

## Research Article

# Application of the Pippard Relations to Cyclohexane near the Melting Point

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The Pippard relations are verified near the melting point for cyclohexane. The experimental data for the thermal expansivity is analyzed according to a power-law formula using the critical exponent and the thermodynamic quantities are calculated close to the melting point for this molecular organic compound. This applies to those compounds showing a second order transition prior to melting.

## 1. Introduction

Various properties of cyclohexane have been studied extensively in the literature. Using different experimental techniques, its thermodynamics [1], dynamic [2–8], and structural [9–11] properties have been investigated.

Cyclohexane undergoes the sequence of phase changes at ambient temperature under high pressures. From liquid to phase I, cyclohexane solidifies as the pressure increases. At 0.5 GPa there occurs I to III transition which follows III to IV at 1.3 GPa, as observed experimentally using X-ray diffraction [9], infrared spectroscopy [3–8], Raman spectroscopy [11–13]. Below 186.1 K, an orientationally ordered structure, namely, phase II, occurs [11]. It has also been indicated that between the liquid phase ( $T > 279.8$  K) and the monoclinic solid phase ( $T < 186$  K), cyclohexane forms an orientationally disordered cubic phase [14]. In a recent study using X-ray diffraction at room temperature for high pressures to 40 GPa [15], a different sequence of phase transitions (i) between 4.14 and 6.91 GPa (phase IV to V), (ii) between 6.91 and 12.3 GPa (phase V to VI), and (iii) above 15.1 GPa (phase VI to VII) have been investigated.

Regarding the structures of the phases that occur in cyclohexane, plastic phase I is cubic, phase III is orthorhombic, and phase IV is monoclinic. It has been reported that phase V retains structural similarities with the monoclinic phase IV [16], as also pointed out previously [12].

It has been observed experimentally that IV-V transition which takes place at 3.2 GPa is accompanied by a large hysteresis [12]. These hysteresis effects have also been observed in cyclohexane [8, 13]. Near the melting point, the thermal expansivity exhibits anomaly at various pressures for a constant temperature ( $T = 299.7$  K), as observed experimentally in cyclohexane [17]. The differential thermal analysis (DTA) measurement has also revealed that cyclohexane confined in metal-organic framework exhibits thermal anomaly at 121, 213, and 306 K [18].

On the basis of the anomalous behaviour of the thermal expansivity  $\alpha_p$ , as observed experimentally [17], we examine in this study the Pippard relations which relate the specific heat  $C_p$  to the thermal expansivity  $\alpha_p$  ( $C_p$  versus  $\alpha_p$ ) and  $\alpha_p$  to the isothermal compressibility  $\kappa_T$  ( $\alpha_p$  versus  $\kappa_T$ ) for cyclohexane close to the melting point. As cyclohexane melts from the solid phase to the liquid when the temperature increases or pressure decreases, the Pippard relations are constructed for this molecular organic compound by analyzing the experimental data for thermal expansivity  $\alpha_p$  at various pressures near the melting point [17] according to a power-law formula. We then calculate the temperature dependence of the thermodynamic quantities, namely,  $\alpha_p$ ,  $\kappa_T$ , and  $C_p$ . By plotting  $C_p$  versus  $\alpha_p$  and  $\alpha_p$  versus  $\kappa_T$  for the same temperature interval, we obtain linear relations close to the melting point for cyclohexane.

## 2. Theory

In order to obtain correlations between the specific heat  $C_p$  and the thermal expansivity  $\alpha_p$  (first Pippard relation), and also correlations between the  $\alpha_p$  and isothermal compressibility  $\kappa_T$  (second Pippard relation), we derive the temperature and pressure dependencies of those thermodynamic quantities. We start with a power-law formula for the pressure dependence of the thermal expansivity  $\alpha_p$  expressed as [17]

$$\alpha_p = A(P - P_m)^{-\gamma}, \quad (1)$$

where  $\gamma$  is the critical exponent for  $\alpha_p$ ,  $A$  is the amplitude, and  $P_m$  is melting pressure. Close to the melting point, one can approximate the rate of change of pressure with the temperature as

