# CALCULATION OF THE THERMODYNAMIC FUNCTIONS USING A MEAN FIELD MODEL FOR THE FLUID-SOLID TRANSITION IN NITROGEN

Özge AKAY[a,b] and Hamit YURTSEVEN[b,*]

[a]Faculty of Arts and Science, Physics Group, Piri Reis University, 34940, Istanbul-Turkey
[b]Department of Physics, Middle East Technical University, 06531, Ankara-Turkey

Temperature and pressure dependence of the thermodynamic quantities are calculated using the Landau phenomenological model for the first order fluid-solid transition in nitrogen. This calculation is performed by fitting the phase line equation as derived from the mean field model to the observed T-P phase diagram of the fluid-solid transition in $N_2$ from the literature. Our calculations show that the order parameter and the inverse susceptibility decrease whereas the entropy, heat capacity, thermal expansion and isothermal compressibility exhibit anomalous behavior as the melting point is approached in nitrogen. This indicates that the first order fluid-solid transition in $N_2$ can be described by the mean field model studied here.
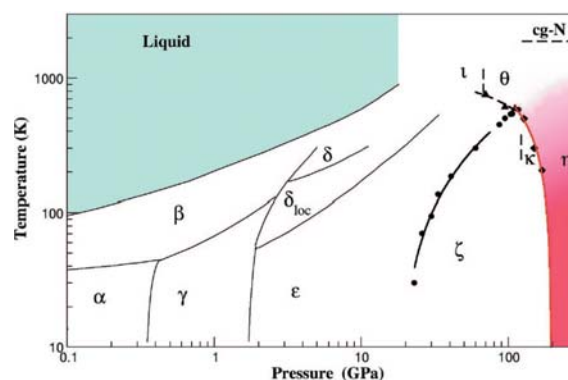
## INTRODUCTION

Nitrogen exhibits the P-T phase boundaries of various crystal forms from about 15 to 300K and 0.6 to 52 GPa as obtained previously by using the Raman scattering.[1] The V-T phase diagram of $N_2$ which has also been obtained by the Raman spectroscopy includes the fluid, vapor and three solid phases ($\alpha,\beta$ and $\gamma$ ) with the temperature range from 0 to 200K and the molar volume range from 23.37 to 27.81 cm[3]/mole.[2] A cubic $\delta$ phase above about 4.5 GPa at room temperature, has been obtained by X-ray[3] and Raman measurements.[4] Also, x-ray measurements have shown a phase transition from the cubic $\delta$ to the trigonal $\delta$ phase at a pressure of $16.3 \pm 0.5$ GPa at room temperature.[3] By using high-pressure Raman spectroscopy, the $\delta$-$\varepsilon$ transition at around 17 GPa and

the transition into the η phase at around 200 GPa have been detected.[5] All those low-temperature and pressure phases of $N_2$ were shown in the P-T phase diagram which we have calculated recently using the mean field model.[6] It has been pointed out by the Raman spectroscopy that the high-pressure phases have closely related structures.[7] Regarding the Raman studies, in our earlier studies,[8-12] we have calculated the Raman frequencies of different modes in various phases of nitrogen.

There occur the θ and i phases, which can be quenched to room temperature, over a wide P-T range from 20 to 100 GPa and 300 to 1000 K, as shown in the P-T phase diagram.[13] The i- phase appears to represent a different kind of lattice consisting of dislike molecules, packed more efficiently compared to the mixed disk- and

spherelike δ-family structures, whereas the θ phase is more complex.[13] An experimental evidence has been presented for the nonmolecular (NM) transformation in the 140-160 GPa range to a disordered single-bonded, threefold-coordinated structure in $N_2$.[14] Experimentally, from the molecular to the polymeric forms of nitrogen the cubic-gauche structure has been found[15,16] and theoretical studies[17–22] have confirmed its stability and highly energetic character as reported from its elastic and vibrational properties at the surface of the crystals.[23] Fig. 1 gives a global T-P phase diagram of nitrogen[24] where we have also studied for the liquid-solid transition in this molecule.

