

Mesomorphic Plastic Phases of Organic Crystals

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Abstract-A thermodynamical approach to the analytical description of transitions “non-plastic phase – plastic phase” in organic crystals is proposed. An analytical expression for temperature dependence of heat capacity is obtained. It is shown that unlike “pre-translational” anomalies commonly observed at structural (polymorphic) transformations, the influence of plasticization on elastic properties of organic crystals amounts to nothing more than abrupt changes of these properties in the plasticization point. Baric dependence of the plasticization temperature is found. Available thermodynamical data on adamantane, 1-aminoadamantane, and pentaerythrityl fluoride are analyzed.

Keywords- Organic Crystals; Crystal Mesomorphism; Plastic Crystal; Plastic Crystalline Phase; Thermodynamic Properties

I. INTRODUCTION

The majority of intensively studied solid-to-solid transformations in organic crystals may be regarded either as a manifestation of structural polymorphism or as a manifestation of conformational polymorphism^[1]. At the same time, a third type of structural transformations of organic solids is known as well^[2, 3]. Namely, some organic solids can pass through an extraordinary intermediate (mesomorphic) state before melting.

Mesomorphism of this kind is appropriate to organic substances formed by molecules of quasi-globular shape with scarce steric hindrance for reorientation. Molecular structures of solids in such states exhibit translational order without orientational order. Therefore, these solids are optically isotropic and may be referred to as “vaporous crystals”. Nevertheless, in practice the mentioned mesomorphic state is usually discovered by high plasticity that makes it possible to force the solid of this kind through an orifice. For this reason, such phases are commonly referred to as plastic crystals.

Mesomorphic crystal plasticity is not a rare phenomenon^[4, 5] and since 1970s plastic crystals have been repeatedly treated monographically (see, for instance, ^[6-9]). However, in these treatments numerous experimental facts prevail, especially, structural, thermo-analytical, and calorimetric data. At the same time, the theory of mesomorphic crystal plasticity has not been built so far.

The first phenomenological description of the orientational disorder in plastic crystals was proposed by Guthrie & McCullough^[2]. Vega et al^[10] advanced some mathematical models of plastic crystals. Energy models of orientational disorder of molecules in plastic crystals are known as well^[11]. In this paper, thermodynamic features of mesomorphic crystal plasticity are studied theoretically.

II. THEORY

We take the following facts^[2, 3, 6-9] as a base of our consideration.

- (i) The plasticization temperature T_λ is as reproducible as the melting temperature T_m .
- (ii) Cooling to temperatures $T < T_\lambda$ reversibly transforms the plastic and optically isotropic state of an organic substance to the non-plastic and optically anisotropic state of the same substance, i.e., to the usual molecular crystal.
- (iii) The plastic state of an organic crystal at temperatures $T_\lambda < T < T_m$ is as stable as the non-plastic state of the same crystal at temperatures $T < T_\lambda$.

Hence, the plasticization of organic crystals at $T = T_\lambda$ may be regarded as the manifestation of their structural dimorphism. Hereafter we will consider the transformation “non-plastic modification – plastic modification” as a structural phase transition that is conditioned by reconstruction of the crystal structure of the organic solid, namely, by orientational disordering of molecules in lattice points.

A transition to the plastic crystalline state is conditioned by rotational activity of molecules, i.e. by their ability to rotate freely in the lattice points^[12]. Therefore we may assume that the transition to the plastic crystalline state is determined by inequality

$$N_d > N_r \quad (1)$$

where N_d is the number of “irregular” positions of molecules in a lattice (molecular orientations in these positions are arbitrary since molecules are rotationally active) and N_r is the number of “irregular” positions of molecules in a lattice

