

Mayer group expansion for solids: application to polymorphic transition in highly compressed nitrogen

E. S. Yakub¹ and L. N. Yakub²

¹*Cybernetics Department, Odessa National Economic University, Odessa 65082, Ukraine*

²*Thermophysics Department, Odessa National Academy of Food Technologies, Odessa 65039, Ukraine*

E-mail: eugene.yakub@gmail.com

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The Mayer group expansion for solids proposed earlier is applied in prediction of the location of polymorphic phase transition line between the cubic and layered phases of polymeric nitrogen. The comparison with existing measurements revealed that theoretical calculations based on the proposed potential model calibrated on *ab initio* energy calculations are in agreement with existing experimental data. Predicted location of the polymorphic transition line and specific behavior of thermal properties of both phases in a wide temperature range is discussed.

Keywords: polymeric nitrogen, polymorph transition, negative thermal expansion.

1. Introduction

In recent years, interest in studying the polymerized phases of highly compressed nitrogen, which began back in the 90s of the last century [1] in connection with the prospect of creating new high-energy-density materials, has significantly increased. Along with experimental studies of various polymeric nitrogen phases [2–7], extensive *ab initio* calculations of their structures were carried out (see, e. g., [8] and references therein). Nevertheless, the problem of the phase diagram configuration of the highly compressed nitrogen remains still open, since usually in experiments mainly the metastable polymeric structures were observed.

Computer simulations and *ab initio* calculation methods have been significantly developed in recent years and have been applied to a wide variety of crystal structures. However, even the most advanced approaches to this kind not always are able to predict the appearance and stability of certain crystalline phases and, moreover, they are unable to explain the unusual behavior of some thermal properties of crystalline solids.

Recently the authors proposed a consistent theoretical approach of the Helmholtz free energy evaluation, based on the Mayer group expansion method [9]. This method treats the average displacements of particles from their crystal lattice sites as a small parameter, and takes into account corrections on pair, triple, etc. correlations between these displacements.

Initially, it was successfully applied to highly anharmonic Lennard-Jones crystal [9]. Lately, this method was

extended on estimation of the Helmholtz free energy of simplest molecular solids, and made it possible to predict the location of polymorphic transition between the phases of heavy methane on its phase diagram [10].

In this work, we present a new illustration of the effectiveness of the above approach in estimating the location of the polymorphic transition in highly compressed nitrogen crystal from the known cubic gauche nitrogen (cg-N) phase to the orthorhombic layered polymeric (LP-N) phase, discovered and experimentally studied recently [4].

We propose a new potential model for both these phases, calibrated on the reliable *ab initio* calculation data [1]. This model is a modification of the model that we proposed earlier and have already been used in Monte Carlo simulation of the solid polymeric nitrogen in cg-N phase [11]. We apply this model not only to assess the stability region of the layered LP-N phase of polymeric nitrogen, but also to predict the behavior of thermal properties in both cg-N and LP-N phases within the Mayer group expansion approach.

2. Technique of the Mayer group expansion

Essentially, the method proposed in [9] is as follows. We consider a perfect crystal of N atoms in volume V . The position of each atom is defined by its radius vector $\mathbf{r}_i = \{x_i, y_i, z_i\}$, and the potential energy U_N of crystalline lattice is assumed to be the sum of pair interatomic potentials:

$$U_N = \sum_{1 \leq i < j \leq N} \Phi(\mathbf{r}_i, \mathbf{r}_j). \quad (1)$$

Within the approach proposed in [9] Eq. (1) can be re-written as

$$U_N = U_N^{(0)} + \sum_{1 \leq i \leq N} u_1(\Delta \mathbf{r}_i) + \sum_{1 \leq i < j \leq N} w_{ij}(\mathbf{r}_i, \mathbf{r}_j), \quad (2)$$

where $U_N^{(0)} = \sum_{1 \leq i < j \leq N} \Phi(\mathbf{r}_i^{(0)}, \mathbf{r}_j^{(0)})$ is the “static energy”, the minimal energy corresponding to all atoms located in their equilibrium cell positions $\mathbf{r}_i^{(0)}$; $u_1(\Delta \mathbf{r}_i)$ is one-particle potential energy of i th atom displaced on $\Delta \mathbf{r}_i = \mathbf{r}_i - \mathbf{r}_i^{(0)}$ from its equilibrium position inside its static environment in the lattice cell, referred to the energy of this atom in its equilibrium position $\mathbf{r}_i^{(0)}$ in the lattice; $w_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ are so-called “pair correlation potentials”, depending on current positions of the displaced atomic pairs i and j .