Thermodynamic properties of the solid nitrogen for various phases have been studied as reported in the literature. Its volume,[2] thermal expansivity,[25,26] isothermal compressibility.[26] specific heat[27–28] and the lattice dynamics of cubic gauche nitrogen in particular,[23] have been studied. It is of interest to study the thermodynamic properties of molecular nitrogen near the melting temperatures at high pressures. By using the measured melting temperatures up to 71 GPa[29] and the experimental T-P data[30] for the fluid-solid transition in $N_2$, the temperature dependence of the thermodynamic quantities such as order parameter, susceptibility, thermal expansion, isothermal compressibility, specific heat etc. can be investigated for this molecular structure.

In this study, we introduce a mean field model with the free energy expanded in terms of the order parameter within the Landau phenomenological theory. By deriving the phase line equation from the free energy for the first order fluid-solid transition and fitting it to the experimental T-P data[29,30] the temperature dependences of those thermodynamic quantities are predicted for $N_2$ near the melting temperature.

Below, in section 2 we give an outline of the mean field model. In section3, our calculations and results are given. In sections 4 and 5, we give our discussion and conclusions, respectively.

## THEORY

The free energy of the solid phase of nitrogen can be expanded in terms of the order parameter Ψ close to the solid-liquid transition according to the Landau phenomenological model by using the cubic term as

$$F_s = a_2\psi^2 + a_3\psi^3 + a_4\psi^4 \qquad (1)$$

where the coefficients $a_2$, $a_3$ and $a_4$ can be temperature and pressure dependent in general. The cubic term in the free energy expansion leads to a first order solid-liquid transition. $a_2$ and $a_4$ are positive constants in $N_2$. Since there is no ordering in the liquid phase, we have

$$F_s = F_L = 0 \qquad (2)$$

where $F_L$ corresponds to the free energy of the liquid phase. By minimizing the free energy with respect to the order parameter ($\frac{\partial F}{\partial \psi} = 0$), we get

$$2a_2 + 3a_3\psi + 4a_4\psi^2 = 0 \qquad (3)$$

By using the first order condition (Eq.2), we have from Eq.1

$$a_2\psi^2 + a_3\psi^3 + a_4\psi^4 = 0 \qquad (4)$$

Solving Eqs.3 and (4) for Ψ gives

$$\psi = -\frac{2a_2}{a_3} \qquad (5)$$

The phase line equation for the solid-liquid transition of $N_2$ can then be obtained as or

$$a_3^2 = 4a_2a_4 \qquad (6)$$

By taking the temperature and pressure dependence of the coefficients, the T-P phase diagram (Eq.6) and the thermodynamic quantities can be calculated close to the solid-liquid transition in nitrogen as functions of temperature and pressure.

In this study, we calculate the order parameter (ψ), the inverse susceptibility of the order parameter ($\chi_\psi^{-1}$), entropy(S), heat capacity ($C_P$), thermal expansion ($\alpha_P$) and the isothermal compressibility ($K_T$) for the solid-liquid transition in $N_2$. The order parameter ψ can be calculated by using Eq.(5).

From the order parameter ψ (Eq.5), the inverse susceptibility ($\chi_\psi^{-1}$) can be calculated according to

$$\chi_\psi^{-1} = \partial^2 F / \partial\psi^2 \qquad (7)$$

which gives from the free energy (Eq.1).

$$\chi_\psi^{-1} = 2a_2 + 6a_3\psi + 12a_4\psi^2 \qquad (8)$$

The thermodynamic quantities of the entropy (S), heat capacity ($C_P$), thermal expansion ($\alpha_P$) and

isothermal compressibility ($\kappa_T$) were also calculated by using their definitions of $S = (\partial V / \partial T)_v$, $C_v = T(\partial S / \partial T)_v$,

$$\alpha_p = (1/V)(\partial V / \partial T)_p \qquad (9)$$

and

$$\kappa_T = \kappa_T = -(1/V)(\partial V / \partial P)_T \qquad (10)$$

respectively, for the solid-liquid transition in $N_2$. The free energy $F_S$ (Eq.1) of the solid phase can be written in terms of the coefficients $a_2$, $a_3$ and $a_4$ through Eq.(5) as

$$F_s = \frac{4a_2^3}{a_3^2}\left(-1 + \frac{4a_2 a_4}{a_3^2}\right)) \qquad (11)$$