(molecular orientations in these positions are translationally invariant). Taking the Inequality (1) as a criterion of “non-plastic modification – plastic modification” allows using as a parameter of this transition the dimensionless quantity

$$q = \frac{N}{N_d - N_r} \quad (2)$$

with $N = N_d + N_r$

The Parameter q enables quantitative characterization of the plasticization (see Fig. 1). At rather low temperatures rotational activity of molecules is notoriously low ($N_d \ll N_r$), and non-plastic phase is maximally stable: $q \rightarrow -1$. With increasing temperature the number N_d increases. This increases the instability of the non-plastic phase structure, hence, an absolute value of the parameter q increases. Nevertheless, until $N_d < N_r$, plasticity and optical isotropy do not manifest ($q < 0$). As $N_d \rightarrow N_r$ at $T \rightarrow T_\lambda$, the structure instability of the non-plastic phase tends to its limit ($q \rightarrow -\infty$), and an abrupt transition to the plastic and optically isotropic phase ($q > 0$) occurs.

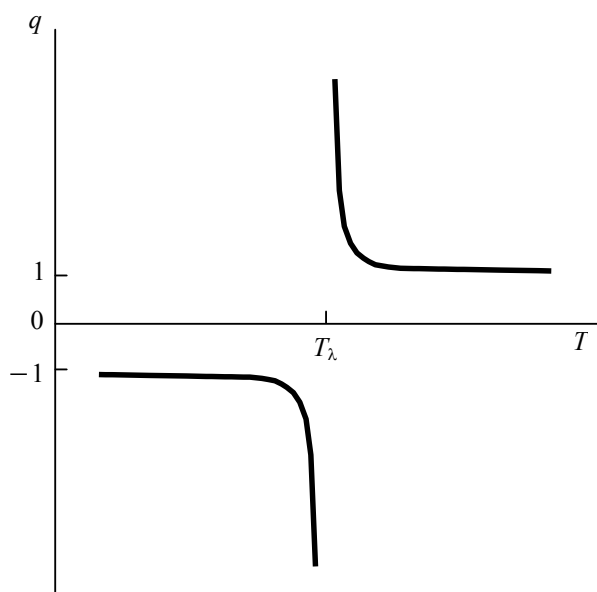


Fig. 1 Temperature dependence of the parameter of transition “non-plastic phase – plastic phase”

It was already mentioned that rotationally active molecules rotate freely in lattice points^[2-6, 12], thus sojourning in the vapor-like state. The latter indicates the “energetic detachment” of N_d molecules occupying irregular positions from the rest of molecules. The energetic detachment of N_d molecules in the crystal consisting of $N = N_d + N_r$ molecules enables to use the Boltzmann correlation

$$\frac{N_d}{N_r} = e^{-\frac{w}{\kappa_B T}} \quad (3)$$

where κ_B is the Boltzmann constant and w is the change of molecular energy at the transition of a molecule from the regular position to the irregular position.

Orientational disordering of molecules is conditioned by reconstruction of the crystal structure as a whole. Therefore it is natural to suppose that isotropic external pressure p equally influences the energy of a molecule in a regular position and the energy of the same molecule in an irregular position. Then the value of w does not depend on p . At the same time, Correlations (1) and (3) point out that

$$w|_{T < T_\lambda} > 0, \quad w|_{T = T_\lambda} = 0, \quad w|_{T > T_\lambda} < 0. \quad (4)$$

On the basis of this we assume

$$w = 2a\kappa_B(T_\lambda - T) \quad (5)$$

where a is dimensionless positive constant.

III. RESULTS AND DISCUSSION

The Definition (2) is equivalent to the equality

$$q = \left(\frac{N_d}{N_r} + 1 \right) / \left(\frac{N_d}{N_r} - 1 \right). \quad (6)$$

Substituting (5) into (6) with account of (3) yields

$$q = -\coth(a\vartheta) \quad (7)$$

where $\vartheta = \frac{T_\lambda}{T} - 1$.