$$\frac{P - P_m(T)}{T_m(P) - T} = \frac{dP_m}{dT}, \quad (2)$$

where the melting pressure  $P_m$  and the melting temperature  $T_m$  depend upon the temperature and pressure, respectively, along the  $P - T$  melting curve. Thus, from (2) the temperature dependence of the thermal expansivity  $\alpha_p$  can be expressed as

$$\alpha_p = A \left( \frac{dP_m}{dT} \right)^{-\gamma} (T_m - T)^{-\gamma} \quad (3)$$

according to (1). Using the thermodynamic relation

$$\frac{\alpha_p}{\kappa_T} = \frac{dP_m}{dT} \quad (4)$$

close to the melting point, the pressure and temperature dependence of the isothermal compressibility  $\kappa_T$  will be obtained as

$$\kappa_T = \frac{A(P - P_m)^{-\gamma}}{(dP_m/dT)}, \quad (5)$$

$$\kappa_T = \frac{A(dP_m/dT)^{-\gamma-1}}{(T_m - T)^{-\gamma}}, \quad (6)$$

respectively. By means of the thermodynamic relation

$$\left( \frac{\partial P}{\partial T} \right)_s = \frac{C_p}{TV\alpha_p} \quad (7)$$

and using the approximate relation

$$\left( \frac{\partial P}{\partial T} \right)_s = \frac{dP_m}{dT} = \left( \frac{\partial P}{\partial T} \right)_v \quad (8)$$

near the melting point [17], the pressure and temperature dependence of specific heat  $C_p$  can be obtained as

$$C_p = ATV \left( \frac{dP_m}{dT} \right) (P - P_m)^{-\gamma}, \quad (9)$$

$$C_p = ATV \left( \frac{dP_m}{dT} \right)^{-\gamma+1} (T_m - T)^{-\gamma}, \quad (10)$$

respectively.

From the pressure and temperature dependence of the specific heat  $C_p$  (see (9) and (10)), the thermal expansivity  $\alpha_p$  (see (1) and (3)), and the isothermal compressibility  $\kappa_T$  (see (5) and (6)), the first and second Pippard relations can be established, respectively, as given below:

$$C_p = TV \left( \frac{dP_m}{dT} \right) \alpha_p + T \left( \frac{dS}{dT} \right)_m, \quad (11)$$

$$\alpha_p = \left( \frac{dP_m}{dT} \right) \kappa_T + \left( \frac{1}{V} \right) \left( \frac{dV}{dT} \right)_m, \quad (12)$$

where the entropy change with the temperature,  $(dS/dT)_m$ , and the volume change with the temperature,  $(dV/dT)_m$ , are taken at the melting point.

## 3. Calculations and Results

The Pippard relations given above (see (11) and (12)) were established in this study by analyzing the experimental data [17] for the thermal expansivity  $\alpha_p$  of cyclohexane at various pressures for  $T = 299.7$  K close to the melting pressure. This analysis of thermal expansivity  $\alpha_p$  was performed according to the power-law formula (1) in the solid phase ( $P > P_m$ ) prior to the melting. By taking the logarithm of (1), we get

$$\ln \alpha_p = \ln A - \gamma \ln(P - P_m). \quad (13)$$

From the analysis of the experimental data, the values we obtained are tabulated in Table 1. Using the values of the critical exponent  $\gamma$ , the amplitude  $A$  (Table 1), and the experimental value of  $dP_m/dT = 5$  MPa/K [17], the temperature dependence of the thermal expansivity  $\alpha_p$  (3), the isothermal compressibility  $\kappa_T$  (6), and the specific heat  $C_p$  (10) were calculated. The temperature dependence of the specific heat per unit volume ( $C_p/V$ ) is plotted against that dependence of the thermal expansivity  $\alpha_p$  near the melting point of cyclohexane according to the first Pippard relation (11) in Figure 1. A plot of the temperature dependence of the thermal expansivity  $\alpha_p$  is given in Figure 2 as a function of the isothermal compressibility  $\kappa_T$  near the melting point according to the second Pippard relation (12) for cyclohexane.