The Mayer group expansion of the excess (with respect to the ideal atomic gas) Helmholtz free energy of the classical monatomic crystal can be written as [9]

$$\Delta F = U_N^{(0)} - NkT \left[\ln(v_f/v) + W_2(v, T) + W_3(v, T) + \dots \right]. \quad (3)$$

Here k denotes Boltzmann constant, $v = V/N$ is the atomic Wigner–Seitz cell volume and T is the absolute temperature. The static potential energy $U_N^{(0)}$ depending only on the volume plays here a role of the zeroth approximation. So-called “free volume” $v_f = v_f(v, T)$ is the first term of the Mayer group expansion Eq. (3). The expression for the free volume is well-known [12]:

$$v_f(v, T) = \int_{v_1} e^{-u_1(\Delta \mathbf{r})/kT} d\mathbf{r}. \quad (4)$$

Integration over atomic coordinates in Eq. (4) is carried out over the atomic Wigner–Seitz cell v_1 . The potential energy $u_1(\Delta \mathbf{r}_i)$ of an atom inside its static environment can be written as

$$u_1(\Delta \mathbf{r}_i) = \sum_{\substack{1 \leq j \leq N \\ j \neq i}} \left[\Phi(\mathbf{r}_i^{(0)} + \Delta \mathbf{r}_i, \mathbf{r}_j^{(0)}) - \Phi(\mathbf{r}_i^{(0)}, \mathbf{r}_j^{(0)}) \right]. \quad (5)$$

The following terms in the Mayer group expansion Eq. (3) represent, correspondingly, contributions of the binary $W_2(v, T)$, triple $W_3(v, T)$ etc. correlations between displacements of atoms from their lattice sites [9]. The pair-correlation term is

$$W_2 = \frac{1}{2v_f^2} \sum_{j>1} \int_{v_1} \int_{v_j} f_{1j} \exp(-[u_1(\Delta \mathbf{r}_1) + u_1(\Delta \mathbf{r}_j)]/kT) d\mathbf{r}_1 d\mathbf{r}_j. \quad (6)$$

Here $f_{ij} = e^{-w_{ij}/kT} - 1$ is an analog of the Mayer’s f -function where the pair interaction potential $\Phi(r)$ is replaced by the so-called pair correlation potential:

$$w_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \Phi(\mathbf{r}_i^{(0)} + \Delta \mathbf{r}_i, \mathbf{r}_j^{(0)} + \Delta \mathbf{r}_j) - \Phi(\mathbf{r}_i^{(0)} + \Delta \mathbf{r}_i, \mathbf{r}_j^{(0)}) - \Phi(\mathbf{r}_i^{(0)}, \mathbf{r}_j^{(0)} + \Delta \mathbf{r}_j) + \Phi(\mathbf{r}_i^{(0)}, \mathbf{r}_j^{(0)}), \quad (7)$$

which turns to zero if at least one of atoms the pair enters its lattice site.

The corresponding expression for the triple correlation contribution is as follows:

$$W_3 = \frac{1}{6v_f^3} \sum_{j>1} \sum_{\substack{l>1 \\ l \neq j}} \int_{v_1} \int_{v_j} \int_{v_l} f_{1j} f_{1l} (3 + f_{jl}) \times \\ \times \exp(-[u_1(\Delta \mathbf{r}_1) + u_1(\Delta \mathbf{r}_j) + u_1(\Delta \mathbf{r}_l)]/kT) d\mathbf{r}_1 d\mathbf{r}_j d\mathbf{r}_l. \quad (8)$$

Integration in Eqs. (7) and (8) is carried out within the corresponding Wigner–Seitz cells and summation is performed over all atomic pairs surrounding the selected (first) one [9].

As it was mentioned above, the ability of this approach (combined with the Monte Carlo method for rotational degrees of freedom) to predict location of polymorphic phase transition lines on phase diagrams of molecular crystals has been recently demonstrated on the example of the heavy methane [10].

In this work we study the effectiveness of this method in calculating the Helmholtz free energy and other thermodynamic properties of the polymeric phases of nitrogen, as well as in predicting their location on phase diagram. Potential model needed to describe interatomic interactions in corresponding crystal structures is discussed in the next section.

3. Potential energy model

We start from the general expression for potential energy of N nitrogen atoms in polymeric phase given by Eq. (1). Each atom is chemically bonded to the three nearest atoms forming the corresponding polymeric structure. Pair potentials $\Phi(\mathbf{r}_i, \mathbf{r}_j)$ expressed in terms of distances between the atoms r_{ij} , bond lengths L_{ij} and the valent angles $\theta_i = \{\theta_i^{(1)}, \theta_i^{(2)}, \theta_i^{(3)}\}$ between pairs of these bonds attached to i th atom can be written as follows:

$$\Phi(\mathbf{r}_{ij}) = \Phi_0(r_{ij}) + u(L_{ij}, \theta_i, \theta_j). \quad (9)$$

