Methodology for Describing Different Phase States of Molecular Nitrogen

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Abstract

A theory-based methodology for describing the thermodynamic properties of molecular nitrogen is presented. The results obtained indicate a successful application of a fully consistent statistical method for the description of a molecular system in different phase states. The method employs a density of states equation for solid nitrogen and a perturbation potential for gaseous and liquid nitrogen. The main characteristics of the calculation method include the need for a minimal number of initial data and the absence of fitting parameters. The adequacy of the physical model that is the basis for the method allows a description of existing experimental data and the peculiarities of the thermodynamic properties.

I. Introduction

A study is presented on the development of a statistical method for the description of thermodynamic characteristics of molecular nitrogen in different phase states. The study is motivated by research on experimental systems that operate using nitrogen in different phase states. Examples of such experimental systems include cryogenic refrigeration systems (e.g., pulse tube, Stirling, etc). There also exist cryogenic heat engine systems. For example, liquid nitrogen is being studied for use as a "fuel" for powering zero emission vehicles [1,2]. The organization of this paper is as follows. In Sec. II, thermodynamic characteristics of solid nitrogen are described taking into account all translational and orientational phonon modes. In Sec. III, thermodynamic characteristics of gaseous and liquid nitrogen are calculated employing a perturbation potential. Concluding remarks are found in Sec. IV

II. Lattice dynamics and heat capacity of solid nitrogen

Thermal properties of solid nitrogen in α- and β-phases are obtained in the framework of a theoretical approach that takes into account all translational and orientational phonon modes, as measured by the

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methods of neutron [3,4] and Raman [5,6] spectroscopy.

As is well known, solid nitrogen has two crystal structure phases: cubic α-phase (Pa3 lattice), which is stable at temperatures lower than $T_{trans} = 35.61$ K and hexagonal β-phase (P6$_3$/mmc lattice), which is stable in the range of temperatures $T_{trans} < T < T_{triple}$. The triple point occurs at $T_{triple} = 63.14$ K, P = 12.53 kPa. Structural α-β phase transition at T = T_{trans} corresponds to the process of orientational disordering in crystalline N_2 and belongs to the phase transition of the second kind. The elementary cell of solid nitrogen consists of 4 molecules, which possess 20 degrees of freedom, 3 translational acoustic, 9 translational optic and 8 orientational, at low temperatures. Neglecting the effects of phonon dispersion and translational-orientational interactions, the spectral phonon density of states (DOS) is approximated by the expression

$$G(\omega) = \frac{3}{20}\frac{3\omega^2}{\omega_D{}^3} + \frac{1}{20}\sum_{i=1}^{9}\delta(\omega - \omega_i) + \frac{1}{20}\sum_{j=1}^{8}\delta(\omega - \omega_j),$$

(1)

where $\omega_D = k\Theta_D/\hbar$ is the cut-off acoustic (Debye) frequency, ω_i and ω_j are the resonant translational optic and orientational frequencies.

The molar lattice heat capacity is determined by the formula

$$C_{ph}(T) = 3nR\int_0^\infty \left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}G(\omega)}{(e^{\hbar\omega/kT}-1)^2}\,d\omega$$

, (2)

where n is the number of atoms entering the chemical formula and R is the universal gas constant.

Using the complete set [7] of translational optic ω_i and orientational ω_j lattice modes measured at the Γ-point at low temperatures

$\omega_i = 46.8$ (A$_u$), 54.0 (E$_u$), 48.6 (T$_u^-$), 69.4 (T$_u^+$)[cm^{-1}];

