

MOLAR HEAT CAPACITY UNDER CONSTANT VOLUME OF MOLECULAR CRYOCRYSTALS OF NITROGEN TYPE WITH HCP STRUCTURE: CONTRIBUTION FROM LATTICE VIBRATIONS AND MOLECULAR ROTATIONAL MOTION

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Abstract. *The analytic expression of molar heat capacity under constant volume of molecular cryocrystals of nitrogen type with hcp structure is obtained by the statistical moment method and the self-consistent field method taking account of the anharmonicity in lattice vibrations and molecular rotational motion. Numerical results for molecular cryocrystals of N_2 type ($\beta-N_2, \beta-CO$) are compared with experiments.*

I. INTRODUCTION

The study of heat capacity for molecular cryocrystals of nitrogen type is carried out experimentally and theoretically by many researchers. For example, the heat capacity of solid nitrogen is measured by Giaouque and Clayton [1], Bagatskii, Kucheryavy, Manzhelii and Popov [2]. The heat capacity of solid carbon monoxide is determined by Clayton and Giaouque [3], Gill and Morrison [4]. Theoretically, the heat capacity of solid nitrogen and carbon monoxide is investigated by the Debye heat capacity theory, the Einstein heat capacity theory, the self-consistent phonon method (SCPM), the self-consistent field method (SCFM), the pseudo-harmonic theory and the statistical moment method (SMM) [5, 6, 7]. In [5, 6] the heat capacities at constant volume and at constant pressure of $\beta-N_2$ and $\beta-CO$ crystals are calculated by SMM only taking account of lattice vibration and the obtained results only agreed qualitatively with experiments. The heat capacity at constant volume of crystals of N_2 type in pseudo-harmonic approximation is considered by SCFM only taking account of molecular rotations [8]. In this report we study the heat capacity at constant volume of $\alpha-N_2$ and $\alpha-CO$ crystals in pseudo-harmonic approximation by combining SMM and SCFM taking account of both lattice vibrations and molecular rotations. In section 2, we derive the heat capacity at constant volume for crystals with hcp structure taking into account lattice vibrations by SMM and for crystals of N_2 type taking into account molecular rotations by SCFM. Our calculated vibrational and rotational heat capacities for $\beta-N_2$ and $\beta-CO$ crystals are summarized and discussed in section 3.

II. THEORY

2.1. The heat capacity at constant volume of crystals with hcp structure by SMM.

The displacement of a particle from equilibrium position on direction x (or direction y) is given approximately [6] by:

$$u_{x0} \approx \sum_{i=1}^4 \left[\frac{\gamma\theta}{(k_x + k_{xy})^2} \right]^i a_i,$$

where:

$$\begin{aligned} a_1 &= \frac{k_{xy}}{k_x} (1 - X) - X, a_2 = \frac{3\gamma}{k_x} a_1 \left(X + \frac{2k_x - k_{xy}}{k_x + k_{xy}} \right), a_3 = \frac{18\gamma^2}{k_x (k_x + k_{xy})} a_1^2 \left(2X - \frac{3k_x + 2k_{xy}}{k_x + k_{xy}} \right), \\ a_4 &= -\frac{108\gamma^3}{k_x (k_x + k_{xy})^2} a_1^3 (X - 1), X \equiv x \coth x, \theta = k_B T, k_x \equiv \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{ix}^2} \right)_{eq} \equiv m\omega_x^2, x = \frac{\hbar\omega_x}{2\theta}, \\ k_{xy} &\equiv \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{ix} \partial u_{iy}} \right)_{eq}, \gamma \equiv \frac{1}{4} \sum_i \left[\left(\frac{\partial^3 \varphi_{i0}}{\partial u_{ix}^3} \right)_{eq} + \left(\frac{\partial^3 \varphi_{i0}}{\partial u_{ix} \partial u_{iy}^2} \right)_{eq} \right], \end{aligned} \quad (1)$$

Here k_B is the Boltzmann constant, T is the absolute temperature, m is the mass of particle at lattice node, ω_x is the frequency of lattice vibration on direction x (or y), k_x, k_{xy} and γ are the parameters of crystal depending on the structure of crystal lattice and the interaction potential between particles at nodes, φ_{i0} is the interaction potential between the i th particle and the 0th particle and $u_{i\alpha}$ is the displacement of i th particle from equilibrium position on direction α ($\alpha = x, y, z$).

The lattice constant on direction x (or y) is determined by $a = a_0 + u_{x0}$, where a_0 is the distance a at temperature 0K and is determined from experiments.