Thermal expansion $\alpha_P$ and the isothermal compressibility $\kappa_T$ can be calculated for the solid-

liquid transition in nitrogen by using the free energy (Eq.1) according to

$$\alpha_p = (\partial^2 F / \partial T.\partial P)/(\partial F / \partial P) \qquad (12)$$

and

$$\kappa_T = -(\partial^2 F / \partial P^2)/(\partial F / \partial P) \qquad (13)$$

## CALCULATIONS AND RESULTS

We calculated the temperature and pressure dependence of the thermodynamic quantities by using the observed T-P phase diagram[29,30] through the phase line equation (Eq.6). The observed P-T data[29,30] which we used for our calculations are given in Table 1.By assuming the temperature and pressure dependence of the coefficient $a_2$ (Eq.6) as

$$a_2^3 = (P - P_t) - a_{20} - a_{21}(T - T_t) + a_{22}(T - T_t)^2 \qquad (14)$$

and $a_4 = 1$, where $a_{20}$, $a_{21}$ and $a_{22}$ are constants, and writing the phase line equation (Eq.6) in the form of

$$a_3 = 2\sqrt{a_2} \qquad (15)$$

with the $a_2$ (Eq.14), we fitted to the experimental T-P phase diagram[29,30] and, the coefficients $a_{20}$, $a_{21}$ and $a_{22}$ were determined as given in Table 2. For this determination, transition temperature ($T_t$) and pressure ($P_t$) were chosen as the maximum values[29,30] for the solid-liquid transition in $N_2$.

Using the values of the coefficients of $a_2$ (T,P) (Table 2), we first calculated the temperature and

pressure dependence of the order parameter $\psi$ as plotted in Figs.(2a) and (2b), respectively, for the solid – liquid transition in $N_2$. By means of Eq.(14) with the values of the coefficients (Table 2), the inverse susceptibility ($\chi_\psi^{-1}$) was calculated as functions of temperature (P=$P_t$) and pressure (T=$T_t$), as plotted in Figs.(3a) and (3b), respectively, for the solid-liquid transition in $N_2$. Also, with Eq.(15) by using $a_2$ (Eq.14), we obtained the entropy S at the transition pressure (P=$P_t$) for the solid-liquid transition in nitrogen. We plot the entropy S as a function of temperature in Fig.(4) for the solid- liquid transition in $N_2$.

*Table 1*

The observed P-T data[29,30] which were used in the phase line equation (Eq.14) to determine the coefficients (see Table 2) for the solid -liquid transition in $N_2$

| (Ref.30) | | (Ref.29) | |
|---|---|---|---|
| P(GPa) | T(K) | P(GPa) | T(K) |
| 1.5 | 241.0 | 816.0 | 15.9 |
| 5.6 | 351.8 | 856.1 | 16.8 |
| 10.0 | 499.7 | 888.2 | 18.1 |
| 13.9 | 721.9 | 987.2 | 20.0 |
| 18.3 | 869.8 | 1078.0 | 24.4 |
| 21.5 | 980.8 | 1182.3 | 27.0 |
| 29.2 | 1165.4 | 1227.6 | 30.8 |
| 36.3 | 1350.1 | 1270.5 | 31.2 |
| 42.8 | 1442.1 | 1342.6 | 35.5 |
| 50.2 | 1552.6 | 1449.4 | 41.2 |
| 57.3 | 1626.0 | 1521.6 | 44.6 |
| 65.0 | 1717.8 | 1556.3 | 45.8 |
| 71.8 | 1791.3 | 1556.2 | 48.8 |
| 79.4 | 1827.5 | 1623.0 | 52.6 |

| | | | |
|---|---|---|---|
| 87.1 | 1882.3 | 1692.4 | 57.8 |
| 94.2 | 1937.1 | 1713.7 | 60.5 |
| 100.4 | 1937.5 | 1748.2 | 67.2 |
| 106.9 | 1972.7 | 1769.4 | 74.3 |

*Table 2*

Values of the coefficients $a_2$, which were obtained by fitting Eq.(14) ($a_2=0$) to the experimental T-P data for the solid $N_2$-liquid $N_2$ transition[29,30] within the temperature and pressure intervals indicated. Values of the transition temperature ($T_t$) and pressure ($P_t$) in Eq.(14), are also given here