The term $\Phi_0(r_{ij})$ takes into account the additive central non-valent interaction of all atomic pairs, and the valent contribution $u(L_{ij}, \theta_i, \theta_j)$ presents the energy of chemical bonding. It depends on the bond length L_{ij} , as well as on six valent angles between the pairs of bonds attached to each atom. Thus, the potential energy of the polymeric crystal is presented in the form

$$U_N = \sum_{1 \leq i < j \leq N} \Phi_0(r_{ij}) + \sum_{1 \leq (ij) \leq N} u(L_{ij}, \theta_i, \theta_j). \quad (10)$$

The first sum here is over all pairs of atoms, and the second only over atoms chemically bonded to each other. The valent contribution in the model applied is specified as a product of three factors:

$$u(L_{ij}, \boldsymbol{\theta}_i, \boldsymbol{\theta}_j) = q(L_{ij}, \boldsymbol{\theta}_i) \cdot q(L_{ij}, \boldsymbol{\theta}_j) \cdot u_V(L_{ij}).$$

The valent contribution $u_V(L_{ij})$ is defined by the Morse potential:

$$u_V(L) = D_e \left[\exp\{-2\beta(L - R_e)\} - 2 \exp\{-\beta(L - R_e)\} \right].$$

The angular dependence of the energy of the valent interaction is determined by factors $q(L_{ij}, \boldsymbol{\theta}_i)$ depending both on the bond length and on three angles between the bonds attached to i th atom. The analytical form of these factors is given as follows [11]:

$$q(L, \boldsymbol{\theta}) = \frac{2}{1 + \exp\{-z(L, \boldsymbol{\theta})\}}, \quad (11)$$

where

$$z(L, \boldsymbol{\theta}_i) = \alpha(L - R_e)^2 + \gamma(c_i - c_e)^2 + \delta(L - R_e)(c_i - c_e) + \varepsilon(1 - 4c_i)\Delta_i. \quad (12)$$

In turn, here

$$c_i = \frac{1}{3} \left(\cos^2 \theta_i^{(1)} + \cos^2 \theta_i^{(2)} + \cos^2 \theta_i^{(3)} \right), \quad (13)$$

$$\Delta_i = \left[\cos^2 \theta_i^{(1)} - \cos^2 \theta_i^{(2)} \right]^2 + \left[\cos^2 \theta_i^{(1)} - \cos^2 \theta_i^{(3)} \right]^2 + \left[\cos^2 \theta_i^{(2)} - \cos^2 \theta_i^{(3)} \right]^2. \quad (14)$$

In the original version of this model, the non-valent atom-atom potential $\Phi_0(r_{ij})$ was purely repulsive and was represented by a simple inverse power function [11].

However, such model cannot be directly applied to the layered LP-N phase, because its stability is largely determined by the mutual attraction of its layers. In this case the energy of non-valent (mainly dispersion) attraction of atoms should be taken into account explicitly.

Hence, in this work the potential model [11] was modified as follows. The non-valent attraction of atoms was represented in the framework of atom-atom interactions, which proved to be effective in describing highly compressed reacting systems [13]. At short interatomic distances this potential approximates the energy of non-valent atom-atom repulsion (i. e., the weighted average energy of interaction of nitrogen atoms in $^1\Sigma$, $^3\Sigma$, $^5\Sigma$, and $^7\Sigma$ states of N_2 molecule [14]), and at longer distances the dispersion contribution added ensuring the stability of the layered LP-N phase structure.

The resulting non-valent interaction was represented by the Buckingham potential:

$$\Phi_0(r_{ij}) = A_0 \exp(-B_0 r_{ij}) - C_0 r_{ij}^{-6}. \quad (15)$$

All parameters of the potential model (9)–(15) were defined first for the layered orthorhombic LP-N crystal and the parameters of the non-valent potential (15) obtained were used for both cg-N and LP-N phases.

It should be noted that in all our calculations of the layered LP-N phase, its structure was represented by the simplified version of the BP (black phosphorus) structure [1] in which all the valent angles $\theta_i^{(k)}$ ($k = 1, 2, 3$) between the bonds attached to each atom are the same. As it was demonstrated in Ref. 1, the differences in energies of such LP-N and BP-N structures are insignificant.

Values of parameters A_0 , B_0 , C_0 , D_e , R_e , α , β , γ , δ and c_e were fitted to reproduce the dependence of the *ab initio* static potential energy of the layered BP-structure [1] within the volume range 3.5–6.75 Å³/at, as well as the following its features at volume corresponding to the minimal energy [1]:

- valent angle between bonds $\theta = 102.2^\circ$;
- bond length $L = 1.54$ Å;
- unit cell parameters $a = 2.299$ Å, $b = 7.268$ Å, $c = 3.036$ Å.