The displacement of a particle from equilibrium position on direction z approximately is as follows [6]:

$$\begin{aligned} u_{z0} &\approx \left[\frac{1}{3} \sum_{i=1}^6 \left(\frac{\theta}{k_z} \right)^i b_i \right]^{1/2}, \text{ where :} \\ b_1 &= \frac{\tau_2 + \tau_3}{k_z} u_{x0}^2, b_2 = \frac{\tau_1}{k_z} + (1 - b_1) C, b_3 = - \left[\frac{\tau_1}{k_z} C + (1 - b_1) C^2 \right], b_4 = \frac{\tau_1}{k_z} C^2 + (1 - b_1) C^3, \\ b_5 &= - \left[\frac{\tau_1}{k_z} C^3 + (1 - b_1) C^4 \right], b_6 = \frac{\tau_1}{k_z} C^4 + C^5, C \equiv \frac{\tau_1}{k_z} (X_z + 1) + \frac{\tau_2}{3k_x} (X + 2), X \equiv x \coth x, \\ X_z &\equiv x_z \coth x_z, k_z \equiv \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{iz}^2} \right)_{eq} = m\omega_z^2, x_z = \frac{\hbar\omega_z}{2\theta}, \end{aligned}$$

$$\tau_1 \equiv \frac{1}{12} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{iz}^4} \right)_{eq}, \tau_2 \equiv \frac{1}{2} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{ix}^2 \partial u_{iz}^2} \right)_{eq}, \tau_3 \equiv \frac{1}{2} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{ix} \partial u_{iy} \partial u_{iz}^2} \right)_{eq}, \quad (2)$$

Here ω_z is the frequency of lattice vibration on direction z and k_z, τ_1, τ_2 and τ_3 also are the parameters of crystal.

The lattice constant on direction z is determined by $c = c_0 + u_{z0}$, where c_0 is the distance c at temperature 0K and is determined from experiments.

The free energy of crystals with hcp structure has the form [6]:

$$\begin{aligned} \psi \approx & U_0 + \psi_0 + \frac{N\theta^2 k_{xy} \gamma^2}{k_x^3 (k_x + k_{xy})} \left[X^2 - \frac{k_{xy}}{k_x + k_{xy}} X - \frac{k_x (k_x + 2k_{xy})}{3(k_x + k_{xy})^2} - \frac{1}{3} \right] + \\ & + \frac{N\theta^2}{4k_z} \left[\frac{\tau_1}{k_z} (X_z + 2) + \frac{\tau_2}{3k_x} (X + X_z + 4) + \frac{6\tau_5 + \tau_6}{3k_z} (X + 2) \right] + \\ & + \frac{N\theta^3}{12} \left\{ \frac{X_z + 5}{k_z} \left[\frac{\tau_1^3}{3k_z^4} (X_z + 1) + \frac{(\tau_2 + \tau_3)\gamma^2}{k_x^4} X^2 \right] + \frac{X + 5}{k_x^2} \left[\frac{\tau_2^2}{18k_z^2} (X + 2) + \frac{(2\tau_4 + 6\tau_5 + \tau_6)\gamma^2}{k_x^3} X^2 \right] \right\} + \\ & + \frac{N\theta^4}{12} \left\{ \frac{\tau_1^5}{15k_z^8} (X_z + 1)^2 + \frac{\tau_2^2 \gamma^2}{3k_x^5 k_z^2} [X^2 (X + 2) + \frac{X + 5}{2}] + \frac{(4\tau_4 + 6\tau_5 + 3\tau_6)\gamma^4}{k_x^8} X^4 \right\} + \\ & + \frac{N\theta^5 \gamma^2}{12k_x^6 k_z^2} X^2 \left\{ \frac{\tau_2^2}{3} \left[\frac{3\gamma^2}{k_x^2} - \frac{\tau_2}{9k_z} (X + 2)(X + 5) \right] + \frac{\tau_2^2 \gamma^2}{k_x^2} X^2 \right\} - \frac{N\theta^6 \tau_2^3 \gamma^4}{54k_x^9 k_z^3} X^4 (X + 2), \\ \tau_4 \equiv & \frac{1}{2} \sum_i \left(\frac{\partial^4 \phi_{i0}}{\partial u_{ix}^3 \partial u_{iy}} \right)_{eq}, \tau_5 \equiv \frac{1}{12} \sum_i \left(\frac{\partial^4 \phi_{i0}}{\partial u_{ix}^4} \right)_{eq}, \tau_6 \equiv \frac{1}{2} \sum_i \left(\frac{\partial^4 \phi_{i0}}{\partial u_{ix}^2 \partial u_{iy}^2} \right)_{eq}, \end{aligned}$$

where:

$$U_0 = \frac{N}{2} \sum_i \phi_{i0}, \psi_0 = N\theta \{ 2[x + \ln(1 - e^{-2x})] + [x_z + \ln(1 - e^{-2x_z})] \}. \quad (3)$$