Let ordering (or disordering) structure of a system be characterized by a Parameter $\tilde{q}$ determining some property that is acquired or lost by this system at the structural transformation accompanying the ordering (or disordering) process (see^[13]). Then at given values of Temperature T and Pressure p the equilibrium value $\tilde{q} = \tilde{q}'$ realizes for which

$$\left(\frac{\partial \tilde{G}}{\partial \tilde{q}} \right)_{T,p} \Big|_{\tilde{q}=\tilde{q}'} = 0, \quad \left(\frac{\partial^2 \tilde{G}}{\partial \tilde{q}^2} \right)_{T,p} \Big|_{\tilde{q}=\tilde{q}'} > 0 \quad (8)$$

where $\tilde{G}$ is the Gibbs energy regarded as a composite function $\tilde{G} = \tilde{G}(T, p; \tilde{q}(T, p))$. As applied to our case with $\tilde{q} = q$ and the Parameter q being given by the Equality (7) for the Gibbs energy G of the plasticizing crystal on the basis of (8) we have

$$\left(\frac{\partial G}{\partial q} \right)_{T,p} = \chi(q + \coth(a\vartheta)), \quad (9)$$

$$\left(\frac{\partial^2 G}{\partial q^2} \right)_{T,p} = \chi \quad (10)$$

where the positive factor χ does not depend on q . Due to this independence the Equation (9) enables to get the following expression for the Gibbs energy of the plasticizing crystal:

$$G = [G] + \chi q \left(\frac{q}{2} + \coth(a\vartheta) \right), \quad (11)$$

Where

$$[G] = [G]_- \equiv G|_{q=-1} \quad \text{at } T < T_\lambda; \quad [G] = [G]_+ \equiv G|_{q=1} \quad \text{at } T > T_\lambda. \quad (12)$$

The independence of χ on q indicates the independence of this factor on the temperature and simultaneously indicates that the convexity of the profile $G(q)$ does not change at the plasticization [see (10)]. Therefore if χ depends on pressure then this dependence is monotonous since the contrary is equivalent to the existence of some low-stability states beyond the line $T_\lambda(p)$. In its turn the monotonous dependence $\chi(p)$ stipulates the pressure value at which χ vanishes. Consequently,

$$\chi = \text{const}. \quad (13)$$

The Expression (11) leads to the conclusion that plasticization exerts an essential influence on the value of the isobaric heat capacity C_p :

$$C_p = [C_p] + \{C_p\}, \quad (14)$$

Where

$$[C_p] = -T \left(\frac{\partial^2 [G]}{\partial T^2} \right)_p, \quad \{C_p\} = \frac{\chi a^2 T_\lambda^2}{T^3 \sinh^4(a\vartheta)}. \quad (15)$$

At the same time, elastic properties of a crystal are not subjected to this influence.

To characterize these properties quantitatively we use thermal expansion coefficient

$$\alpha = \frac{1}{V^\circ} \left(\frac{\partial V}{\partial T} \right)_p$$

and compressibility

$$\beta = \frac{-1}{V^\circ} \left(\frac{\partial V}{\partial p} \right)_T$$

where V is the molar volume; superscript $^\circ$ here and henceforth refers the corresponding values to the standard pressure. The Expression (11) gives:

$$\alpha = \frac{1}{V^\circ} \frac{\partial^2 [G]}{\partial T \partial p}; \quad \beta = \frac{-1}{V^\circ} \left(\frac{\partial^2 [G]}{\partial p^2} \right)_T. \quad (16)$$

According to (12), the value $[G]$ does not depend on q . Therefore Quantities α and β manifest rather weak temperature dependence with a jump in the plasticization point:

$$\Delta\alpha = \frac{1}{V^\circ} \left(\frac{\partial^2 [G]_+}{\partial T \partial p} - \frac{\partial^2 [G]_-}{\partial T \partial p} \right); \quad \Delta\beta = \frac{-1}{V^\circ} \left[\left(\frac{\partial^2 [G]_+}{\partial p^2} \right)_T - \left(\frac{\partial^2 [G]_-}{\partial p^2} \right)_T \right]. \quad (17)$$

