional order (\( q \neq 0 \)) but orientationally are disordered (\( s = 0 \)). In Fig. 2(b), for the same value of \( v \) but for a higher temperature it has the PS–IL transition.

For larger values of \( v \), the two kinks in the curve become closer together as illustrated in Fig. 2(c). In this case the CS–IL transition isotherm is such that the two types of disordering, positional and orientational, both occur together in a single first-order transition at the point A, \( s \neq q \neq 0 \) and at B, \( s = q = 0 \). The total pressure \( P \), the contribution ordering of pressure \( P' \) and the contribution disordering of pressure \( P'' \) are shown together in Fig. 2(c). As shown from the figures of the theoretical isotherms, there will be CS–PS transition at the low temperature and PS–IL transition at the higher temperature for a material characterized by values of \( v < 0.315 \) at zero pressure.

Similarly the entropy of CS–PS and PS–IL transition \( \Delta S_e \) can be found by calculating the entropies of the two phases in equilibrium from \( S_e = S'_e + S''_e \)
\[ = -(\partial F'/\partial T)_V - (\partial F''/\partial T)_V, \quad (15) \]
where \( S'_e \) is the contribution of ordering and the tabulation will be taken from Wentorf et al. [26] and \( S''_e \) disordering and can be calculated in terms of the long-range order parameters using Eqs. (3), (6) and (7) as
\[ \frac{S''_e}{R} = -[S \ln S + 2Q \ln Q + (1 - S) \ln(1 - S) \]
\[ + (1 - Q) \ln(1 - Q)], \quad (16) \]
where \( R \) is the gas constant.
We can obtain reduced transition temperature $kT/\varepsilon_0$ by examining various theoretical isotherms at zero pressure for each value of $n$ parameter. These are shown in Fig. 3. There is a critical value $v = 0.315$ below which two separate transitions corresponding to the CS–PS transition at lower reduced temperature and PS–IL transition at higher reduced temperature. If $v$ is greater than 0.315, the two transitions merge into CS–IL (ordinary melting) transition at zero pressure.

Volume change is also easily determined from the isotherms at transition temperatures at zero pressure, so we can plot $\Delta V/V^*$ against $v$ in Fig. 4, where $\Delta V$ is the change in volume and $V^*$ is the volume of the phase immediately below the transition. It was seen for which there is a volume change of the CS–PS transition and PS–IL transition for values of $v < 0.315$ and higher.
volume change of CS–IL transition for values of $v > 0.315$.

The change of entropy in the transitions at the zero pressure can be found in a similar manner in Fig. 5. An entropy change of CS–PS transition and PS–IL transition for values of $v < 0.315$ and higher entropy change of CS–IL transition for values of $v > 0.315$ were seen. For $v \leq 0.1$, the CS–PS transition becomes second order and the volume and entropy change is zero and all other transitions are first-order transitions.

3.1. Theoretical phase diagrams

We can find the theoretical phase diagrams using reduced pressure and temperature coordinates for various $v$ values. These are constructed by drawing the summed $P' + P''$ isotherms for given $v$ and for a range of temperatures $kT/\nu_0$ and applying the “equal area principle” to the sigmoid portions to find the equilibrium pressures for the CS–PS, PS–IL and CS–IL (ordinary melting) transitions. Figs. 6(a–e) illustrates the typical behavior.

Fig. 6 (a) shows the phase diagram for $v = 0$. There is no CS–PS transition and we obtain a single CS–IL phase boundary. For $v > 0$ and up to $v = 0.315$, we find two phase boundaries, CS–PS and PS–IL boundaries in equilibrium at all pressures, e.g. see Fig. 6(b), $v = 0.25$.

Fig. 6(c) shows the phase diagrams for $v = 0.315$ which is the critical value where the two transitions merge at zero pressure. It can be seen that for all $P > 0$ and temperature, the transitions have separated and we obtain a phase diagram that is essentially similar to that shown in Fig. 6(b). For $v > 0.315$, the CS–IL phase boundary at the low reduced pressure and temperature, but at a higher reduced pressure and temperature, the CS–PS and PS–IL transition boundaries again separate, as can be seen in Fig. 6(d), $v = 0.4$. Finally, Fig. 6(e) shows the behavior for $v = 0.7176$. This is a special value of $v$ in the present theory and we find one single combined transition for all reduced pressures and temperatures.

It is worthwhile to mention that for $1.565 > v > 0.7176$ for the lower pressure, the theory predicts only the CS–IL boundaries but for the higher pressure the theory predicts the CS–nematic liquid crystal and the nematic liquid crystal–IL boundaries. $v = 1.565$ is the second critical value where all the phases separate at zero pressure. For $v > 1.565$, the theory predicts the CS–nematic liquid crystal and nematic liquid crystal–IL boundaries even at zero pressure. Therefore, $v > 1.565$ corresponds to the liquid crystal and we will consider this region for another study.