For cg-N structure, the same values of A_0 , B_0 , and C_0 in Eq. (15) as for the LP-N phase were kept, and the numerical values of D_e , R_e , α , β , γ , δ and c_e parameters were fitted to reproduce the following *ab initio* calculations [1] results:

- volume dependence of the static energy in the same range 3.5–6.75 Å³/at;
- values of the valent angle $\theta = 114^\circ$ and bond length $L = 1.40$ Å at zero pressure;
- energy variation at the valent angles change from 114° to 103° (presented in Ref. 1 as a sensitivity study result).

The only parameter on which the energy of the static lattice does not depend at all is ε . Its value was determined, as in the original version of this model [11] first for cg-N structure, from the requirement of isotropy of the individual atom potential field when it displaces from its equilibrium position in the static cg-N lattice at zero pressure. The sensitivity study performed for LP-N phase showed that the results are only weakly dependent on the variation of this parameter. Therefore, for the LP-N phase we set the same value ($\varepsilon = -190$) as was obtained for cg-N phase. The potential model parameters determined for both phases are presented in Table 1.

To assess the quality of the adopted model in description of the input *ab initio* data [1] we calculated bulk compression moduli B_0 near the energy minimum estimated in Ref. 1 as $B_0 = 340.7$ GPa for cg-N phase and $B_0 = 316.9$ GPa for the layered phase. Corresponding values calculated on the basis of the potential model with parameters presented in Table 1 are $B_0 = 335$ GPa in cg-N and $B_0 = 285$ GPa in LP-N phase that is in reasonable agreement with the original *ab initio* data [1], as well as with estimates made in Ref. 4.

Table 1. Parameters of the potential model (9)–(12) for cubic gauche (cg-N) and layered orthorhombic (LP-N) polymeric structures

Phase	D_e , eV	R_e , Å	α , Å ⁻²	β	γ	δ , Å ⁻¹	c_e	A_0 , eV	B_0 , Å ⁻¹	C_0 , eV·Å ⁶
cg-N	2.165	1.502	-2.524	1.938	-222.5	-16.11	0.0416	8772	5.061	8.738
LP-N	2.507	1.367	10.526	3.784	-36.33	-15.87	0.1632			

4. Calculating the Helmholtz free energy of polymeric nitrogen

We evaluated the Helmholtz free energy and other thermodynamic functions in both cg-N and LP-N phases applying potential model (10)–(15) and Mayer group expansion (3).

In our calculations we used generated fragments of cg-N and LP-N crystal structures, containing $N = 216$ atoms located in the sites of the corresponding lattices (Fig. 1).

The energy of the static lattice per atom was determined by summing the pair interaction energies of single atoms ($i = 1$) located in centers of these fragments with all other atoms of the corresponding fragments:

$$U_N / N = \frac{1}{2} \sum_{2 \leq j \leq N} \Phi(\mathbf{r}_1^{(0)}, \mathbf{r}_j^{(0)}).$$

At each given value of the atomic volume, the static energy of the fragment was minimized by varying: 1) valent angles between the bonds, 2) the bond length, and 3) ratios a/c and b/c between the unit cell parameters (for LP-N structure only).

When calculating the free volume $v_f(v, T)$ according to Eq. (4) (triple integral), as well as correlation corrections W_2 [Eq. (6)] and W_3 [Eq. (8)] (six- and nine-fold integrals, correspondingly) we applied the same Chebyshev–Hermite numerical integration method of the highest algebraic degree of precision [15] with the $\exp(-x^2)$ weight function which was used in our earlier calculations of the Helmholtz free energy of the Lennard-Jones crystal [9].

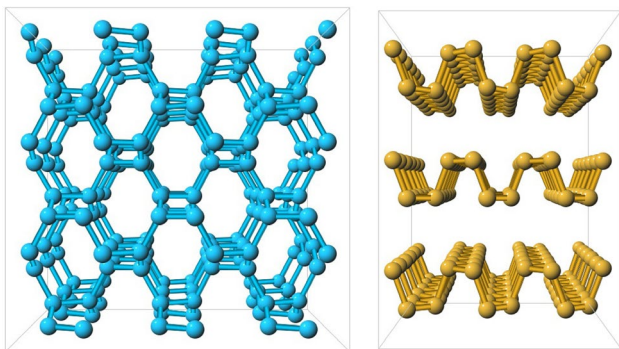


Fig. 1. Fragments of the cg-N (left) and LP-N (right) polymeric phase structures used in calculations.

These calculations came down to evaluating the weighted amount $\sum_{1 \leq i \leq n} w_i g(\xi_i)$ of the integrands values at

n nodes of the reduced coordinates $\xi_i = \sqrt{\alpha_i / kT} \Delta x_i$, where the elastic constants α_i ($i = 1, 2, 3$), corresponding to the first (harmonic) approximation to the single-particle potential $u_1^{(\text{harm})}(\Delta \mathbf{r}) = \sum_{1 \leq i \leq 3} \alpha_i \Delta x_i^2$, were determined by

setting small displacements of the central atom and computing $u_1(\Delta \mathbf{r})$ according to Eq. (5).