An analogous equation is valid for the heat capacity jump. Indeed, according to (15)

$$\lim_{T \rightarrow T_\lambda - 0} \{C_p\} = \lim_{T \rightarrow T_\lambda + 0} \{C_p\}.$$

Consequently, the heat capacity jump in the plasticization point is described by the equation

$$\Delta C_p = \Delta[C_p] = T \left[\left(\frac{\partial^2 [G]_-}{\partial T^2} \right)_p - \left(\frac{\partial^2 [G]_+}{\partial T^2} \right)_p \right]. \quad (18)$$

Equations (17) and (18) indicate that molar heat Θ of the transformation “non-plastic modification – plastic modification” and molar volume jump ΔV accompanying this transformation do not depend on the Parameter q . We assume linear dependence of these quantities on pressure and substitute the equations

$$\Delta V = \Delta V^\circ + B(p - p^\circ), \quad \Theta = \Theta^\circ + \xi(p - p^\circ) \quad (19)$$

[where B and ξ are constant] into the Clausius-Clapeyron equation. Then the dependence of plasticization temperature on pressure will be expressed as follows:

$$\ln \left[\frac{T_\lambda(p)}{T_\lambda^\circ} \right] = \frac{Bp}{\xi} + \Gamma \ln(\Theta^\circ + \xi(p - p^\circ)) \quad (20)$$

where $\Gamma = \frac{\Delta V^\circ \xi - B(\Theta^\circ + 2\xi p^\circ)}{\xi^2}$. If we additionally assume that

$$\frac{\xi(p - p^\circ)}{\Theta^\circ} \ll 1 \quad (21)$$

(i.e. that variations of pressure scarcely affect the transformation heat), then instead of the Equation (20) we get an approximate equation

$$T_\lambda(p) \approx T_\lambda^\circ \left[1 + \frac{2\Delta V^\circ(p - p^\circ) + B(p - p^\circ)^2}{2\Theta^\circ} \right]. \quad (22)$$

It is worth noting that the case (21) is appropriate for the most widely known plastic crystal adamantane $C_{10}H_{16}$. Indeed, according to^[14, 15], plasticization temperature of adamantane varies with pressure as

$$T_{\lambda}(p) = 208.6 + 21.1p - 0.0734p^2$$

[here p is in kilobars] just as it is specified by the Equation (22).

Side by side with the Formula (22) the analytical expression for temperature dependence of heat capacity [Formulas (14) and (15)] is in good agreement with available experimental data as well. Figures 2 and 3 present the results of calculations according to Formulas (14) and (15) in comparison with experimental measurements^[16-18] of heat capacity of adamantane ($T_{\lambda}^{\circ} = 208.6\text{ K}$; $\chi = 4.55 \cdot 10^{-7}$; $a = 48.967$) and pentaerythrityl fluoride ($T_{\lambda}^{\circ} = 244.1\text{ K}$; $\chi = 6.28 \cdot 10^{-10}$; $a = 2.21$).