Applying the Gibbs-Helmholtz relation and using (3), we find the expression for the energy of crystal

$$\begin{aligned} E \approx & U_0 + E_0 + \frac{N\theta^2}{12} \left[\left\{ \frac{4k_{xy} \gamma^2}{k_x^3 (k_x + k_{xy})} 1 + \frac{k_x (k_x + 2k_{xy})}{(k_x + k_{xy})^2} + \frac{3k_{xy}}{k_x + k_{xy}} Y^2 + 3X (X - 2Y^2) \right\} - \right. \\ & - \left. \frac{6\tau_5 + \tau_6}{k_x^2} (2 + Y^2) - \frac{3\tau_1}{k_z^2} (2 + Y_z^2) - \frac{\tau_2}{k_x k_z} (2 + Y^2 + Y_z^2) \right] - \\ & - \frac{N\theta^3}{12} \left\{ \frac{2\tau_1^3}{3k_z^5} (3X_z + X_z Y_z^2 + 3Y_z^2 + 5) + \frac{(\tau_2 + \tau_3)\gamma^2}{k_x^4 k_z^2} X [X (-X_z + Y_z^2) + Y^2 (X - 2Y^2)] + \right. \\ & \left. + \frac{\tau_2^2}{18k_x^2 k_z^2} (7X + 2XY^2 + 7Y^2 + 20) + \frac{2\tau_4 + 6\tau_5 + \tau_6}{k_x^5} X (-X^2 + 3XY^2 + 10Y^2) \right\}, \end{aligned}$$

where:

$$E_0 = N\theta (2X + X_z), Y \equiv \frac{x}{\sinh x}, Y_z \equiv \frac{x_z}{\sinh x_z}. \quad (4)$$

The vibrational molar heat capacity at constant volume is determined by [6]:

$$\begin{aligned} C_V^{vib} \approx & Nk_B \left\{ 2Y^2 + Y_z^2 + \frac{k_{xy} \gamma^2 \theta}{k_x^3 (k_x + k_{xy})} \left[\frac{2}{3} + \frac{2k_x (k_x + 2k_{xy})}{3(k_x + k_{xy})^2} + \left(\frac{2k_{xy}}{k_x + k_{xy}} - 5 \right) XY^2 - Y^2 (Y^2 - 3X^2) \right] - \right. \\ & \left. - \frac{\theta}{6} \left[\frac{6\tau_5 + \tau_6}{k_x^2} (2 + XY^2) + \frac{3\tau_1}{k_z^2} (2 + X_z Y_z^2) + \frac{\tau_2}{k_x k_z} (4 + XY^2 + X_z Y_z^2) \right] \right\} \quad (5) \end{aligned}$$

2.2. The heat capacity at constant volume of crystals with hcp structure by SCFM.

Using SCFM, only taking account of molecular rotation, the rotational free energy of crystals with fcc and hcp structures in pseudo-harmonic approximation (when $U_0\eta/B \gg 1$ or $T/\sqrt{U_0 B \eta} \ll 1$) is determined by [7]:

$$\frac{\psi_{rot}}{k_B N} = 2T \ln \left[4 \sinh \left(\frac{\varepsilon}{2T} \right) \right] - U_0 \eta + \frac{U_0 \eta^2}{2}, \varepsilon = \sqrt{6U_0 B \eta}, \quad (6)$$

where U_0 is the barrier, which prevents the molecular rotation at $T = 0$ K, $B = \hbar^2/(2I)$ is the intrinsic rotational temperature or the rotational quantum or the rotational constant.

The rotational molar heat capacity at constant volume in pseudo-harmonic approximation is determined by the following expression [7]:

$$C_V^{rot} = -T \left(\frac{\partial^2 \psi_{rot}}{\partial T^2} \right)_V = \frac{Nk_b}{2} \frac{(\varepsilon/T)^2}{\sinh^2(\varepsilon/2T)} \left(1 - \frac{T}{\varepsilon} \frac{\partial \varepsilon}{\partial T} \right). \quad (7)$$

The total molar heat capacity at constant volume in pseudo-harmonic approximation is determined by the following expression:

$$C_V = C_V^{vib} + C_V^{rot} = -T \left(\frac{\partial^2 \psi}{\partial T^2} \right)_V = -T \left(\frac{\partial^2 \psi_{vib}}{\partial T^2} \right)_V - T \left(\frac{\partial^2 \psi_{rot}}{\partial T^2} \right)_V. \quad (8)$$