## 4. Discussion

The Pippard relations were constructed in this study for cyclohexane close to the melting point according to (11) and (12), as shown in Figures 1 and 2, respectively. For these plots ( $C_p/V$  versus  $\alpha_p$  and  $\alpha_p$  versus  $\kappa_T$ ), the experimental data [17] for the thermal expansivity  $\alpha_p$  was analyzed using

TABLE 1: Values of the critical exponent  $\gamma$  for thermal expansivity  $\alpha_p$  and the amplitude  $A$  for cyclohexane according to a power-law formula (1). The experimental ( $dP_m/dT$ ) value [17] is also given here.

$\gamma$	$A[\text{K}^{-1}(\text{GPa})^\gamma]$	Pressure interval (GPa)	$dP_m/dT$ (MPa)
1.3	1.764	$0.023 < (P - P_m) < 0.143$	5

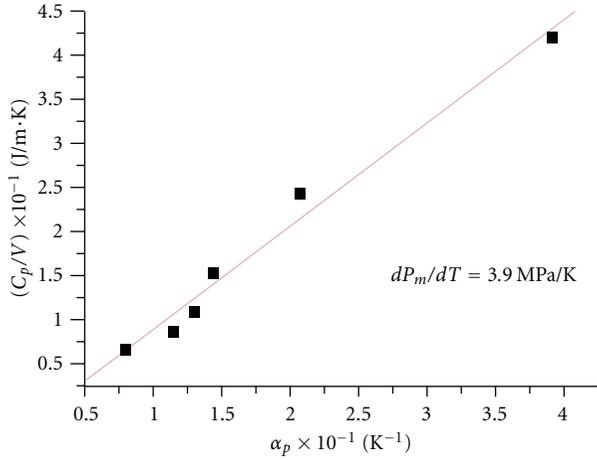


FIGURE 1: The specific heat ( $C_p/V$ ) as a function of the thermal expansivity  $\alpha_p$  according to the first Pippard relation (11) for cyclohexane near the melting point.

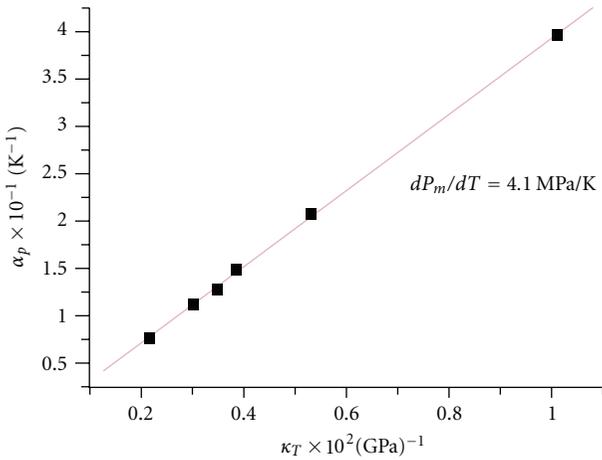


FIGURE 2: The thermal expansivity  $\alpha_p$  as a function of the isothermal compressibility  $\kappa_T$  according to the second Pippard relation (12) for cyclohexane near the melting point.

a power-law formula (1) with the critical exponent value of  $\gamma = 1.3$  within the pressure interval  $0.023 < P - P_m < 0.143$  (GPa) (Table 1) close to the melting point in cyclohexane. This analysis of the thermal expansivity was also performed previously by Pruzan et al. [17] using a power-law formula (1). They obtained values of the critical exponent  $\gamma$  for thermal expansivity as follows:  $\gamma_s = 0.2$  (solid phase),  $\gamma_p = 0.7$  (precursor zone), and  $\gamma_m = 2$  (melting zone). They described the pressure ranges on the basis of their experimental measurements as follows:  $P_1$  beginning

of the precursor zone,  $P_2$  change of regime, and  $P_L$  end of melting, with the difference in pressure as  $P_1 - P_L = 35$  MPa and  $P_2 - P_L = 15$  MPa [17]. Thus, the experimental  $\alpha_p$  versus  $P$  plot gives that a straight line in the solid phase changes to a curve at  $P_1$  followed by a reverse  $\lambda$ -type peak at  $P_2$  [17]. Below  $P_2$  as the pressure decreases down to the liquid pressure  $P_L$ , this peak disappears and the homogenous liquid phase appears [17]. So, the solid-liquid transformation occurs in the melting zone ( $P_2 - P_L$ ) by taking  $P_L$  very close to the melting pressure  $P_m$  and from the liquid state, the crystallization takes place at around  $P_2$  in cyclohexane [17].