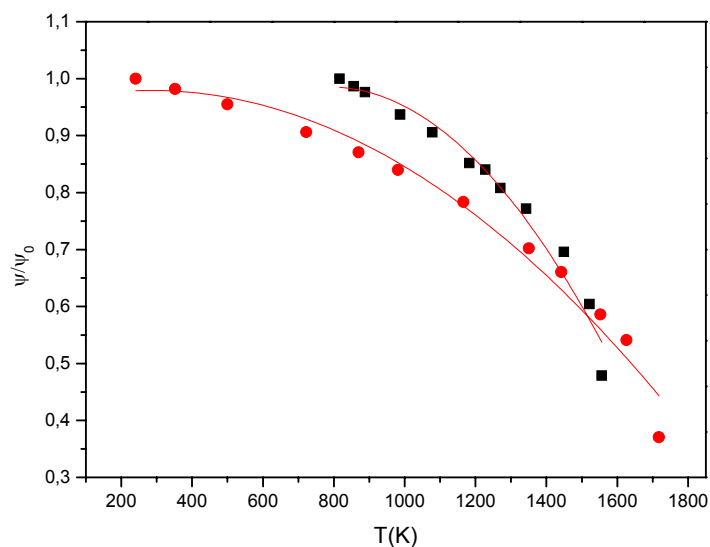| $T_t$ (K) | $P_t$ (GPa) | $a_{20}$ (GPa) | $a_{21}x10^{-2}$ (GPa/K) | $a_{22}x10^{-5}$ (GPa/K$^2$) | Temperature Interval (K) | Pressure Interval (GPa) | Ref. |
|---|---|---|---|---|---|---|---|
| 1769.4 | 74.3 | -8.70 | 8.80 | 3.90 | 816.0<T<1769.4 | 15.9<P<74.2 | 29 |
| 1972.7 | 106.9 | 11.29 | 11.34 | 3.59 | 241.0<T<1972.7 | 1.5<P<106.9 | 30 |



Fig. 2(a) – Variation of the order parameter ψ (normalized) with the temperature at the transition pressures of $P_t$ =74.3 GPa and $P_t$=106.9 GPa by using the observed T-P data (circles)[30] and (squares),[29] respectively, for the solid–liquid transition in $N_2$ according to Eq.(5) through Eq.(14).
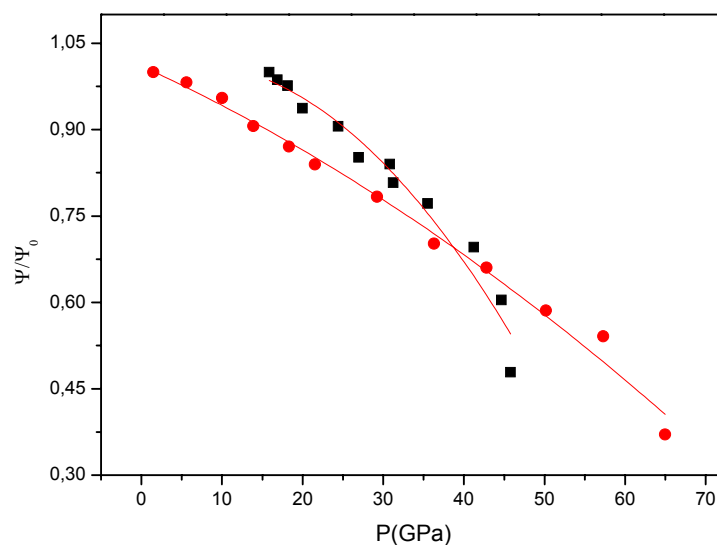


Fig. 2 (b) – Variation of the order parameter ψ (normalized) with the pressure at the transition temperatures of $T_t$ =1769.4 and $T_t$=1972.7 K by using the observed T-P data (circles)[30] and (squares)[29] respectively, for the solid–liquid transition in $N_2$ according to Eq.(5) through Eq.(14).