The same scheme with the same dimensionless variables was applied in evaluation of pair W_2 and triple W_3 correlation contributions. Numbers of the integrand values needed to evaluate v_f , W_2 , and W_3 were corresponding-

ly: n^3 , n^6 and n^9 . Calculations carried out with different numbers of nodes n showed that the increase in the number of nodes over $n = 7$ along each Cartesian coordinate leads to the refinement of the results only in fourth decimal place, so in all our final calculations the number of Chebyshev–Hermite nodes was set to $n = 7$. The results of the free volume calculations were compared with their values calculated in harmonic approximation, and the contribution of the anharmonicity was estimated. Detailed calculations of the Helmholtz free energy $F(V, T)$, pressure $P = -\partial F / \partial V$, as well as the heat capacity and coefficient of thermal expansion $\beta_T = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ were performed at temperatures $T = 100\text{--}2000$ K in the volume range $3.5\text{--}6.75$ Å³/at.

5. Results and discussion

Analyzing the results of these calculations, it should be noted that at low temperatures the main contribution to the Helmholtz free energy, as well as to pressure and compressibility, gives the zeroth-order term in Mayer group expansion (static lattice). The contribution of the first term in Mayer group expansion (free volume) at $T = 300$ K is only about -10 %, and both correlation corrections are small (about 0.1 % for the LP-N phase and about -1.5 % for the cg-N phase).

The calculated thermodynamic properties of the polymerized phases of nitrogen were compared with available limited experimental data [3–5]. This comparison is presented in Fig. 2.

As one can see, the agreement is quite satisfactory, although most of the available experimental data refer to metastable regions of both phases (dashed lines in Fig. 2).

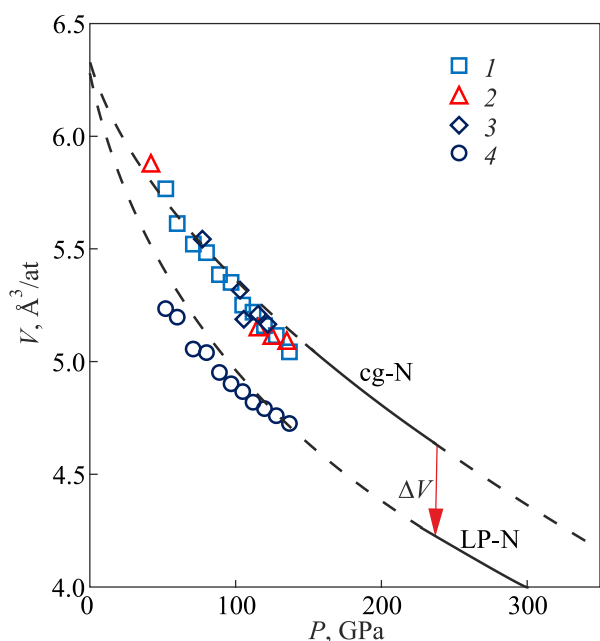


Fig. 2. Volumes in polymeric phases of nitrogen at room temperature. Comparison of our calculations with experimental data in cg-N phase (1 — [4], 2 — [3], 3 — [5]) and in LP-N phase (4 — [4]). Solid parts of lines correspond to stable, dashed lines — to metastable states.

However, this agreement is primarily due to the reliability of the underlying *ab initio* calculations of Mailhot *et al.* [1], because the thermal contribution to the P - V dependence in both polymeric phases here is rather small.

Prediction of the pressure-temperature dependence of the cg-N to LP-N phase transition line, as mentioned above, was of the greatest interest in this work. According to the underlying *ab initio* data [1], at zero temperature this transition should occur at pressure of about 250 GPa, what was confirmed by recent experiments [8].

We used the well-known Maxwell method, constructing the common tangent to the curves of the Helmholtz free energy as a function of volume on each isotherm. It should be stressed that these calculations were performed without using any experimental data, but only on the basis of the described above models calibrated on *ab initio* calculations [1].

The predicted phase transition line is shown in Fig. 3 by the solid line, where it is compared with the location of this transition proposed by Tomasino *et al.* [4] (dashed line). Authors of Ref. 4 supposed a positive slope of the boundary between the cg-N and the LP-N phases, reasoned by the “higher density of the LP-N phase compared to cg-N and the strong presence of cg-N in the region of stability of LP-N (not vice versa), and the lack of LP-N in the region of cg-N stability between 100 and 125 GPa” [4].