$\omega_j = 32.1$ (E$_g$), 36.4 (T$_g^-$), 60.0 (T$_g^+$) [cm^{-1}],
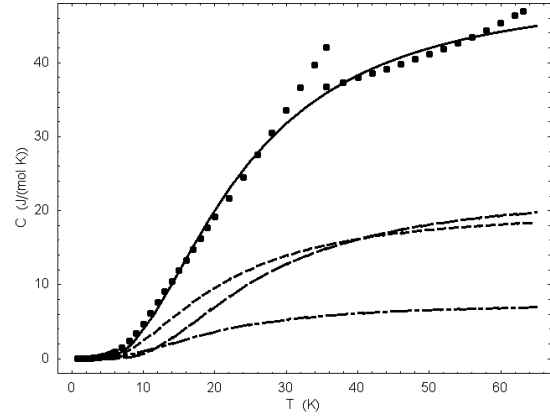
Fig. 1. Calculated (solid curve) heat capacity of solid nitrogen in comparison with measurements (points) [9]. The contributions of acoustic (dot-dashed curve), optic translational (long-dashed curve) and orientational (short-dashed curve) modes are shown.

with taking into account their degree of degeneration in accordance with the number of dispersion curves calculated in Ref. [8] for each mode and the value of the Debye temperature $\Theta_D = 83.5$ K (Ref. [7]), the phonon DOS (1) and heat capacity (2) have been calculated without using fitting parameters.

The results of the heat capacity calculations are presented in Fig.1, along with the corresponding experimental data [9]. The agreement is better than in Ref. [8], where the interaction potential between N_2 molecules with a set of fitting parameters was used. The contributions to the heat capacity of the acoustic translational, optic translational and orientational phonon modes are clearly obtainable with the approach presented here, as shown in Fig.1. Within the approach proposed it is possible also to separate the heat capacity jump in the α-β transition region. As a result, its theoretical investigation can provide more detailed information on the critical fluctuations and peculiarities of the structural phase transition. Thus, the proposed phonon DOS (1), based on the measured characteristic lattice frequencies, allows the calculation of phonon energy, entropy and

other thermodynamic functions of solid nitrogen.

III. Thermodynamic properties of gaseous and liquid nitrogen

Until the 70's, creation of efficient calculational procedures for obtaining thermodynamic properties applicable both for gaseous and liquid states was a problem. In fact, the possibilities for extrapolation of empirical equations to regions of states uninvestigated experimentally were limited. There were various kinds of predictive procedures or simplified methods of simulations, as reviewed in Refs. [10,11]. These calculation methods provided satisfactory results for some thermodynamic characteristics in certain regions of states; however, they were often found to be unsatisfactory because the computational errors for the set of properties exceeded substantially the experimental errors. On the other hand, the attempts to apply modern statistical methods to the specified purposes had not yet been undertaken.

The situation has changed during the last 25 years, when methods of thermodynamic perturbation theory (PT) began to evolve intensively. This line of investigation, being both rigorous and workable, made it possible to build successful theoretical models of non-uniform (including dense) molecular media [12]. The results were necessary for the development of general computational procedures and algorithms for a complex of thermodynamic quantities, phase equilibria, and kinetics, surface and other properties of gases and liquids – both for individual substances and mixtures.

The main idea of PT is to divide of the initial potential of inter-molecular interaction into the sum of two terms, one of which is small in certain respect when compared to the other and can be considered as a perturbation $u = u_B + u_I$. It is known that structural properties of dense molecular systems are generally determined by repulsive interactions. Thus, it is possible to take into account thermodynamic effects associated with an attraction potential u_I by means of a statistical averaging of the states of the basic system with repulsive interaction u_B.

The main requirements imposed for the present work on models for pair potentials of interaction are that they completely represent the inter-molecular interaction for a broad class of substances and that they have simple analytical forms. Many studies [12] have shown that the application of very complicated and, as expected, "accurate" potentials for a specified substance, does not necessarily improve the accuracy of the description of its thermodynamic properties in a wide region of states. In addition, the universality of expressions for a set of investigated substances is lost.

The traditional and widely used Lennard-Jones potential

$$u(r) = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^{6} \right] \qquad (3)$$

is an isotropic two-parameter potential of the form $u(r) = \varepsilon \varphi(r/\sigma)$,

where $r = |r_{12}|$ is the inter-molecular separation,

ε is the depth of the potential well,

σ is the separation of the pair of molecules at which the interaction energy vanishes: $u(\sigma) = 0$.

