ANALYTIC EXPRESSION OF THERMODYNAMIC QUANTITIES FOR MOLECULAR CRYOCRYSTALS OF NITROGEN TYPE WITH FCC AND HCP STRUCTURES IN HARMONIC, CLASSICAL AND ANHARMONIC APPROXIMATIONS

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Abstract. The analytic expressions of thermodynamic quantities such as the Helmholtz free energy, the internal energy, the entropy, the molar heat capacity at constant volume for molecular cryocrystals of N\textsubscript{2} type with face-centered cubic (FCC) and hexagonal close-packed (HCP) structures in harmonic, classical and anharmonic approximations are obtained by combining the statistical moment method (SMM) and the self-consistent field method (SCFM).

Keywords: Statistical moment method, self-consistent field method, cryocrystal.

1. Introduction

Molecular crystals, comprising a vast and comparatively little investigated class of solids, are characterized by a diversity of properties. Up to now only solidified noble gases have systematically been investigated and this is due to the availability of relevant theoretical models and the ease of comparing theories with experimental results. Recently, experimental data have been obtained for simple non-monoatomic molecular crystals as well, and this in turn has stimulated the appearance of several theoretical papers on that subject.

This paper deals with the analysis of thermodynamic properties of the group of non-monoatomic molecular crystals including solid N\textsubscript{2} and CO that have similar physical properties. These crystals are formed by linear molecules and in their ordered phase, the molecular centers of mass are situated at the site of a face-centered cubic (FCC) pattern, the molecular axes being directed to the four spatial diagonals of a cube (space group Pa3). The characteristic feature of the intermolecular interaction in such crystals is that the non-central part of the potential results from quadrupole forces and from the part of valence and dispersion forces having analogous angular dependence as quadrupole forces, and further, that dipole interaction either does not exist (N\textsubscript{2}) or is negligible (CO) to influence the majority of thermodynamic properties. In addition, all crystals considered have a common feature, namely their intrinsic rotational temperatures \( B = \hbar^2/(2I) \) (\( I \) is the momentum of inertia of the corresponding molecule) are small compared to the energy of non-central interaction.
In the low-temperature range, it is reasonable to apply an assumption successfully used by the authors [1, 2] that translational motions of the molecular system are independent. As shown [3] there are two types of excitations in molecular crystals - phonons and librons and, furthermore, the thermodynamic functions can be written as a sum of two independent terms corresponding to each subsystem. In such a treatment, the translational–orientational interaction leads to a renormalization of the sound velocity and of the libron dispersion law only.

The investigation of the librational behavior of molecules is usually carried out within the framework of the harmonic approximation. However, anharmonic effects for the thermodynamic properties are essential at temperatures substantially lower than the orientational disordering temperature. The effect of molecular rotations in N\(_2\) and CO crystals not restricted by the assumption of harmonicity of oscillations has been calculated numerically in the molecular field approximation by Kohin [4]. Full calculations on thermodynamic properties of molecular crystals of nitrogen type are given by the statistical moment method (SMM) in [5] and by self-consistent field method (SCFM) in [6]. This paper represents the analytic expressions of thermodynamic quantities for molecular cryocrystals of nitrogen type with FCC and hexagonal close-packed (HCP) structures such as the free energy, the energy, the entropy and the heat capacity at constant volume in harmonic, classical and anharmonic approximations.

2. Content

2.1. Analytic expression of thermodynamic quantities for crystals of N\(_2\) type from the combination of SMM and SCFM

2.1.1. Free energy

By combining the SMM and the SCFM, the free energy of molecular crystals of N\(_2\) type with FCC and HCP structures is the sum of the vibrational free energy and the rotational free energy. In harmonic approximation (harmonic approximation of lattice vibration and pseudo-harmonic approximation of molecular rotational motion) for FCC crystal [6, 7],

\[
\psi_{\text{fcc, har}} = \psi_{\text{vib, fcc, har}} + \psi_{\text{rot, fcc, har}},
\]

\[
\psi_{\text{vib, fcc}} = V_{0}^{\text{fcc}} + \psi_{0, \text{vib}} + 3N\theta \left[ x^{\text{fcc}} + \ln(1 - e^{-2x^{\text{fcc}}}) \right],
\]

\[
\psi_{\text{rot, fcc}} = k_B N \left\{ 2T \ln \left[ 4 \sinh \left( \frac{\xi}{2T} \right) \right] - U_0 \eta + \frac{U_0 \eta^2}{2} \right\},
\]