III. NUMERICAL RESULTS AND DISCUSSION

In order to apply the theoretical results in Section 2 to molecular cryocrystals of nitrogen type, we use the Lennard-Jones (LJ) potential

$$\varphi(r) = 4\varepsilon_1 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (9)$$

where $\varepsilon_1/k_B = 95.1$ K, $\sigma = 3.708 \cdot 10^{-10}$ m for β -N₂; $\varepsilon_1/k_B = 100.1$ K, $\sigma = 3.769 \cdot 10^{-10}$ m for β -CO [6]. In the approximation of two first coordination spheres, the crystal parameters are given by [6]:

$$\begin{aligned} k_x &= \frac{4\varepsilon_1}{a^2} \left(\frac{\sigma}{a} \right)^6 \left[384.711 \left(\frac{\sigma}{a} \right)^6 - 95.9247 \right], k_{xy} = \frac{4\varepsilon_1}{a^2} \left(\frac{\sigma}{a} \right)^6 \left[229.8912 \left(\frac{\sigma}{a} \right)^6 - 66.9288 \right], \\ k_z &= \frac{4\varepsilon_1}{a^2} \left(\frac{\sigma}{a} \right)^6 \left[286.3722 \left(\frac{\sigma}{a} \right)^6 - 64.7487 \right], \gamma = -\frac{4\varepsilon_1}{a^3} \left(\frac{\sigma}{a} \right)^6 \left[161.952 \left(\frac{\sigma}{a} \right)^6 - 24.984 \right], \\ \tau_1 &= \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[6288.912 \left(\frac{\sigma}{a} \right)^6 - 473.6748 \right], \tau_2 = \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[11488.3776 \left(\frac{\sigma}{a} \right)^6 - 752.5176 \right], \\ \tau_3 &= \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[8133.888 \left(\frac{\sigma}{a} \right)^6 - 737.352 \right], \tau_4 = \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[43409.3184 \left(\frac{\sigma}{a} \right)^6 - 4550.04 \right], \\ \tau_5 &= \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[11315.6064 \left(\frac{\sigma}{a} \right)^6 - 1006.0428 \right], \tau_6 = \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[40782.6048 \left(\frac{\sigma}{a} \right)^6 - 4189.6536 \right], \end{aligned} \quad (10)$$

where a is the nearest neighbour distance (or the lattice constant on direction x or y) at temperature T . The LJ potential has a minimum value corresponding to the position $r_0 = \sigma \sqrt[6]{2} \approx 1.2225\sigma$. However, since there is interaction of many particles, the nearest neighbour distance a_0 in the lattice is smaller than r_0 . It is equal to $a_0 = r_0 \sqrt[6]{A_{12}/A_6} \approx 1.0865\sigma$, where A_6 and A_{12} are the structural sums and they have the values $A_6 = 14.1601$, $A_{12} = 11.648$ for a hcp crystal [6]. From the above mentioned results, we obtain the values of crystal parameters at 0 K. From that, we calculate the nearest neighbour distances of the lattice, the vibrational molar heat capacities at constant volume in different temperatures by SMM as in [5, 6]. The values of B , U_0 and the values of η at various temperatures are given in Tables 1, 2 and 3. Our calculated results for the lattice constant a and the molar heat capacities C_V^{vib} , C_V^{rot} , C_V for β -N₂ and β -CO crystals are shown in Figures 1-3. In comparison with experiments, the heat capacity

calculated by both SMM and SCFM is better than the heat capacity calculated by only SMM or only SCFM. Both the lattice vibration and the molecular rotation have important contributions to thermodynamic properties of molecular cryocrystals of nitrogen type.