The two parameters in the pair potential (3) account for the contributions to the thermodynamic properties caused by multi-particle interactions, anisotropy of fields of force, quantum and other effects. These parameters are determined [10] from the data on properties of substances in liquid-vapor equilibrium. The Lennard-Jones potential, as well as more complicated anisotropic potentials, have been used [11] for calculations of the thermodynamic quantities of more than 30 substances and their multi-component mixtures in the gaseous and liquid states. The application of the potential (3) for nitrogen

is so well substantiated that one can see it clearly from the results given below.

The thermodynamic properties of the molecular system under study are presented in the form of PT series in parameters that characterize the differences between the real (original) $u(r)$ potential and the $u_0(r)$ potential of the system of zero order approximation. A hard sphere (HS) system is usually used as a system for zero order approximation. This method has advantages over other methods, as there are a large number of numerical experiments and exact analytical expressions for the HS system properties.

The main problem is going from the transition of repulsive potential $u_B(r)$ to the HS potential $u_0(r/d)$ as a zero order approximation (d is a HS diameter). Different versions of such conversion were proposed [12], but in this case d always depends on the parameters of state (T,V). This makes further calculations based on the u_0 [r/d (T,V)] potential incorrect [13].

In the present approach we are using the proposed in Ref. [14] modified PT procedure (MPT), in which the perturbation potential $u_1(r) = \varepsilon \varphi_1(r)$ is chosen in the form:

$$u_1(r) = \begin{cases} 0, & r < a(T^*); \\ u(r), & r > a(T^*), \end{cases} \quad (4)$$

so that the division of the original potential into a basic potential u_B and perturbation (4) takes place at the "floating" point $a(T^*)$, where $T^* = kT/\varepsilon$ is a dimensionless (reduced) temperature. Such a choice of the $a(T^*)$ should provide a temperature independent HS diameter

$$d = \int_0^{a(T^*)} [1 - \exp(-\varphi(r)/T^*)]dr = const, \quad (5)$$

as well as HS potential $u_0(r/d)$.

The free energy $F = N f$ of the system of N particles interacting through the initial potential $u(r)$ at the temperature T and particle density $\rho = N/V$ can be transformed into a series:

$$\beta f = \beta f_0 + \rho^* (I_1 + I_2/T^*)/T^* + \dots, \quad (6)$$

where $\beta = 1/kT$; $\rho^* = \rho\sigma^3$ is a dimensionless (reduced) density; I_1 and I_2 are the MPT group integrals of the 1st and 2nd order, respectively. The quantity f_0 is a specific free energy (per one particle) of the HS system:

$$\beta f_0 = \psi(T^*) + ln\,\rho^* + \eta\,(4\text{-}3\eta)/(1\text{-}\eta)^2, \quad (7)$$

where $\psi(T^*)$ is a temperature function in the ideal-gas part f_0;

$$\eta = (\pi/6)\rho_0^*; \quad \rho_0^* = \rho\,d^3 = \xi^3\rho^*.$$

In particular, the advantages of the MPT procedure are rapid convergence of the series of the (6) type and an essential facilitation of the calculations, especially for phase equilibrium and for the properties of mixtures. This allows us to restrict consideration of the MPT series for terms of an order not higher than the first (for the thermal properties) or not higher than the second (for the thermal or mixed properties - C_v, C_p, sound velocity V_s, etc.).

The group integral $I_1(T^*, \rho^*)$ is of the form,

$$I_1 = 2\pi \int_0^\infty \varphi_1(x)g_0(x)x^2 dx, \quad (8)$$

where $g_0(r/d; \rho_0^*)$ is a radial distribution function of the HS system; $x = r/\sigma$. The expression for $I_2(T^*, \rho^*)$ is more complicated and was presented in Ref. [14].