\[
k_{\text{fcc}} = \frac{1}{2} \sum_i \left( \frac{\partial^2 \varphi_{i0}}{\partial u_{i\alpha}^2} \right)_{eq} \equiv m\omega_{\text{fcc}, \alpha}^2, \alpha = x, y, z, x = \frac{\hbar \omega_{\text{fcc}}^2}{2\theta}, \theta = k_B T, V_{0}^{\text{fcc}} = \frac{N}{2} \sum_i \varphi_{i0}
\]

for the HCP crystal [7, 8],

\[
\psi_{\text{hcp, har}} = \psi_{\text{vib, hcp, har}} + \psi_{\text{rot, hcp, har}},
\]

\[
\psi_{\text{vib, hcp}} = V_{0}^{\text{hcp}} + \psi_{0, \text{vib}} + 2N\theta \left[ x^{\text{hcp}} + \ln \left( 1 - e^{-2x^{\text{hcp}}} \right) \right] + N\theta \left[ x_{z}^{\text{hcp}} + \ln \left( 1 - e^{-2x_{z}^{\text{hcp}}} \right) \right],
\]

\[
k_{\text{hcp}} = \frac{1}{2} \sum_i \left( \frac{\partial^2 \varphi_{i0}}{\partial u_{ix}^2} + \frac{\partial^2 \varphi_{i0}}{\partial u_{iz} \partial u_{iy}} \right)_{eq} \equiv m\omega_{\text{hcp}, x}^2, x^{\text{hcp}} = \frac{\hbar \omega_{\text{hcp}}^2}{2\theta}, V_{0}^{\text{hcp}} = \frac{N}{2} \sum_i \varphi_{i0},
\]
In classical approximation for FCC crystal [6, 7],

\[
\psi_{fcc,cla} = \psi_{fcc,cla}^{vib} + \psi_{rot}^{vib},
\]

\[
\psi_{fcc,cla}^{vib} \approx V_0^{fcc} + \psi_{0vib}^{fcc} + 3N \left\{ \frac{\hbar^2}{k_{f,c}^2} \left( \gamma_2^{fcc} - \gamma_1^{fcc} \right) \right. \\
\left. + \frac{4\theta^3}{k_{f,c}^4} \left[ \gamma_2^{fcc} - 3 \left( \gamma_1^{fcc} + 2 \gamma_1^{fcc} \gamma_2^{fcc} \right) \right] \right\},
\]

\[
\psi_{fcc} = N\theta \left[ x^{fcc} + \ln(1 - e^{-2x^{fcc}}) \right],
\]

\[
x^{fcc} \approx 0.283, \quad \psi_{rot}^{fcc} - \psi_{rot}^{fcc} = -U_0\eta + \frac{U_0\eta^2}{2} + 2T \ln \left( \frac{\sqrt{6BU_0\eta}}{T} \right),
\]

\[
\gamma_1^{fcc} = \frac{1}{48} \sum_i \left( \frac{\partial^4 \psi_{0i}^{f1}}{\partial u_{i\alpha}^2} \right)_{eq}, \quad \gamma_2^{fcc} = \frac{1}{8} \sum_i \left( \frac{\partial^4 \psi_{0i}^{f1}}{\partial u_{i\alpha}^2 \partial u_{i\beta}} \right)_{eq}, \quad \alpha \neq \beta, \alpha, \beta = x, y, z
\] (2.3)

and for HCP crystal [7, 8],

\[
\psi_{hcp,cla}^{vib} = \psi_{hcp,cla}^{vib} + \psi_{rot}^{vib}, \quad \psi_{hcp,cla}^{vib} = V_0^{hcp} + \psi_{0vib}^{hcp},
\]

\[
+ \frac{N\theta^4}{4} \left[ \frac{6\tau_5^{hcp}}{k_x^{hcp^2}} + \frac{3\tau_1^{hcp}}{k_x^{hcp^2}} + \frac{2\tau_2^{hcp}}{k_x^{hcp^2}} \right] + \frac{3N\theta^3}{4k_x^{hcp^2}} \left[ \frac{\tau_1^{hcp}}{k_x^{hcp^2}} + \frac{\tau_2^{hcp}}{9k_x^{hcp^2}} \right] \\
- \frac{N\theta^4}{36k_x^{hcp^3}} \left[ \frac{33\tau_1^{hcp}}{k_x^{hcp^3}} + \frac{2\tau_2^{hcp}}{k_x^{hcp^3}} \right],
\]