Fig. 3 (a) – Inverse susceptibility $\chi_\psi^{-1}$ of the order parameter $\psi$ as a function of temperature at the transition pressures of $P_t = 74.3$ GPa and $P_t = 106.9$ GPa by using the observed T-P data (circles)[30] and (squares)[29] respectively, for the solid–liquid transition in $N_2$ according to Eq.(8).
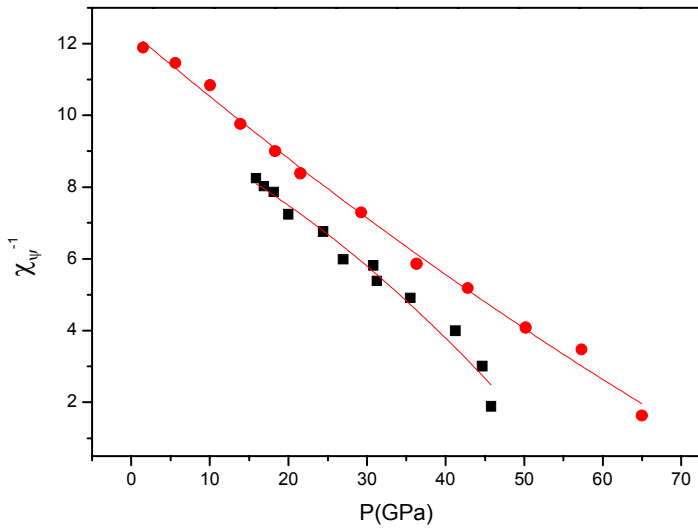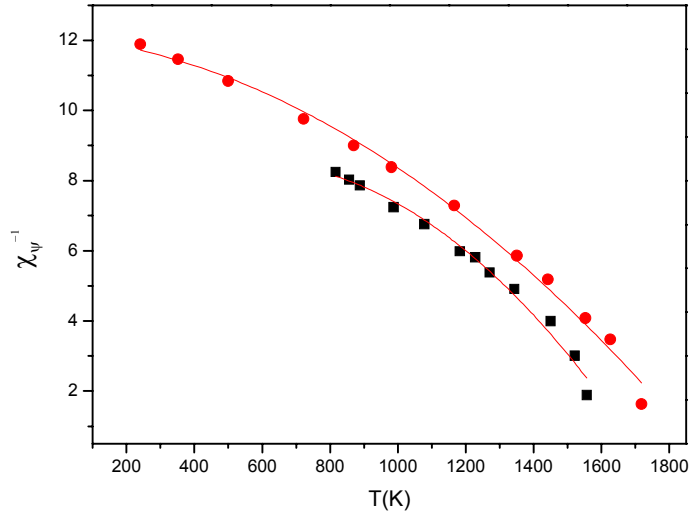


Fig. 3 (b) – Inverse susceptibility $\chi_\psi^{-1}$ of the order parameter $\psi$ as a function of pressure at the transition temperature of $T_t = 1769.4$ K and $T_t = 1972.7$ K by using the observed T-P data (circles)[30] and (squares)[29] respectively, for the solid–liquid transition in $N_2$ according to Eq.(8).



Fig. 4 – Entropy S (normalized ) calculated from the free energy (Eq.11) as a function of temperature at the transition pressures of $P_t = 74.3$ GPa and $P_t = 106.9$ GPa by using the observed T-P data (circles)[30] and (squares)[29] respectively, for the solid–liquid transition in $N_2$.
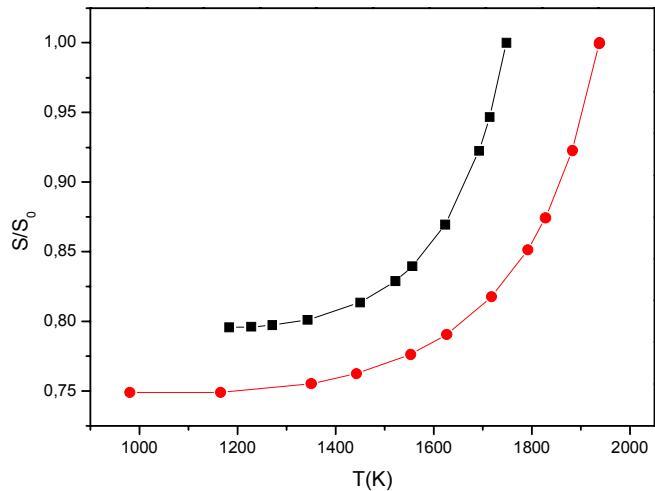