Table 1. Values of B and U_0 for β -N₂ and β -CO crystals

Crystal	β -N ₂	β -CO
B (K)	2.8751	2.7787
U_0 (K)	325.6	688.2

Table 2. Values of η at various temperatures for β -N₂ crystal

T (K)	36	38	40	42	44	45.354
η	0.8633	0.8617	0.8544	0.8404	0.8244	0.8038

Table 3. Values of η at various temperatures for β -CO crystal

T (K)	62	64	66	68
η	0.9100	0.9099	0.9060	0.8942

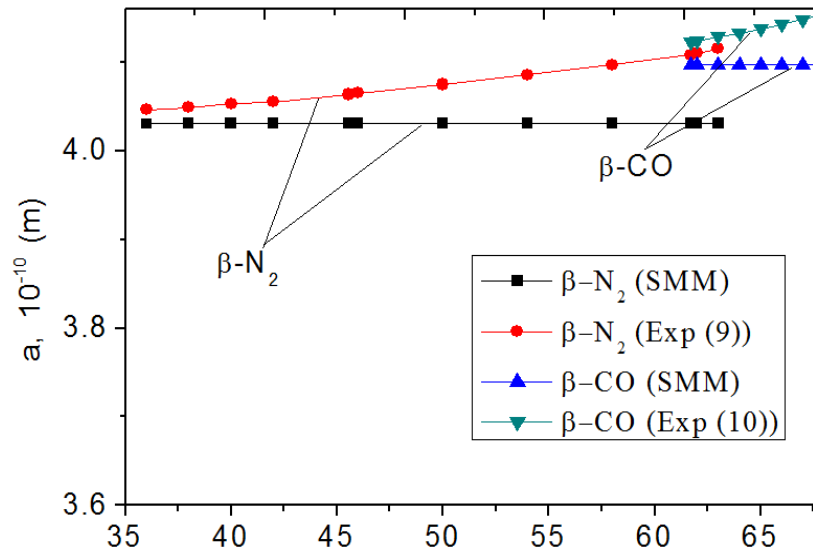


Figure 1. Nearest neighbour distances a at various temperatures for β -N₂ and β -CO crystals

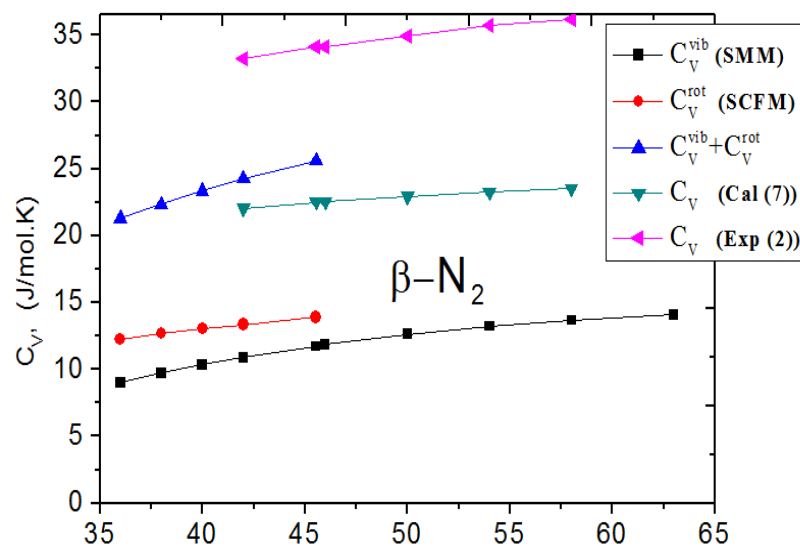


Figure 2. Heat capacities at constant volume C_V^{vib} , C_V^{rot} , C_V in different temperatures for β -N₂ crystal

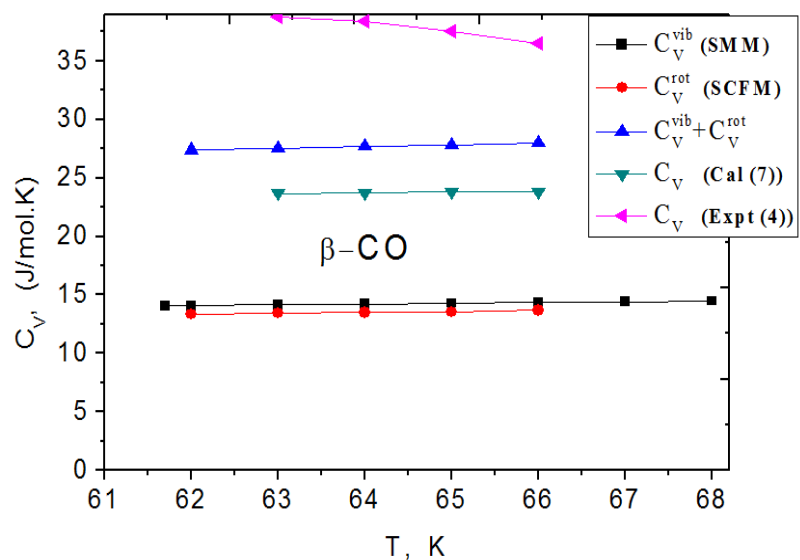


Figure 3. Heat capacities at constant volume C_V^{vib} , C_V^{rot} , C_V in different temperatures for β -CO crystal

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