\[
k_x \equiv \frac{1}{2} \sum_i \left( \frac{\partial^2 \psi_{0i}}{\partial u_{iz}^2} \right)_{eq}, \quad \tau_1 \equiv \frac{1}{12} \sum_i \left( \frac{\partial^4 \psi_{0i}^{f1}}{\partial u_{iz}^4} \right)_{eq}, \quad \tau_2 \equiv \frac{1}{2} \sum_i \left( \frac{\partial^4 \psi_{0i}^{f1}}{\partial u_{ix}^2 \partial u_{iz}^2} \right)_{eq},
\]

\[
\tau_5 \equiv \frac{1}{12} \sum_i \left( \frac{\partial^4 \psi_{0i}^{f1}}{\partial u_{ix}^4} \right)_{eq}, \quad \tau_6 \equiv \frac{1}{2} \sum_i \left( \frac{\partial^4 \psi_{0i}^{f1}}{\partial u_{ix}^2 \partial u_{iz}^2} \right)_{eq}.
\] (2.4)

In anharmonic approximation (anharmonic approximation of lattice vibration and self-consistent libron approximation of molecular rotational motion) for FCC crystal [6, 7],

\[
\psi_{fcc,anh} = \psi_{vib}^{fcc,anh} + \psi_{rot}^{fcc,anh},
\]

\[
\psi_{vib}^{fcc,anh} = V_0^{fcc} + \psi_{0vib}^{fcc} + 3N \left\{ \frac{\hbar^2}{k_{f,c}^2} \left[ \frac{\gamma_2^{fcc}}{X^{fcc}} - \frac{2\gamma_1^{fcc}}{3} \left( 1 + \frac{X^{fcc}}{2} \right) \right] \right. \\
+ \frac{2\theta^3}{k_{f,c}^4} \left[ \frac{4}{3} \gamma_2^{fcc} X^{fcc} \left( 1 + \frac{X^{fcc}}{2} \right) - 2 \left( \gamma_1^{fcc} + 2 \gamma_1^{fcc} \gamma_2^{fcc} \right) \left( 1 + \frac{X^{fcc}}{2} \right) \left( 1 + X^{fcc} \right) \right] \right\},
\]

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\[
\frac{\psi_{\text{anh}}}{k_B N} = 2T \ln \left[ 4 \sinh \frac{\xi}{2T} \right] - \frac{\xi}{2} \coth^2 \frac{\xi}{2T} \frac{B}{2} - \frac{U_0 \eta^2}{2} \tag{2.5}
\]

and for HCP crystal [7, 8],

\[
\psi_{\text{hcp,anh}} = \psi_{\text{eib}}^{\text{hcp}} + \psi_{\text{rot}}^{\text{hcp}},
\]

\[
\psi_{\text{eib}}^{\text{hcp}} = V_0^{\text{hcp}} + \psi_{00b}^{\text{hcp}} + \frac{N \theta^2}{12} \left[ \frac{6 \tau_5^{\text{hcp}} + \tau_6^{\text{hcp}}}{k_x^{\text{hcp}2}} (X^{\text{hcp}} + 2) + \frac{3 \tau_4^{\text{hcp}}}{k_z^{\text{hcp}2}} (X_z^{\text{hcp}} + 2) \right] + \frac{N \theta^3}{24k_z^{\text{hcp}2}} \left[ \frac{\tau_1^{\text{hcp}}}{k_z^{\text{hcp}3}} (X_z^{\text{hcp}} + 2) (X_z^{\text{hcp}} + 5) \right]
\]

\[
+ \frac{\tau_2^{\text{hcp}}}{9k_x^{\text{hcp}2}} \left( X^{\text{hcp}} + 2 \right) \left( X^{\text{hcp}} + 5 \right) \right] - \frac{N \theta^4}{108k_z^{\text{hcp}3}} \left[ \frac{\tau_3^{\text{hcp}}}{k_z^{\text{hcp}3}} (X_z^{\text{hcp}} + 2) (3X_z^{\text{hcp}} + 17X_z^{\text{hcp}} + 13) \right]
\]

\[
+ \frac{\tau_2^{\text{hcp}}}{9k_x^{\text{hcp}3}} \left( X^{\text{hcp}} + 2 \right)^2 (X^{\text{hcp}} + 5) \right],
\]

\[
X^{\text{hcp}} \equiv x^{\text{hcp}} \coth x^{\text{hcp}}, X_z^{\text{hcp}} \equiv x_z^{\text{hcp}} \coth x_z^{\text{hcp}}. \tag{2.6}
\]