Our calculations, in contrast, show the negative slope of the transition line. This is due to the fact that in LP-N phase entropy is higher and volume is less than in the coexisting cg-N phase. The predicted jumps of the volume and entro-

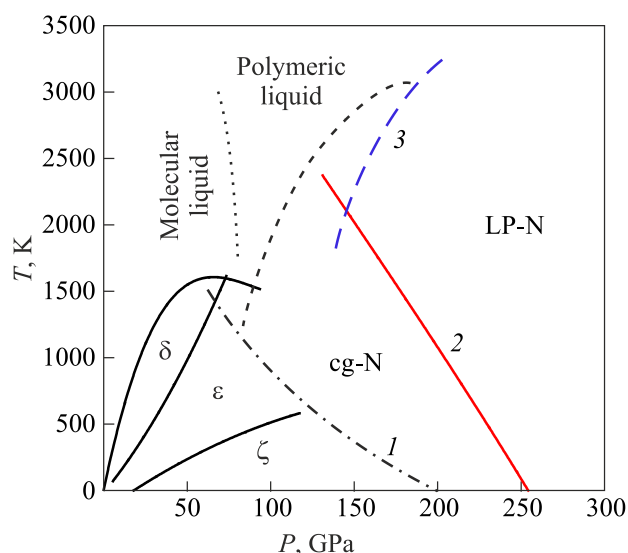


Fig. 3. Phase diagram of highly compressed solid nitrogen: 1 — the predicted transition from molecular N_2 to cg-N phase [11] (dash-dotted line), 2 — cg-N to LP-N phase transition line (this work), 3 — location of the cg-N to LP-N transition proposed in Ref. 4.

py along the transition line are approximately constant: $\Delta v \cong 0.4 \text{ \AA}^3/\text{at}$ and $\Delta S/R \cong 2.5$ ($R = Nk$ is gas constant), up to its intersection with the melting line.

Another point of considerable interest in this work was behavior of other thermodynamic properties of polymerized nitrogen, especially the thermal expansion coefficient β_T . Estimations of β_T in cg-N solid made in our early Monte Carlo simulations [16] showed its essential decrease with the increasing pressure up to negative values at $P > 100$ GPa. This effect was explained by the fact that increasing temperature leads to the increase of atomic vibration amplitudes which in turn lead to decreasing the length of valent bonds and valent angles, and, as a result, atoms become closer to each other.

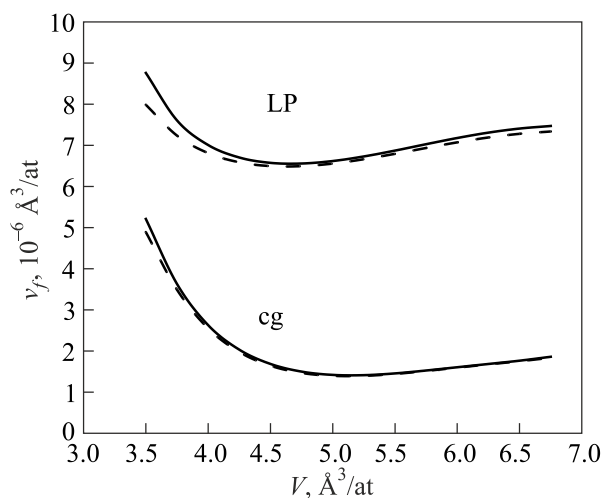


Fig. 4. Free volumes in LP-N (above) and cg-N (below) phases at room temperature (solid lines). Dashed lines — harmonic approximation.