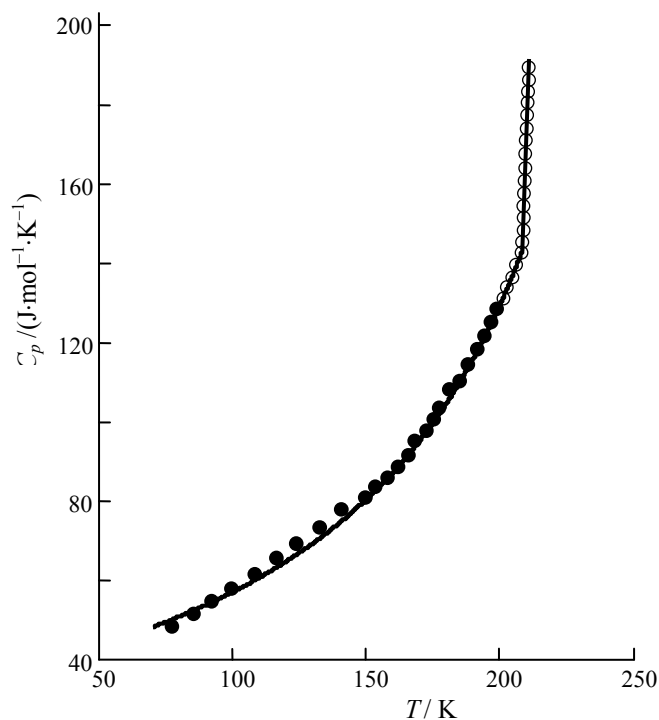


Fig. 2 Temperature dependence of heat capacity of adamantane

Solid line is obtained by calculations from formulas (14) and (15), black circles are the results of measurements^[16], empty circles are the results of measurements^[17]

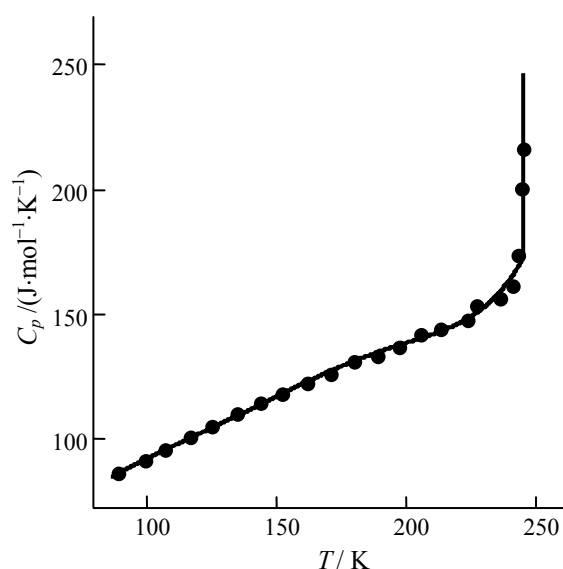


Fig. 3 Temperature dependence of heat capacity of pentaerythrityl fluoride

Solid line is obtained by calculations according to formulas (14) and (15), circles are the results of measurements^[18]

The figures show that our formulas enable high-accuracy description of the principal thermodynamical peculiarity of plasticizing crystals. Namely, we managed to give analytical description of relatively streamline increase of their heat capacity at heating beyond the vicinity of the plasticization point with an extremely abrupt (bend-like) transition to impetuous grow of heat capacity at $T \rightarrow T_{\lambda}$. This temperature behavior differs greatly from the behavior of heat capacity in the region of an

“ordinary” polymorphic transformation. This distinction is especially clear when one takes notice of 1-aminoadamantane whose plasticization ($T_{\lambda}^{\circ} = 284.6\text{ K}$) is in close neighborhood with an “ordinary” polymorphic transition occurring at the temperature 244.1 K (see^[19]).

IV. CONCLUSIONS

A thermodynamical approach to the analytical description of transitions “non-plastic phase – plastic phase” in organic crystals is proposed [Formulas (1) – (7), (11) – (13)]. The application of this approach has yielded the following.

1. An analytical expression for temperature dependence of heat capacity is obtained [Formulas (14), (15)].
2. Thermal expansion and compressibility of organic crystals have in the vicinity of the plasticization point no “pre-translational” anomalies commonly observed at structural (polymorphic) transformations. It is shown that the influence of plasticization on elastic properties of organic crystals amounts to nothing more than abrupt changes of these properties in the plasticization point [Formulas (16), (17)].
3. Baric dependence of the plasticization temperature is found [Formula (20)]. In the particular case when variations of the plasticization heat under pressure are negligible [Correlation (21)], this dependence acquires the Form (22).

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