In above mentioned expressions, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( m \) is the mass of particle at lattice node, \( \omega^{\text{fcc}}, \omega^{\text{hcp}}, \omega^{\text{hcp}} \) are the frequencies of lattice vibration, \( k^{\text{fcc}}, \gamma_1^{\text{fcc}}, \gamma_2^{\text{fcc}}, k_x^{\text{hcp}}, k_z^{\text{hcp}}, \gamma_1^{\text{hcp}}, \gamma_2^{\text{hcp}}, \gamma_5^{\text{hcp}}, \gamma_6^{\text{hcp}} \) are the parameters of FCC and HCP crystals depending on the structure of crystal lattice and the interaction potential between particles at nodes, \( \varphi_0 \) is the interaction potential between the \( i \)th particle and the \( 0 \)th particle, \( u_{\text{eq}} \) is the displacement of the \( i \)th particle from equilibrium position in direction \( \alpha \) and \( N \) is the number of particles per mole or the Avogadro number, \( U_0 \) 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, \( \xi \) is the energy of rotational excitation and \( \eta \) is the ordered parameter.

In the harmonic, classical and anharmonic approximations, the rotational free energy, the rotational energy, the rotational entropy and the rotational heat capacity at constant volume of HCP crystal are identical to that of FCC crystal. This is a common property of crystals of nitrogen type [7].

In the harmonic approximation of lattice vibration, the quantities such as \( V_0^{\text{fcc}}, V_0^{\text{hcp}}, k^{\text{fcc}}, k_x^{\text{hcp}}, k_z^{\text{hcp}} \) are expressed in terms of the nearest neighbor distance \( a_0 \) at 0 K. The pseudo-harmonic approximation of molecular rotational motion corresponds to the condition \( \frac{T}{\sqrt{U_0 B \eta}} << 1 \) [7].

In the classical approximation of lattice vibration, \( x e^h x \equiv X = 1, x_z e^h x_z = X_z = 1 \) or \( x = x_z \approx 0.283 \). Then the formulae of \( \psi, E, S, C_V \) obtained in anharmonic approximation
give the classical results. From that we can determine the temperature \( T_{\text{lim}} \approx 1.3494.10^{-11} \) corresponding to that where the quantum effects can be neglected [6]. The classical approximation of molecular rotational motion corresponds to the condition \( \frac{T}{\sqrt{\omega \theta}} >> 1 \) [7].

In the anharmonic approximation of lattice vibration, the quantities such as \( k_{\text{fcc}}, \gamma_{\text{fcc}}, k_{\text{hcp}}, \gamma_{\text{hcp}}, k_{x}, \gamma_{x}, k_{z}, \gamma_{z}, k_{6}, \gamma_{6} \) are expressed in terms of the nearest neighbor distance \( a_{i}^{\text{fcc}} = a_{0}^{\text{fcc}} + u_{x0}^{\text{fcc}}, a_{i}^{\text{hcp}} = a_{0}^{\text{hcp}} + u_{x0}^{\text{hcp}} \), where \( a_{0}^{\text{fcc}}, a_{0}^{\text{hcp}} \) respectively are the nearest neighbor distance of FCC and HCP crystals at 0 K and the displacements \( u_{x0}, u_{x0} \) of a particle from the equilibrium position are calculated by

\[
u_{x0}^{c} = \sqrt{\frac{2g_{x}^{2}}{3K^{2}}} A_{i}^{c}, \quad \gamma_{c}^{c} = \frac{1}{12} \sum_{i} \left[ \left( \frac{\partial^{4} \varphi_{ij}}{\partial u_{i}^{4}} \right)_{\text{eq}} + 6 \left( \frac{\partial^{4} \varphi_{ij}}{\partial u_{i}^{2} \partial u_{j}^{2}} \right)_{\text{eq}} \right], \quad \beta \neq \gamma, \beta, \gamma = x, y, z,
\]

\[
A = a_{1} + \sum_{i=2}^{6} \left( \frac{g_{c}^{2}}{K^{2}} \right)^{i} a_{i}^{c}, \quad u_{x0}^{c} = \sum_{i=1}^{6} \left[ \gamma_{c}^{c} \left( \frac{g_{c}^{2}}{K^{2}} \right)^{i} \right] a_{i}^{c},
\]

\[
\gamma_{c}^{c} = \frac{1}{4} \sum_{i} \left[ \frac{\partial^{3} \varphi_{ij}}{\partial u_{i}^{3}} \right]_{\text{eq}} + \left( \frac{\partial^{3} \varphi_{ij}}{\partial u_{i} \partial u_{j}^{2}} \right)_{\text{eq}},
\]

