

Amorphous polymeric nitrogen – toward equation of state

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The thermodynamic properties of amorphous polymeric nitrogen are analyzed theoretically basing on free energy expansion. An approach allowing estimating Helmholtz free energy of high-pressure disordered condensed phases of nitrogen is proposed. The approach is based on expansion of the excess entropy on interatomic correlations and tested on existing Monte Carlo simulation data. Some specific problems arising on this way and their possible solutions are discussed.

PACS: 65.20.De General theory of thermodynamic properties of liquids, including computer simulation;
65.20.Jk Studies of thermodynamic properties of specific liquids;
64.30.Jk Equations of state of nonmetals.

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1. Introduction

The anomalous behavior of the shock-compressed nitrogen was discovered many years ago by Radouski, Nellis and Ross [1]. It was interpreted as a dissociation of N_2 molecules with formation of non-molecular phase. First theoretical calculations of McMahan and LeSar [2] of the solid nitrogen atomic phase predict a stable layered arsenic-like $A7$ polymeric structure, where each atom is bound to three neighbours by ordinary chemical bonds. Later *ab initio* calculations of Martin and Needs [3] show the three-fold coordinated *cubic gauche* (cg) structure must be more stable. The first experimental evidence of non-molecular solid nitrogen at megabar pressures and low temperatures was found later by Goncharov, Grigorianz, Mao, Liu, and Hemley [4]. Analysis of spectra of this phase performed by Grigorianz, Goncharov, Hemley, and Mao [5] reveals the possibility of existence of the metastable amorphous nitrogen solid. The problem of high-pressure phase diagram of nitrogen was discussed by Grigorianz, Goncharov, Hemley, Mao, Somayazulu, and Shen [6]. Eremets, Hemley, Mao, and Grigorianz [7] confirmed that the crystalline phase very likely has the cubic gauche structure.

Equation of state of disordered polymeric nitrogen at high pressures and temperatures was first proposed on the basis of the simplest potential model of sticky spheres [8]. In our earlier Monte Carlo calculations [9], we predicted the thermodynamic functions of polymeric nitrogen at non-zero temperatures in the $A7$ arsenic-like structure us-

ing simple atom-atom potential model. Later, a more sophisticated potential model was proposed [10]. It represents the total energy of polymeric nitrogen as a function of both interatomic distances and angles between single chemical bonds attached to each atom. The calibration of the model was based on the *ab initio* quantum mechanical calculations of Mailhot, Yang, and McMahan [11] at $T=0$. This model was used in prediction of thermodynamic behavior of both crystalline [10] and amorphous [12] polymeric solid nitrogen at high pressures and non-zero temperatures. Equilibrium properties of polymerized solid nitrogen have been computed using Metropolis' Monte Carlo method [10]. These simulations revealed that the polymeric cg-crystalline structure of nitrogen at high densities and elevated temperatures has negative thermal expansion coefficient. It was found that the negative thermal expansion appears in both threefold-coordinated polymeric nitrogen structures studied: in cg-crystalline and amorphous phase, but not in the layered $A7$ structure. Polymeric phases exhibit not only negative thermal expansion, like other covalent structures, but also essential deviations from the Dulong–Petit law [12]. Prediction of the high-pressure phase equilibrium between molecular and non-molecular condensed nitrogen require adequate equations of state for all phases, including fluid, amorphous and crystalline polymeric phases [13]. The proposed modification of the Mie–Grüneisen model was applied in explanation of thermodynamic behavior of the polymeric high-pressure cg-phase of the solid nitrogen. The problem

of equation of state for amorphous phase is more complicated. The amorphous nitrogen solid can be modelled [12] using averaging over a number of simulations with cells containing overheated and then quenched polymeric nitrogen. To achieve the accuracy comparable to that characteristic for Monte Carlo simulation of cg crystalline structure [10], one needs much more efforts. At the same time, due to spatially uniform structure of the amorphous phase the modified Mie–Grüneissen model [13] can be applied here only formally and its parameters would have little sense.

Here we propose an approach providing an alternative possibility to determine equation of state of amorphous polymeric nitrogen using results of Monte Carlo calculations [12].

2. Excess entropy of amorphous polymeric nitrogen

Fortunately, this type of structure allows applying another approach, suitable for fluids and other disordered condensed phases [14]. This approach uses expansion of free energy in series on interatomic correlations:

$$F = F^{(1)} + \Delta F^{(2)} + \Delta F^{(3)} + \dots, \quad (1)$$

where $F^{(1)}$ is the single-particle (ideal-gas) contribution, and $\Delta F^{(2)}$, $\Delta F^{(3)}$, ... are contributions of pair, triple etc. interatomic correlations. In the context of the computer simulation data, internal energy is usually easy available and the problem reduces to the entropy contribution to Helmholtz free energy in (1).

$$S = S^{(1)} + \Delta S^{(2)} + \Delta S^{(3)} + \dots, \quad (2)$$

where $S^{(1)}$ is entropy of an ideal-gas, and the following terms provide pair-, triple-, etc. correlation contributions to entropy of a spatially uniform system.