The integrals I_1 and I_2 for the MPT procedure are calculated and presented in the form of analytic expression $I_1 = T^*\chi_1[1]/\rho^*$, $I_2 = T^*\chi_2[1]/\rho^*$ in a wide region of states of the substances under study including gaseous and liquid nitrogen. Coefficients

a_{ik}, b_i, c_j of the $\chi_1[n]$ and $\chi_2[n]$ forms, determined according to

$$\chi_1[n] = \sum_{i,k} n\, a_{ik} (\rho^*)^{i+1} /(T^*)^{k+1},$$

$$\chi_2[n] = \sum_{i} b_i (\rho^*)^{i+1} \sum_{j} n\, c_j /(T^*)^{j+1}, \quad (9)$$

were presented in Ref. [11].

The thermodynamic properties of the fluids under study are obtained on the basis of surfaces of free energy $f(T, V)$ or $F(T, \rho)$ calculated according to Eq. (6), using standard thermodynamic relations. Further we shall deal with the mass density D, heat capacity C_p, and sound velocity V_s of gaseous and liquid nitrogen. In general, the calculations of C_p and V_s are a severe test for the theoretical models developed as they are described by second derivatives (and besides that, by the derivatives with respect to temperature) of the thermodynamic potentials – in our case, $F(T, \rho)$. Moreover, the sound velocity occupies a special position because it relates thermal (compressibility β_T) and caloric (C_p/C_v) properties.

The initial stage of calculations of the properties is the determination of the mass density D. In the single-phase region of states with T and p given, the density is determined from the numerical solution of the equation

$$p(T,D) - p = 0, \quad (10)$$

and for the two-phase region (for example, along the line of liquid-vapor equilibrium) – from the solution of the well-known set of equations for phase equilibrium [10]. In the latter case the dependencies $D_L(T)$ and $D_V(T)$ are determined for liquid (L) and vapor (V) phases along the line of the equilibrium, i.e., at the pressure of saturated vapor $p_s(T) = p(T, D_L) = p(T, D_V)$, which is determined according to (10).

The equation of state $p(T, D)$, the heat capacity C_p and the sound velocity V_s for the MPT procedure are as follows:

The pressure

$$p = \widetilde{P} T^* \rho^* \{1 + 2\eta \frac{2-\eta}{(1-\eta)^3} + \chi_1[i+1]\}. \quad (11)$$

The heat capacity

$$C_p = R\, c_p,$$

$$c_p = c_v + \rho^* T^* \beta_T^* \{1 + 2\eta \frac{2-\eta}{(1-\eta)^3} - \chi_1[(i+1)k]\}^2. \quad (12)$$

The sound velocity

$$V_s = (10^3 R E)^{1/2}\, v_s, \qquad v_s = [(c_p/c_v)/\rho^* \beta_T^*]^{1/2}. \quad (13)$$

In these expressions the reduced isothermal compressibility $\beta_T^* = \beta_T \widetilde{P}$ and heat capacity $c_v = C_v/R$ are equal to

$$\beta_T^* = \frac{1}{T^* \rho^*} \{1 + 2\eta \frac{4-\eta}{(1-\eta)^4} - \chi_1[(i+1)(i+2)]\}^{-1}, \quad (14)$$

$$c_v = c_p^0 - 1 - \chi_1[k(k+1)] - \chi_2[j(j+1)]. \quad (15)$$

Here $T^* = T/E$, $\rho^* = D/\widetilde{D}$, $\eta = (\pi \xi^3/6)\rho^*$, $\xi = 0.9274$ [10], c_p^0 is the heat capacity of the substance in the state of the ideal gas, M is the molar mass, N_A is Avogadro's number, R is the gas constant.

The parameters used above are defined as: $E = \varepsilon/k$, $\widetilde{D} = M/(N_A \sigma^3)$, $\widetilde{P} = R E \widetilde{D}$.

In the expressions (11) - (15) the properties are given in the following units:

p (MPa); D (kg/m^3); T (K);

C_p, C_v (kJ/(kg K)); V_s (m/s).