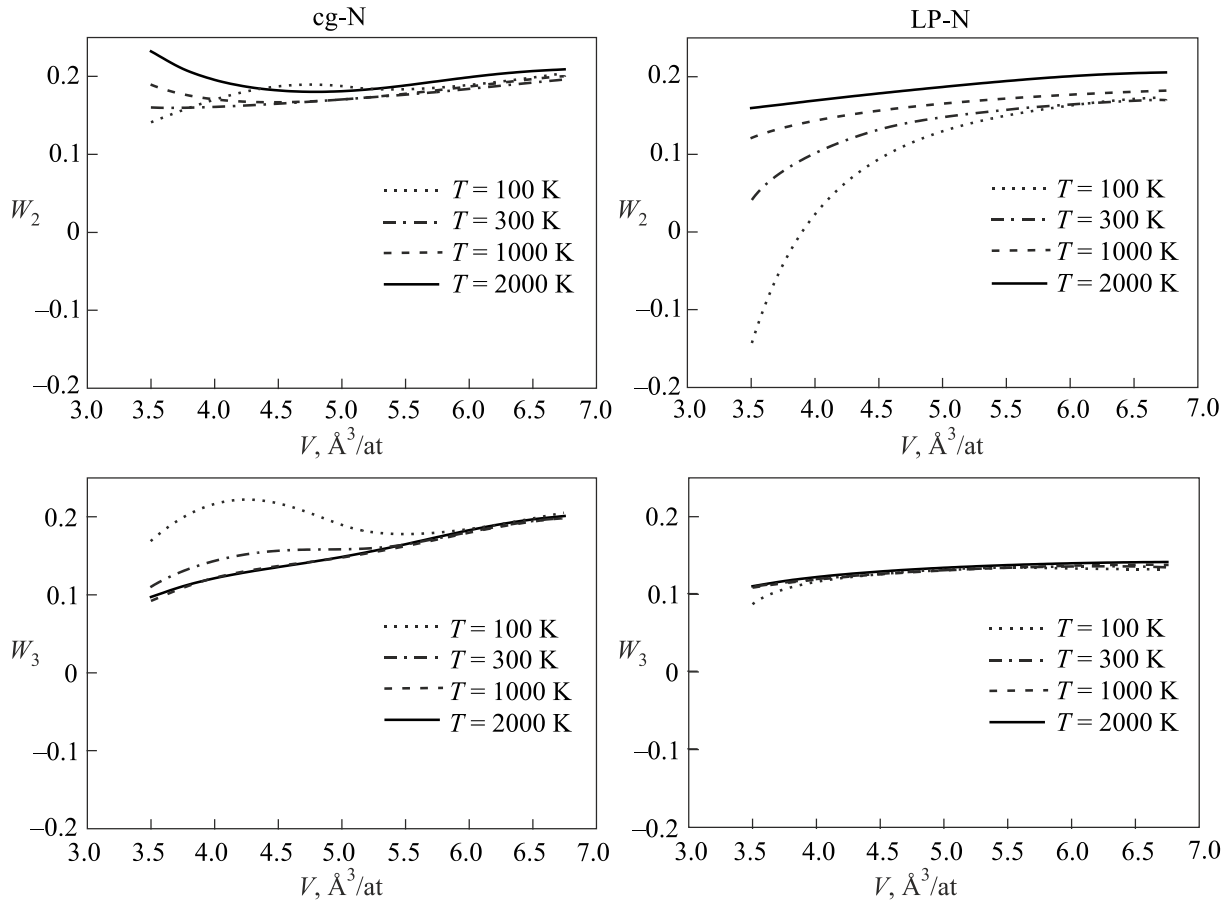


Fig. 5. Volume dependence of the pair W_2 (above) and triple W_3 (below) correlation contributions at different temperatures.

Within the framework of the Mayer group expansion approach, it is possible to study the behavior of the thermal expansion in more detail and find out what factors determine its behavior. In the first approximation, the value of the thermal expansion coefficient β_T is determined by the dependence of the free volume $v_f(v, T)$ Eq. (4) from both the atomic volume and temperature. Analysis of our results showed that the anharmonicity of the atomic vibrations in static environment, which determine the free volume, is very small in both cg-N and LP-N phases (Fig. 4). At the same time, the anharmonic contribution remains very noticeable both in binary and triple correlation corrections (Fig. 5).

This means that the contribution of the first term of the Mayer group expansion Eq. (3) to the coefficient β_T is determined in both phases mainly by the unusual volume dependence of the harmonic contributions to the free volume represented by dashed lines in Fig. 4.

The peculiarity of these dependences is their nonmonotonicity. In the region of strong compression, the free volume begins to increase with increasing pressure instead of the usual decrease. This unusual behavior is mainly due to decrease of the elastic constants α_i at strong compression which leads to decrease in the contribution of the first term of Mayer group expansion to β_T with increasing pressure in both phases.

It should also be mentioned that the contributions to β_T from the next terms of the Mayer group expansion: pair W_2 and triple W_3 correlations between the atomic displacements are very different. The coefficient of thermal expansion in both polymeric phases turned out to be especially sensitive to the pair correlations between displacements of neighboring atoms. The main contribution to β_T in cg-N phase (more than 90 %) is due to these pair correlations. The contribution of triple correlations to the thermal expansion coefficient is much smaller, it is about 2 % in the cg-N phase and about 0.5 % in LP-N phase. This is clearly seen when comparing these contributions along the transition line as it illustrated in Fig. 6.

We have also evaluated the corresponding contributions to the heat capacity of polymeric phases both with pressure (at room temperature) and with temperature (along the transition line). It was found that the pressure practically does not affect the heat capacity, which remains close to its classic harmonic value $3R$. The heat capacity increases along the transition line with increasing temperature, but only slightly (by 7 % in cg-N phase and by 4 % in LP-N phase when temperature reaches 2000 K). This is also due to small anharmonicity of the atomic vibrations in both polymeric structures.