From our analysis given here, the exponent value ( $\gamma = 1.3$ ) lies on the pressure range between precursor and melting zones, which is a small pressure range in comparison with that of the solid phase. In fact, the exponent value of  $\gamma_s = 0.2$  describes a second order transition in the solid phase as obtained by Pruzan et al. [17], which is followed by the melting process. The exponent values of  $\gamma_p = 0.7$  (precursor zone) and  $\gamma_m = 2$  (melting zone) due to Pruzan et al. [17] or our value of  $\gamma = 1.3$  describe this melting process which occurs below the pressure  $P_2$  where instability takes place and the solid state is transformed into the homogenous liquid state.

Using our value of  $\gamma = 1.3$  and the experimental value of the slope  $dP_m/dT = 5$  MPa/K [17], the temperature dependence of the thermal expansivity  $\alpha_p$ , specific heat  $C_p$ , and the isothermal compressibility  $\kappa_T$  were calculated, which gave us as straight lines when plotted  $C_p/V$  versus  $\alpha_p$  (Figure 1) and  $\alpha_p$  versus  $\kappa_T$  (Figure 2) near the melting point in cyclohexane. Since we used the experimental  $dP_m/dT$  value to calculate  $\alpha_p$  (3),  $\kappa_T$  (6), and  $C_p$  (10) as functions of temperature, the same slope value was deduced from our plots (Figures 1 and 2), as expected. This linear relationship between the specific heat  $C_p$  and the thermal expansivity  $\alpha_p$  (Figure 1) expresses the validity of the first Pippard relation (11) close to the melting point in cyclohexane. Also, the second Pippard relation (12) was verified by a linear variation of  $\alpha_p$  with the isothermal compressibility  $\kappa_T$ , as shown in Figure 2 near the melting point in this compound.

## 5. Conclusions

Linear variations of the specific heat  $C_p$  with the thermal expansivity  $\alpha_p$ , and also  $\alpha_p$  with the isothermal compressibility  $\kappa_T$  were established close to the melting point in cyclohexane. This was obtained by analyzing the thermal expansivity data from the literature near the melting point in this molecular organic compound. From a power-law analysis,  $C_p$ ,  $\alpha_p$ , and  $\kappa_T$  were calculated as functions of temperature close to the melting point, and the Pippard relations were verified.

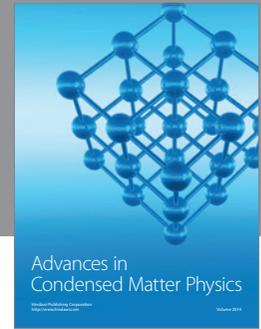
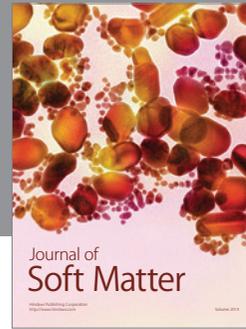
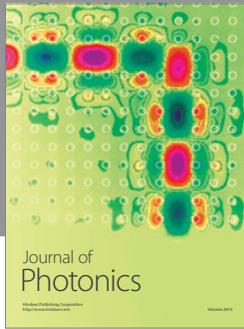
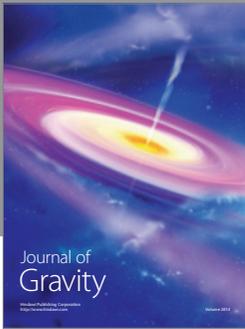
This shows that the thermodynamic quantities can be calculated and the Pippard relations can be constructed close to the melting point for those molecular organic compounds which exhibit a second order phase transformation prior to melting.

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