For nitrogen: $E = 97.55$ K, $\sigma = 3.5996 \cdot 10^{-10}$ m [11], $\widetilde{D} = 997.38$ kg/m^3, $\widetilde{P} = 28.877$ MPa, $R = 0.2968$ kJ/(kg K), $C_p^0 = (7/2)R$.
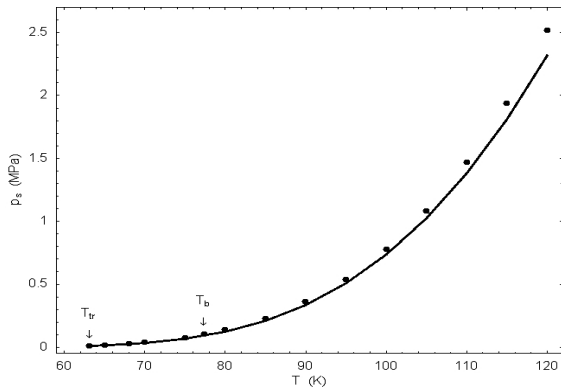
Fig. 2. The temperature dependence of the saturated vapor pressure of nitrogen: 1 - calculations from the MPT procedure according to (11); [15] - values based on experimental data.
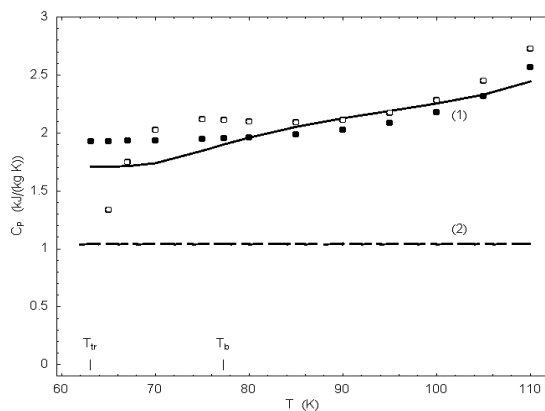

Fig. 3. The heat capacity Cp of liquid nitrogen along the line of liquid-vapor equilibrium: 1 - calculations from the MPT procedure according to (12); 2 - ideal gas [= 1.0388 kJ/(kg K)]; [15] and [16] - values based on experimental data

Fig. 4. The heat capacity Cp of nitrogen at 5 MPa pressure. Calculations from the MPT procedure according to (12): 1 - liquid phase, 2 - gaseous state. Values based on the experiments - [15].

3 - the ideal gas state.

Fig. 5. The sound velocity in gaseous and liquid nitrogen. The values Vs at the pressure p = 5 MPa:

1 - calculations from the MPT procedure according to (13); - experimental data extrapolation [15]. The values of Vs along the line of the liquid-vapor equilibrium:

2 - calculations from the MPT procedure; [16] - treatment of the experimental data.

Curve 3 corresponds to the ideal gas, in this case =20.384 T1/2 m/s from eq. (16).

