An investigation of the thermodynamic properties of long-chain molecular crystals and the possibility of their application as phase change materials

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Abstract. The thermodynamic properties of \( n \)-alkanes have been investigated by using differential scanning calorimetry. The impact of the chain length on the thermodynamic characteristics of the first order phase transitions in \( n \)-alkanes has been estimated. The \( n \)-alkanes homologous series has been analyzed using the theory of diffused phase transitions. The nuclei sizes of a new phase within the bulk of the initial phase have been estimated.

1. Introduction

Currently, phase change materials (PCM) have widely been used for consumption, storage, and release of heat energy from various heat sources due to their own thermal effects during phase transitions (PT). The use of PCM is extremely important for creating comfortable living conditions for people in the temperature from \(-40^\circ\text{C}\) to \(70^\circ\text{C}\). In addition, PCM are completely environmentally friendly.

The long-chain molecular crystals (LMC), in particular, \( n \)-alkanes, are among the most effective PCM. In \( n \)-alkane mixtures, which are of the greatest practical interest, as was shown experimentally [1], a significant decrease in the magnitude of thermal effects was observed due to a decrease in one of the components of PT. This reduces the efficiency of \( n \)-alkane mixtures as compared to a set of the same, but isolated component of the mixture. To clarify the mechanism of "work" of PCM based on \( n \)-alkane mixtures, it is necessary to investigate the phase transformations in the individual components. Moreover, for a better understanding of the physics of processes, it is necessary to consider them at the nanoscale.

The objects of the study are \( n \)-alkanes with a chain length of 3-5 nm. The chains of \( n \)-alkanes comprise of the methylene \( \text{CH}_2 \) trans-sequences groups, as well as of the chain-terminated methyl \( \text{CH}_3 \) groups. The interaction between the chains is due to the weak van der Waals forces [2]. In this work, the samples of \( n \)-alkanes with a chain length consisting of 21 to 25 \( \text{C} - \text{C} \) bonds were studied. Geniecose C\(_{21}\)H\(_{44}\), docosane C\(_{22}\)H\(_{46}\), tricosane C\(_{23}\)H\(_{48}\), tetracosane C\(_{24}\)H\(_{50}\) and pentacosan C\(_{25}\)H\(_{52}\) samples were acquired from the Sigma Company.

By changing the chain length of \( n \)-alkanes, one can vary the ratio between the volume and the surface energies of crystals. Thus, a model series with variable thermodynamic properties can be investigated.

The amount of heat absorbed in the LMC consists of two components: the heat absorbed by increasing thermal motion of molecules and the heat absorbed during phase transitions in narrow temperature ranges. In more detail, phase transitions have been investigated.
2. Experiment

The dependence of the heat capacity on the temperature for \( n \)-alkanes \( C_{21}H_{44}, C_{22}H_{46}, C_{23}H_{48}, C_{24}H_{50}, C_{25}H_{52} \) was determined by differential scanning calorimetry (DSC) (figure 1). On these curves, endothermic \( T_{max1}, T_{max2} \) (when heated) and exothermic \( T_{min1}, T_{min2} \) (when cooled) peaks are observed corresponding, as was shown in [3], to first-order phase transition (PT-1) and second-order phase transition (PT-2). In some cases, the peaks of the first and second-order transitions on the DSC curves can be partially or fully merged. So, the real shape of the PT-1 peak should be determined. For this purpose, we developed an original technique that allows one to separate the solid-phase transition experimentally in a “pure” form.

![DSC curves for n-alkanes.](image)

**Figure 1.** DSC curves for \( n \)-alkanes.

The basis of this method is the use of temperature hysteresis of the PT-1, i.e. the differences between the transition temperatures during heating and cooling (figure 2 curves 1 and 4). For the experimental separation of the transitions for all the studied \( n \)-alkane samples, the procedures identical to that shown in figure 2 for docosane were performed — the sample was heated to the melt state at \( T = 324 \) K (curve 1), and then cooled, bypassing the exothermic peak, \( T \sim 317 \)K (curve 3). In this way, an intermediate phase state was formed, during which a solid phase first-order transition did not occur in the cooling cycle, and the ordering associated with the second-order transition was already realized. Reheating the sample to the melting temperature (curve 2) should show a “pure” PT-2, and thus the peak of the heat capacity will be associated only with an order-disorder phase transition. According to the difference between the peaks on the primary and repeated heating curves, endothermic effects can be distinguished, which should correspond only to PT-1.
Thus, according to the difference between the peaks on the primary and repeated heating curves, endothermic effects resembling $\Lambda$-shaped peaks were identified. The half width of these peaks is about 1 K, which is substantially larger than the PT interval for the low molecular weight substances. Such large half widths of the peaks indicate that the PT process is heterogeneous. These PT are called diffuse phase transitions.

3. Theoretical calculations

The fact that the transition becomes diffuse means that the change in the phase state occurs not instantly but gradually, and within a certain temperature range.

For the analysis of $\Lambda$-shaped peaks, a self-consistent field theory was developed [4]. The theory provides the possibility to analyze the change in the phase state of a system of interacting particles of different phases, including the formation and further growth of stable nuclei of a new phase in the matrix of the old phase. The nucleation mechanism is heterogeneous, and new phase nuclei are formed on crystal defects of different type, thus leading to the appearance of a phase interface, which is the characteristic sign of the first-order transition.