4. Conclusions

In this paper, we investigated crystalline solid–plastic solid (CS–PS), plastic solid–isotropic liquid (PS–IL) and crystalline solid–isotropic liquid (CS–IL) (ordinary melting) transitions on molecular crystals. The Pople–Karasz model is modified using a new energy parameter and the equilibrium properties of the modified Pople–Karasz model is studied in the lowest approximation of the CVM. Thermal variations of $s$ orientational and $q$ positional order parameters for several values of $v$ are plotted in Figs. 1. For $0 \leq v \leq 0.7176$ values, first $s$ becomes zero at low reduced temperature followed by $q$. These values of $v$ correspond to CS–PS phase transition, because PSs have positional order but no orientational order. We have obtained two separate transitions for values of $v \leq 0.315$ under zero
pressure, the CS–PS transition for low temperature and PS–IL transition for the higher temperature. For \( n \geq 0.315 \), the two transitions coalesce and there occurs a single CS–IL (ordinary melting) transition with much greater entropy and volume changes. For \( n < 0.1 \), CS–PS transition becomes second order while the volume and entropy change is zero but all other transitions are of first order. The ranges of \( n \) that defines the different types of transitions are given in Table 1 along with Pople and Karasz and Chandrasekhar et al.’s theories.

The theoretical phase diagrams using reduced pressure and temperature coordinating for various values of \( n \) were studied. For special values of \( n \), \( n = 0 \) and 0.7176, there is a single CS–IL phase boundary but there is no CS–PS transition. For \( 0 < n < 0.7176 \), there are two phase boundaries,
CS–PS and PS–IL transition at the higher pressure.

Temperature, entropy and volume changes of transitions for some values of \( n \) for the present and Pople and Karasz theories are given in Table 2. The modification theory has upper entropy and volume changes in CS–PS transitions but lower in CS–IL transitions than the Pople and Karasz theory. In CS–IL (ordinary melting) transition, volume changes are bigger and entropy changes are lower than the Pople and Karasz theory. The theory predicts the CS–nematic liquid crystal and nematic liquid crystal–IL boundaries at zero pressure for \( n > 1.565 \), but we have not dealt with the liquid crystal region in this paper.

References


Table 1
The ranges of physical realistic coupling constant \( v \) defining the different types of transitions are given in Table 1 along with Pople and Karasz and Chandrasekhar et al. theories

<table>
<thead>
<tr>
<th>( v )</th>
<th>Present theory</th>
<th>Pople and Karasz theory</th>
<th>Chandrasekhar et al.’s theory</th>
<th>Types of transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt; 0.315)</td>
<td>(&lt; 0.325)</td>
<td>(&lt; 0.298)</td>
<td></td>
<td>Two transitions, CS–PS transition preceding the PS–IL transition</td>
</tr>
<tr>
<td>(&lt; 0.1)</td>
<td>(&lt; 0.17)</td>
<td>(&lt; 0.264)</td>
<td></td>
<td>Second-order CS–PS transition</td>
</tr>
<tr>
<td>(0.1 &lt; v &lt; 0.315)</td>
<td>(0.17 &lt; v &lt; 0.325)</td>
<td>(0.264 &lt; v &lt; 0.298)</td>
<td></td>
<td>First-order CS–PS transition</td>
</tr>
<tr>
<td>(0.315 &lt; v &lt; 1.565)</td>
<td>(0.325 &lt; v &lt; 1.925)</td>
<td>(0.298 &lt; v &lt; 0.975)</td>
<td></td>
<td>Single, CS–IL transition</td>
</tr>
<tr>
<td>(v &gt; 1.565)</td>
<td>(v &gt; 1.925)</td>
<td>(v &gt; 0.975)</td>
<td></td>
<td>Two transitions, positional melting preceding the rotational melting</td>
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<tr>
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<td>No second order</td>
<td></td>
<td></td>
<td>Second-order mesomorphic–isotropic transition</td>
</tr>
<tr>
<td>(v &gt; 1.565)</td>
<td>(v &gt; 1.925)</td>
<td>(v &gt; 1.047)</td>
<td></td>
<td>First-order mesomorphic–isotropic transition</td>
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Table 2
Temperature, entropy and volume changes of transitions for some values of physical realistic coupling constant \( v \) for present and Pople and Karasz theories are given in Table 2.

<table>
<thead>
<tr>
<th>( v )</th>
<th>Present theory</th>
<th>Pople and Karasz theory</th>
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<tr>
<td>(v \leq 0.315)</td>
<td>(v \leq 0.325)</td>
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<tr>
<td>(v \leq 0.1)</td>
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<td>(0.315 &lt; v \leq 1.565)</td>
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<td>(v &gt; 1.565)</td>
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