The densities of nitrogen in the single-phase region calculated according to (10) are given in Table 1. The portion of data that are related to the liquid phase of N_2 are marked with an asterisk *. As the values of density obtained in practice reproduce the experimental data within the accuracy of the experiments (usually 0.1%) a question arises about the discrepancies in experimental data obtained by different authors. These discrepancies are due to systematic experimental errors. Further, we will compare the calculated values of the thermodynamic properties with the data given in Refs. [15,16], which are mainly the treatment and correlation of the most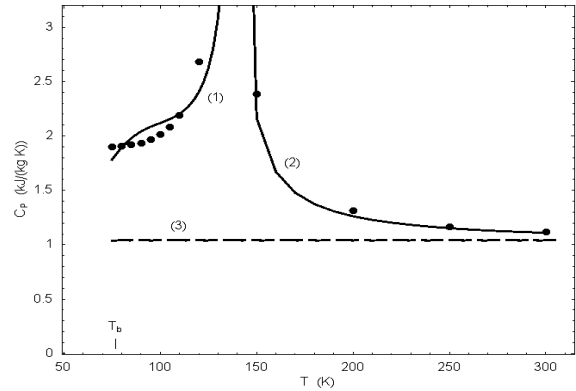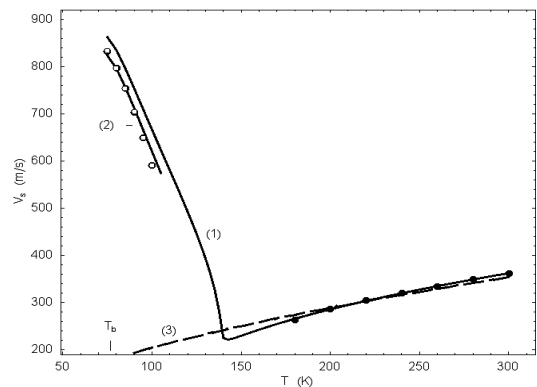 reliable experimental values. The comparison of the results for the density of nitrogen (Table 1) in the range of temperature from 80 to 300 K and pressure from 0.1 to 5 MPa with the results given in [16] shows that the average absolute magnitude of their differences for 132 density values is 0.12%. It is significant that the discrepancies of the different experimental data on the density of nitrogen are as much as 0.22% [11].

The calculations of saturated vapor pressure $p_s(T)$ according to the MPT procedure also agree very well with the experimental data as one can see in Fig. 2. It turns out, that very small deviations from the Clapeyron-Clausius equation is observed up to the temperature of 120 K.

The temperature dependencies of the heat capacity at constant pressure both for liquid N_2 along

the line of liquid-vapor equilibrium and for the 5 MPa isobar are presented in Figs. 3 and 4. It should be noted that in the liquid nitrogen region, in which we are interested, from the triple point $T_{tr} = 63.15$ K to the boiling point $T_b = 77.35$ K (at standard conditions), the differences based on the experimental results [15] and [16] are even more significant (one can say, unusually large). Besides that, as it is seen in the Figs. 3 and 4, the ideal gas approximation for the heat capacity C_p^0 is extremely poor at low temperatures as it gives the values of C_p about two times lower, and does not describe properly the observed temperature dependencies. One can see that peculiarities of the properties (more or less distinct peaks of $C_p(T)$) are observed when approaching the vicinity of the critical point ($T_c = 126.2$ K, $p_c = 3.40$ MPa, where $C_p(T_c, p_c) = \infty$) in the phase plane (T, p).

The ideal gas approximation for the sound velocity in liquid nitrogen is easily obtained according to (13):

$$V_s^0 = \sqrt{10^3 (c_p^0 / c_v^0)\, R\,T} \qquad \text{m/s,}$$

$$(16)$$

where $(c_p^0 / c_v^0) = 1.4$.

This approximation for sound velocity as opposed to the heat capacity, C_p, gives adequate values in the region of the gaseous state of N_2 not only at room temperatures (Fig. 4) but even at $T > 150$ K (Fig.5). The experimental data are presented in the Ref. [15] only for temperatures above 180 K. As in

Refs. [15,16] there are no data on the sound velocity in the liquid phase at the given pressure we also performed calculations of $V_s(T)$ along the line of equilibrium with the vapor phase, and compared them with the experimental ones. These data are shown in the Fig. 5. It can be seen that the ideal gas approximation $V_s^0(T)$ for the N_2 liquid phase is completely inapplicable.

IV. Conclusion

The results obtained show the possibility of a successful application of fully consistent statistical methods to the description of molecular systems in different phase states. Summarizing the main characteristics of the method for calculations of thermodynamic properties, one can note the minimal number of initial data necessary for calculations and the absence of fitting parameters. The adequacy of the physical model, that is the basis for the method, allows one to describe the existing peculiarities of the thermodynamic properties and to analyze factors responsible for causing of the peculiarities. Finally, it is necessary to point out the applicability of the calculation procedure proposed to a wide class of substances and their mixtures, the workability of the procedure in a wide region of states, and low level of errors for the thermodynamic characteristics under study.

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