From the entropy S, the heat capacity $C_v$(normalized) was calculated at various temperatures ($P = P_t$), as plotted in Fig. (5) for the solid-liquid transitions in $N_2$. Similarly, we also calculated the temperature dependence of the thermal expansion $\alpha_P$ (Fig. 6) and the isothermal compressibility $\kappa_T$ (Fig. 7) according to Eqs.(12) and (13), respectively, for the solid- liquid transition in $N_2$.
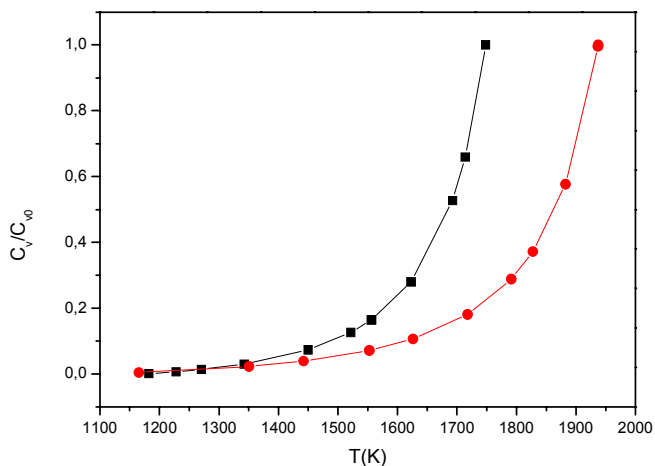
Fig. 5 – Heat capacity $C_v$ (normalized) calculated from the free energy (Eq.11) as a function of temperature at the transition pressures of $P_t = 74.3$ GPa and $P_t = 106.9$ GPa by using the observed T-P data (circles)[30] and (squares)[29] respectively, for the solid–liquid transition in $N_2$.

Fig. 6 – Thermal expansion $\alpha_p$ (normalized) as function of temperature at the transition pressures of $P_t = 74.3$ GPa and $P_t = 106.9$ GPa using the observed T-P data (circles)[30] and (squares)[29] respectively, for the solid–liquid transition in $N_2$ according to Eq.(12).
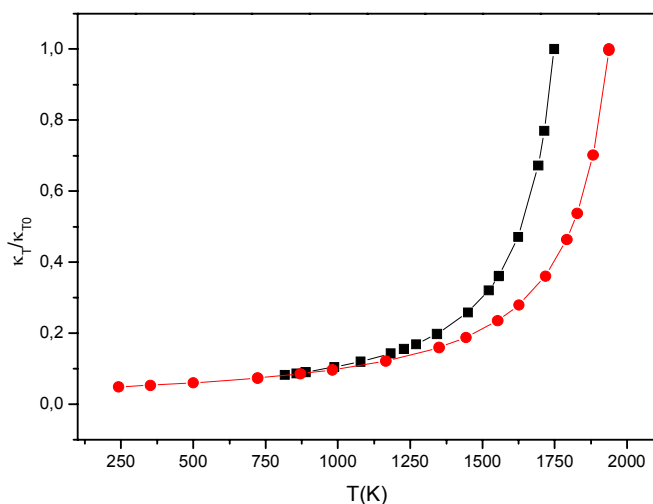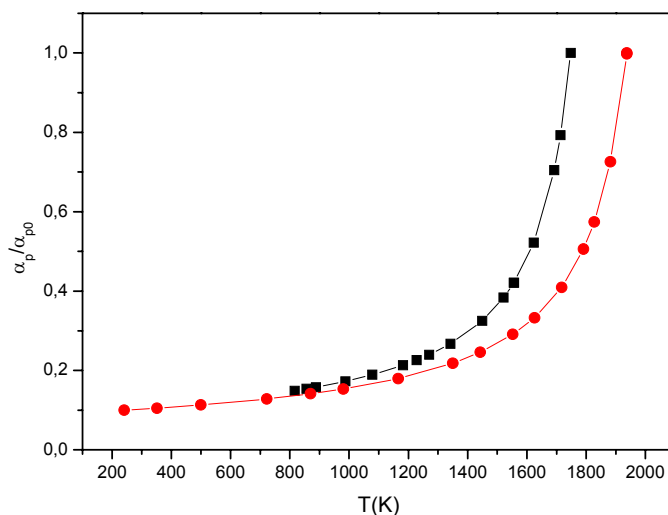




Fig. 7 – Isothermal compressibility $\kappa_T$ (normalized) as a function of temperature at the transition pressures of $P_t = 74.3$ GPa and $P_t = 106.9$ GPa by using the T-P data (circles)[30] and (squares)[29] respectively, for the solid–liquid transition in $N_2$ according to Eq.(13).