Many attempts have been made to develop effective expansion of excess entropy on density fluctuations and particle correlation [14–17].

The most successful expansion [18] provides the pair-correlation contribution $\Delta S^{(2)}$ expressed via atom–atom radial distribution function:

$$\Delta S^{(2)}/k = -2\pi\rho \int \{g(R) \ln g(R) - [g(R) - 1]\} R^2 dR. \quad (3)$$

This contribution appears to be the most important one both at low densities (where (3) is exact) and at high densities, where the pair correlation contribution, according to Ref. 18, captures 85–90% of the excess entropy, with the largest discrepancy occurring at intermediate densities. It was successfully applied in estimating entropy of various liquids (silica, beryllium fluoride and water) from their atom–atom radial distribution functions, computed using conventional molecular dynamics or Monte Carlo simulations [17].

Amorphous polymerized nitrogen is extremely dense and spatially uniform, its pair correlation functions are known from Monte Carlo simulations [12], and hence this approach seems a promising alternative to construction of a semi-empirical Mie–Grüneissen-like equation of state.

At the same time, an immediate application of (3) encounters a difficulty related to the presence of strong, short-range and saturative valence forces, acting between nitrogen atoms. These forces are responsible for formation of three ordinary chemical bonds per each atom both in crystalline and amorphous polymeric nitrogen. In atom–atom distribution function these forces produce extremely narrow and high peaks like that shown in Fig. 1.

The contribution of such a peak to the excess binary entropy (3) is essential and evaluation of $\Delta S^{(2)}$ by direct numerical integration of $g(R)$ may be related to a serious error.

To overcome this difficulty we adopt the separation of atom–atom radial distribution functions into bonded $g_B(R)$ and non-bonded parts $g_{\text{non-B}}(R) = g(R) - g_B(R)$ [19]. The last one is shown in Fig. 2. Except of a few small peaks reflecting the indirect chemical bonding with atoms in the second coordination sphere, it behaves smooth enough to be used in numerical integration procedure immediately.

The bonded contribution $g_B(R)$ differs from zero only in a rather narrow range of distances near equilibrium chemical bond length L . It satisfies the normalization condition [19]:

$$4\pi\rho \int g_B(R) R^2 dR = \nu. \quad (4)$$

Here $\nu=3$ is atomic valence (the number of chemical bonds per atom).

Another important point is: both contributions to $g(R)$ almost do not overlap. This peculiarity provides the possibility to represent the pair-correlation contribution $\Delta S^{(2)}$ as an approximate sum of «bonded» and «non-bonded» parts: $\Delta S^{(2)} \approx \Delta S_B^{(2)} + \Delta S_{\text{non-B}}^{(2)}$, where

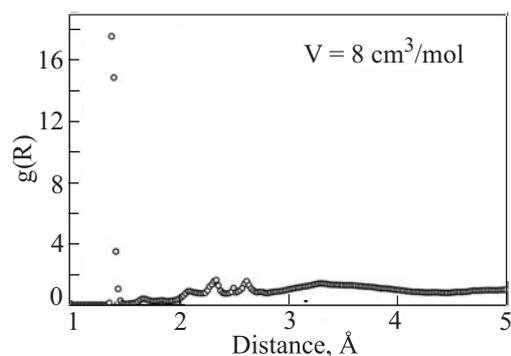


Fig. 1. Atom–atom radial distribution function of amorphous nitrogen at room temperature (MC simulation [12]).

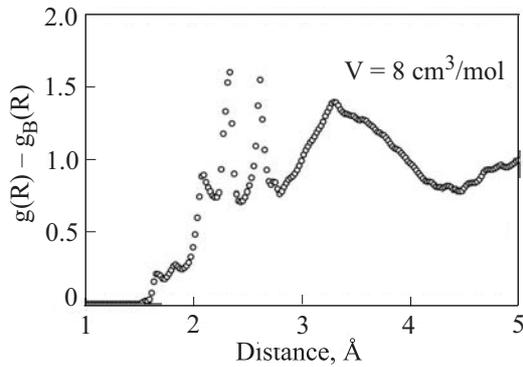


Fig. 2. Non-bonded part of atom–atom radial distribution function (amorphous nitrogen at room temperature [12]).

$$\frac{\Delta S_{\text{non-B}}^{(2)}}{k} = -2\pi\rho \int \{g_{\text{non-B}}(R) \ln g_{\text{non-B}}(R) - [g_{\text{non-B}}(R) - 1]\} R^2 dR, \quad (5)$$

$$\frac{\Delta S_B^{(2)}}{k} = -2\pi\rho \int \{g_B(R) \ln g_B(R) - g_B(R)\} R^2 dR. \quad (6)$$