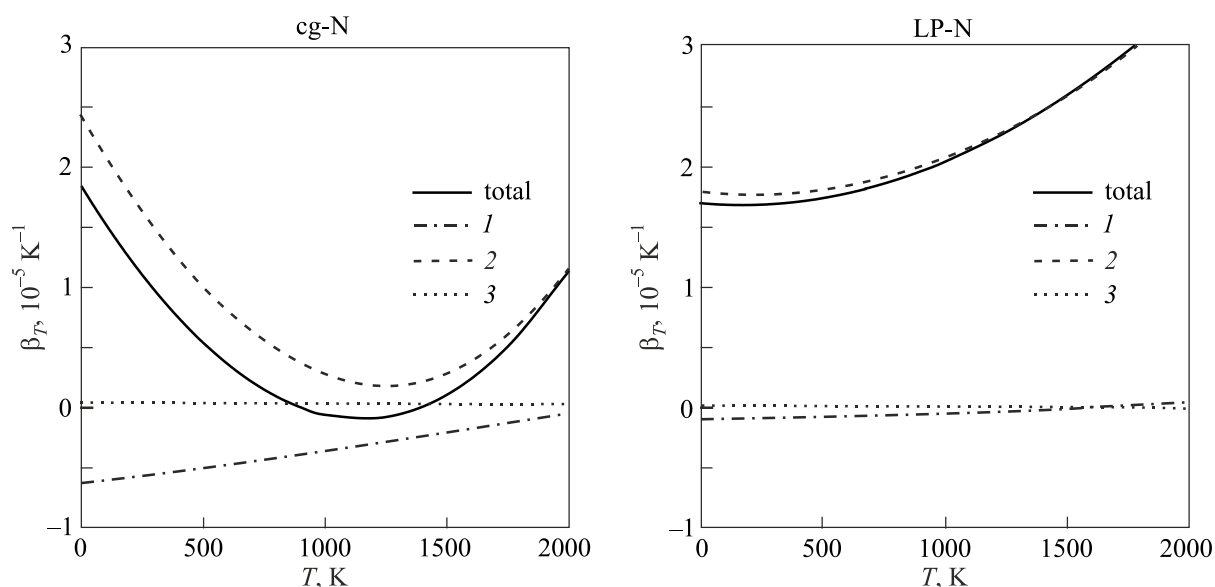


Fig. 6. Temperature dependence of the thermal expansion coefficient along the phase transition (solid line) and Mayer group expansion terms contributions: 1 — first (free-volume) term, 2 — second (W_2) term, 3 — third (W_3) term.

6. Conclusions

Characterizing the above results in general, it should be noted that they clearly demonstrate the effectiveness of the Mayer group expansion method in predicting the behavior of thermodynamic properties of the polymeric phases of crystalline nitrogen. A good agreement was found between the predicted and measured properties of both phases at room temperature.

Unfortunately, it is not yet possible to compare the predicted location of the cg-N to LP-N phase transition line with direct measurements, because in all existing experiments [6–9, 17] mainly the metastable polymeric structures were studied.

As it follows from our calculations, the predicted negative slope of the transition line is mainly determined by the contribution of the first terms of the Mayer group expansion Eq. (3), corresponding to the well-known free-volume theory of Lennard-Jones and Devonshire [12].

Despite this, the next term in the expansion Eq. (3), which takes into account pair correlations between atomic displacements in the crystal lattice, turned out to be very important in assessing the behavior of thermal properties, in particular, of the thermal expansion. This gives the main contribution to β_T both in the cg-N and LP-N phases, and together with the first-order term, determines the area of its negative values in cg-N phase.

At the same time, the contribution of the triple correlations to both the thermal and caloric properties appears to be insignificant in both polymeric phases. This can be regarded as a sign of sufficiently rapid convergence of the Mayer group expansion at least in the region of state parameters considered in this paper.

It should also be emphasized that when using the proposed approach it is important to have reliable *ab initio* data for calibration of the potential model. Our attempt to use for this purpose recent *ab initio* calculations [18] instead of the classical results [1], did not lead to a reasonable agreement with experimental data [3–5] as it presented in Fig. 3.

In conclusion, we note that the successful prediction of the polymorphic transition in both molecular [6] and polymerized crystals based on the Mayer group expansion method increases the interest to verifying its effectiveness in predicting other polymorphic phase transitions, e. g., to assessing the location of the transition lines between the ϵ - and ζ -phases of molecular nitrogen and the polymeric cg-N phase, as well as to extending this approach to quantum crystals.

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Групове розкладання Майєра для твердих тіл:
застосування до поліморфного переходу у сильно
стисненому азоті

Є. С. Якуб, Л. М. Якуб

Групове розкладання Майєра для кристалічних твердих тіл, запропоноване раніше, застосовується для прогнозування лінії поліморфного фазового переходу між кубічною та шаруватою фазами полімерного азоту. Порівняння з існуючими експериментами виявило, що теоретичні розрахунки на основі запропонованої потенційної моделі, відкаліброваної на неемпіричні розрахунки енергії, узгоджуються з існуючими експериментальними даними. Обговорюється прогнозоване розташування лінії поліморфного переходу на фазовій діаграмі та специфіка поведінки теплових властивостей обох фаз у широкому температурному діапазоні.

Ключові слова: полімерний азот, поліморфний перехід, негативне теплове розширення.