## DISCUSSION

A mean field model with the cubic term (Eq.1) was employed to calculate the thermodynamic quantities of the order parameter $\psi(T,P)$ (Figs. 2a,b), the inverse susceptibility $\chi_\psi^{-1}(T,P)$

(Figs. 3a,b), entropy S (Fig. 4), heat capacity $C_v$ (Fig. 5), thermal expansion $\alpha_p$ (Fig. 6) and isothermal compressibility $\kappa_T$ (Fig. 7) for the solid-liquid transition in nitrogen. In a wider temperature and pressure region, calculated $\psi$ (T,P) decreases

smoothly with the lower values as the temperature or pressure increases, which we obtained by using the observed T-P data[30] in comparison with the one decreasing with the larger slope, that was calculated from the experimental T-P data,[29] as shown in Fig. (2a,b). Almost linear decrease of the inverse susceptibility $\chi_\psi^{-1}$ with increasing temperature and pressure (Figs.3a,b) and, a large increase in the entropy S (Fig. 4), in the heat capacity $C_v$ (Fig. 5), in the thermal expansion $\alpha_p$ (Fig.6) and in the isothermal compressibility $\kappa_T$ (Fig. 7) with increasing temperature in particular, close to the melting point, indicate a first order liquid-solid transition in nitrogen. This is associated with a sharp drop in the melting slope which also indicates the appearance of a liquid denser than the solid and of a liquid- liquid phase transition.[31] As stated above, for the calculation of the thermodynamic quantities, we used two sets of experimental T-P data[29,30] for the first order solid-liquid transition in $N_2$. For the $C_v$ (Fig. 5) and $\alpha_p$ (Fig. 6), and $\kappa_T$ (Fig. 7), we obtained nearly the same values up to about 1400K by using both the observed T-P data[29,30] in a large temperature interval ( ~200 to 1400 K),(for $C_v$, the temperature range from ~1150 to 1400 K). They exhibit similar critical behavior and above about 1400K, those thermodynamic quantities ($C_v$, $\alpha_p$ and $\kappa_T$) show anomalous behavior close to the melting point in $N_2$. This critical behavior of the heat capacity ($C_v$) ,thermal expansion ($\alpha_P$) and the isothermal compressibility ($\kappa_T$) indicates that the first order solid-liquid transition in nitrogen can be described adequately by the mean field model with the cubic term in the order parameter ($\psi^3$) in the free energy expansion (Eq.1).

## CONCLUSIONS

The thermodynamic quantities of the order parameter inverse susceptibility, entropy, heat capacity, thermal expansion and the isothermal compressibility were calculated as a function of temperature for the solid-liquid transition in nitrogen using the Landau phenomenological model. We also calculated the pressure dependence of he order parameter and the inverse susceptibility. The observed T-P data from the literature were used for this calculation. A continuous decrease of the order parameter and almost a linear decrease of the inverse susceptibility with the increasing temperature and pressure were obtained toward the melting point in

this crystal. We also find that the entropy, heat capacity, thermal expansion and isothermal compressibility show an anomalous behavior in the vicinity of the melting point ,which can be described adequately with the Landau phenomenological model with the cubic term ( in the order parameter) for the first-order solid-liquid transition in nitrogen. This suggests that the critical behavior of the thermodynamic quantities can be predicted from the observed phase diagrams (T-P or T-X ) of various crystalline materials close to their solid-liquid transitions as we studied here for nitrogen.