Numerical calculation of $\Delta S_{\text{non-B}}^{(2)}$ is straightforward. To calculate $\Delta S_B^{(2)}$, we propose the following procedure. To a first approximation, the bonded contribution $g_B(R)$ may be represented by a Gauss function:

$$g_B(R) \approx A \exp[-\alpha(R-L)^2]. \quad (7)$$

Equation (7) contains three constants: A , α and L . The normalization condition (4) gives the possibility to exclude one of them. Substituting (7) into (4) one gets:

$$A = \frac{v\alpha^{3/2}}{2\rho\pi^{3/2}(1+2\alpha L^2)}. \quad (8)$$

Table 1. «Bonded» and «non-bonded» contributions to excess entropy calculated using Monte Carlo atom–atom distribution function at room temperature and $V = 8.04 \text{ cm}^3/\text{mol}$ [12] shown in Figs. 1 and 2

L	α	A	$\Delta S_{\text{non-B}}^{(2)}/k$	$\Delta S_B^{(2)}/k$	$\Delta S^{(2)}/k$
1.37	1650	19.33	-3.08	-2.19	-5.27

Two other constants one may easily adjust to represent the pronounced first $g(R)$ peak height and position. Substituting (7) into (6) and taking into consideration (8) one gets:

$$\frac{\Delta S_B^{(2)}}{k} \approx \frac{v}{4} \left(3 + \frac{2}{1+2\alpha L^2} + \ln \left[\frac{4\pi^3 \rho^2 (1+2\alpha L^2)^2}{\alpha^3 v^2} \right] \right). \quad (9)$$

This expression for the bonded contribution $\Delta S_B^{(2)}$ is the more accurate the higher and narrower is the $g_B(R)$ peak, i.e. for large α . In the case $\alpha \gg \rho^2 L^4$, Eq. (9) simplifies:

$$\frac{\Delta S_B^{(2)}}{k} \approx \frac{v}{4} \left(3 + \ln \left[\frac{16\pi^3 \rho^2 L^4}{\alpha v^2} \right] \right). \quad (10)$$

The above approach allows estimating the excess entropy of amorphous nitrogen using immediately only atom–atom radial distribution functions, easily computable in Monte Carlo simulation [12]. Results of $\Delta S_B^{(2)}$ calculations at room temperature and $V = 8.04 \text{ cm}^3/\text{mol}$ are presented in Table 1.

It is to be noted that the analogous calculation for $V = 6.0 \text{ cm}^3/\text{mol}$ gives higher value of entropy. This is an indication of the negative thermal expansion, characteristic for both crystalline and amorphous polymeric nitrogen [10,12]. From thermodynamic relation $\partial S / \partial V = \partial P / \partial T$, it is possible to estimate the average thermal pressure $P_T = T(\partial P / \partial T)$ in the volume interval 6–8 cm^3/mol as: $P_T = -65 \text{ MPa}$.

This value is just in between values determined in Monte Carlo simulation [12]: -160 MPa (6 cm^3/mol) and -45 MPa (8 cm^3/mol).

3. Conclusions

Computer simulation of the metastable amorphous high-pressure polymeric phase of condensed nitrogen is a more complicated task than the simulation of the molecular or cg-crystalline phases [10] and requires much more efforts and computation time. In this work, an approximate way of calculating excess entropy of amorphous phase is tested, which uses only atom–atom radial distribution functions determined in Monte Carlo simulations [12]. This approach was developed for estimation of excess entropy of fluids and has never been tested on amorphous solids yet. If successful, it provides an easy solution of the problem of equation of state for this phase. Our estimations prove the effectiveness of the above approach, despite of difficulties on account of interatomic chemical bonding and related to a specific shape of radial distribution function.

More efforts are required to estimate theoretically the location of the $P-T$ equilibrium line between the molecular and non-molecular phases of nitrogen. One of problems unsolved yet is the absence of the common origin of a scale for interatomic potentials used in simulations of both phases. Hopefully, this problem may be solved in the

short run invoking precise *ab initio* calculations, available now [20].

Another point is determination of the relative stability and abundance ratio of the high-pressure amorphous phase of nitrogen in samples recovered from diamond-anvil experiments [4–7], because it may be a mixture of crystalline and amorphous solid nitrogen. *Ab initio* calculations predict that the metastable low-pressure phase is amorphous, i.e. has predominantly 3-folded bonded atoms in a disordered configuration [20]. This result confirms the initial suggestion [5] that the high-pressure and high-temperature non-molecular phase is amorphous as well, and the P – T phase transition line must be determined taking this circumstance into consideration. In this case the excess entropy estimation provided in this work may help in solution of the general phase equilibrium problem.

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