The main idea of the theory consists in the notion that numerous fluctuations are located in a limited volume in the old phase in the form of stable nuclei of a new phase, i.e., the so-called elementary transition volumes $\omega$. Further, as the transition develops, the motion of the phase interface occurs via the sequential additions of nuclei with a volume $\omega$ to the formed phase interface. The formation of domain nuclei requires the change in the temperature at a small value, which is determined by the energy required for the appearance of such domains. Namely this factor leads to broadening of the transition peak.

The sizes of stable nuclei $\omega$ can be determined from the shape of $C_p$ peaks corresponding to PT-1. In reference [5], the temperature dependence of the heat capacity in a diffusive phase transition is derived in the form

$$\Delta C_p(T) = 4\Delta C_m \exp\left[B(T-T_0)/T_0\right]\left[1+\exp\left[B(T-T_0)/T_0\right]\right]^{-2}$$

(1)

where $T_0$ is the temperature of a PT-1, $\Delta C_m$ is the maximum heat capacity at $T=T_0$, and $B$ is the parameter not depending on the temperature.

Asymmetric peaks were divided into two symmetric $\Lambda$-shaped peaks, assuming the equality of the
enthalpy of an experimentally obtained peak and the sum of the enthalpies of two symmetric peaks. Varying the parameters $T_0$, $\Delta C_{\text{max}}$, and $B$ for each symmetric peak, it was possible to attain coincidence with either the right (high-temperature) or left (low-temperature) shoulder of the peak. The best coincidence between the experimental and calculated dependences was observed for the parameters given in Table 1 (peaks 1 and 2). The results of the calculation of $\Lambda$-shaped peaks by equation (1) and the experimental dependences of the heat capacity $\Delta C_p(T)$ for tricosane are plotted in figure 3.

\[ \Delta C_p = 50 \text{ J/gK} \]

\[ \text{Figure 3. The decomposition of the PT-1 peak for tricosane.} \]

The parameter $B$ in equation (1) contains the most interesting information about the physical nature of a PT, as it is related with the maximum heat capacity $\Delta C_m$ as

\[ \Delta C_m = q_0 B / (4T_0) \]  

(2)

where $q_0$ is the transition heat, and $B$ is expressed as

\[ B = \omega \rho q_0 / (k T_0) \]  

(3)

where $\omega$ is the elementary transition volume, $k$ is the Boltzmann constant, and $\rho$ is the density. The parameter $B$ proved to be structurally sensitive, as it characterizes the volumes of new phase nuclei in materials with diffusive phase transitions [4]. The specific transition heat (enthalpy) can be determined from equation (2), and the elementary transition volume $\omega$ can be estimated from equation (3) (assuming, at first approximation, that the density of $n$-alkane crystals $\rho \sim 0.8 \text{ g/cm}^3$ [6]). The results of calculations with these equations are listed in Table 1.

| Sample     | Stage of the PT-1 | Fraction in the transition energy (%) | $T_0$ (K) | $B$ | $\Delta C_{\text{max}}$ (J/gK) | $q_0$ (J/g) | $\omega$ (nm$^3$) |
|------------|-------------------|--------------------------------------|-----------|----|-------------------------------|-------------|------------------|
| Geneicosane| 1                 | 72                                   | 305.5     | 1750 | 55                           | 39          | 240              |
| Geneicosane| 2                 | 28                                   | 305.8     | 6000 | 75                           | 15          | 2000             |
| Docosane   | 1                 | 100                                  | 319.5     | 3600 | 240                          | 86          | 230              |
| Tricosane  | 1                 | 87                                   | 315.9     | 1650 | 70                           | 54          | 128              |
| Tricosane  | 2                 | 13                                   | 316.03    | 4000 | 25                           | 8           | 2700             |
| Tetracosane| 1                 | 44                                   | 323.05    | 1800 | 55                           | 39          | 250              |
| Tetracosane| 2                 | 56                                   | 323.45    | 2600 | 100                          | 50          | 290              |
| Pentacosane| 1                 | 91                                   | 322.76    | 1250 | 55                           | 68          | 100              |
| Pentacosane| 2                 | 9                                    | 322.97    | 3500 | 20                           | 7           | 2800             |
4. Conclusion

The estimation of the number of molecules participating in the formation of a new phase in docosane and in the first stage PT-1 in the geneicosane shows that the elementary transition volumes $\omega \sim 230–240$ nm$^3$ contain $\sim 450–500$ molecules, i.e. the transition covers a rather great domain. A much greater number of molecules ($\sim 4000$) participate in the formation of new phase nuclei at the second stage PT-1 in geneicosane. The estimation of the number of molecules participating in the formation of a new phase in tricosane and pentacosane shows that the elementary transition volumes $\omega \sim 100–130$ nm$^3$ at the first stage PT-1 contain $\sim 200–250$ molecules. The phase transition in tetracosane also occurs in two stages, which appreciably differ from each other by their elementary transition volume containing $\sim 500–600$ molecules. A much greater number of molecules ($\sim 5000$) participate in the formation of new phase nuclei at the second stage PT-1 in tricosane and pentacosan.

Thus, it has been shown that the homologous series of $n$-alkanes has a wide temperature range of PT. This allows one to select the PCM components for a desirable temperature range. For example, to maintain a temperature in the range of 320–325 K, three $n$-alkanes are sufficient: docosane, tricosane, pentacosan, whereas to maintain the room temperature, it is possible to dispense with $n$-alkanes with a chain length consisting of 16 to 19 C–C bonds. The use of $n$-alkanes in phase change materials opens the possibility to maintain an exactly specified temperature under almost any external conditions. In particular, they can be used to create comfortable living conditions for people at external temperatures from $-40$ to 70°C.

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