## REFERENCES

1. S. Buchsbaum, R. L. Mills and D. Schiferl, *J. Phys. Chem.*, **1985**, *88*, 2522.
2. F. D. Medina and W. B. Daniels, *J. Chem. Phys.*, **1976**, 64, 150.
3. D. T. Crommer, R. L. Mills, D. Schiferl and L. A. Schuralbe, *Acta Crystallogr. B*, **1981**, *3*, 78.
4. R. Le Sar, S. A. Ekberg, L. H. Jones, R. L. Mills, L. A. Schuralbe and D. Schiferl, *Solid State Commun.*, **1979**, *32*, 131.
5. T. Westerhoff, A. Witttig and R. Feile, *Phys. Rev. B*, **1996**, *54*, 14.
6. Y. Enginer, G. Algul and H. Yurtseven, *Int. J. Mod. Phys. B*, **2017**, *31*, 1750245.
7. H. Olijnyk and A. P. Jephcoat, *Phys. Rev. Lett.*, **1999**, *83*, 332.
8. M. Kurt and H. Yurtseven, *Int. J. Mod. Phys. B* , **2011**, *25*, 3679.
9. E. Çetinbaş İşeri and H.Yurtseven, *High Temp. Mater. Process.*, **2013**, *32*, 25.
10. H. Yurtseven and M. Kurt, *Trends App. Spectrosc.*, **2013**, *19*, 2243.
11. H. Yurtseven and A. Aslantaş, *Int. J. Mod. Phys. B*, **2013**, *27*, 1350125.
12. O. Akay and H. Yurtseven, *Optik*, **2018**, *160*, 227.
13. E. Gregoryanz, A. F. Goncharov, R. J. Hemley, H. K. Mao, M. Somayazulu and G. Shen, *Phys. Rev. B*, **2002**, *66*, 224108.
14. A. F. Goncharov, E. Gregoryanz, H. K. Mao, Z. Liu and R. J. Hemley, *Phys. Rev. Lett.*, **2000**, *85*, 1262.
15. M. I. Eremest, A. G. Gavriliuk and I. A. Trojen, D. A. Dzivenko and R. Boehler, *Nat. Matter.*, **2004**, *3*, 558.
16. M. I. Eremest, A. G. Gavriliuk and I. A. Trojen, *Appl. Phys. Lett.*, **2007**, *90*, 171904.
17. R. Reichlin, D. Schiferl, S. Martin, C. Vanderborgh and R. L. Mills, *Phys.Rev.Lett.*, **1985**, *55*, 1464.
18. C. Mailhiot, L. H. Yang and A. . McMahan, *Phys. Rev. B*, **1992**, *46*, 14419.
19. T. W. Barbee III, *Phys .Rev. B*, **1993**, *48*, 9327.
20. M. M. G. Alemany and J. L. Martins, *Phys. Rev. B*, **2003**, *68*, 024110.
21. W. D. Mattson, D. Sanchaz-Portal, S. Chiesa and R. M. Martin, *Phys. Rev. Lett.*, **2004**, *93*,125501.
22. F. Zahariev, A. Hu, J. Hooper, F. Zhang and T. Woo, *Phys .Rev. B*, **2005**, *72*, 214108.

23. R. Caracas, *J. Chem. Phys.*, **2007**, *127*, 144510.
24. E. Gregoryanz, A. F. Goncharov, C. Sanloup, M. Somayazulu, H. Mao, and R. J. Hemleyett, *J. Chem. Phys.,* **2007**, *126,* 184505.
25. V. G. Manzhelii, A. M. Tolkachev and E. I. Vortovich, *Phys. Stat. Solid*, **1966**, *13*, 351.
26. D. C. Heberlein, E. D. Adams and T. A. Scott, *J. Low Temp. Phys.*, **1970**, *2*, 449.
27. M. I. Bagatskii, V. A. Kutcheryavy, M. G. Manzhalii and V. A. Popov, *Phys. Stat. Solid*, **1968**, *26*, 453.
28. N. Q. Hoc, N. N. Anh, N. T. Hung, N. D. Hien and N. D. Quyen, P*roc. Natl. Conf. Theor. Phys.*, **2012**, *37*, 150.
29. D. Tomasino, Z. Jenei, W. Evans and C. S. Yao, *J. Chem. Phys*., **2014**, *140*, 244510.
30. M. Ross and F. Rogers, *Phys. Rev. B*, **2006**, *74*, 024103.
31. G. D. Mukherjee and R. Boehler, *Phys. Rev. Lett*., **2007**, *99*, 225701.