(2.7)

where \( a_{i}^{c}, a_{i}^{c} \) \( (i = 1 - 6) \) are determined in [8]. The anharmonic approximation of molecular rotational motion corresponds to the condition \( \frac{T}{\sqrt{\omega \theta}} \approx 1 \) [7].

2.1.2. Energy

The energy of molecular crystals of \( N_{2} \) type with FCC and HCP structures is the sum of the vibrational energy and the rotational energy. In harmonic approximation for FCC crystal [6, 7],

\[
E_{\text{vib},\text{har}} = \psi_{\text{vib},\text{har}} - T \left( \frac{\partial \psi_{\text{vib},\text{har}}}{\partial T} \right)_{V} = E_{\text{vib}} + E_{\text{har}},
\]

\[
E_{\text{vib}} = V_{0}^{\text{fcc}} + E_{0\text{vib}}^{\text{fcc}} = V_{0}^{\text{fcc}} + 3N \theta X_{\text{fcc}},
\]

\[
E_{\text{rot}} = -N k_{B} U_{0} \left[ 1 - \frac{3B}{\xi} \coth \frac{\xi}{2T} \right] + \frac{N k_{B} U_{0}}{2} \left[ 1 - \frac{3B}{\xi} \coth \frac{\xi}{2T} \right]^{2}
\]

\[
- Nk_{B} \left( T \frac{\partial \xi}{\partial T} - \xi \right) \coth \frac{\xi}{2T}
\]

\[
+ \frac{3N k_{B} U_{0} B T}{2 \xi^{2}} \left[ 1 + \frac{3B}{\xi} \coth \frac{\xi}{2T} \right] \left\{ \frac{\xi}{2T^{2}} \left( T \frac{\partial \xi}{\partial T} - \xi \right) \left[ 1 - \coth^{2} \frac{\xi}{2T} \right] - \frac{\xi}{2T} \coth \frac{\xi}{2T} \right\}
\]

and for HCP crystal [7, 8],

\[
E_{\text{har}} = E_{\text{vib}} + E_{\text{rot}}, \quad E_{\text{vib}}^{\text{har}} = V_{0}^{\text{hcp}} + E_{0\text{vib}}^{\text{hcp}} = V_{0}^{\text{hcp}} + N \theta (2X_{\text{hcp}} + X_{z}^{\text{hcp}}).
\]

In classical approximation for FCC crystal [6, 7],
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\[ E_{\text{fcc,cla}}^{\text{vib}} = E_{\text{fcc,cla}}^{\text{rot}} + E_{\text{vib}}^{\text{rot}}, \]
\[ E_{\text{vib}}^{\text{rot}} = V_0^{\text{vib}} + N k_B \left( -U_0 \eta + \frac{1}{2} U_0 \eta^2 + 2 T \ln \left( \frac{\sqrt{6} B U_0 \eta}{T} \right) \right) - T \frac{\partial}{\partial T} \left\{ \psi^{\text{rot}} + k_B N \left[ -U_0 \eta + \frac{1}{2} U_0 \eta^2 + 2 T \ln \left( \frac{\sqrt{6} B U_0 \eta}{T} \right) \right] \right\} \]
\[ + \frac{1}{2} U_0 \eta^2 + 2 T \ln \left( \frac{\sqrt{6} B U_0 \eta}{T} \right) \right\} = E_{\text{vib}}^{\text{cla}} + k_B N U_0 \eta (\eta^2 - 1) \]
\[ - 2 k_B N T \left( \frac{T}{2 \eta} \frac{\partial \eta}{\partial T} - 1 \right), \eta = \frac{1}{2} \left( 1 - \sqrt{1 - \frac{4 T}{U_0}} \right), \frac{\partial \eta}{\partial T} = - \frac{2}{U_0 \sqrt{1 - \frac{4 T}{U_0}}} \] (2.10)
and for HCP crystal [7, 8],

\[ E_{\text{hcp,cla}}^{\text{vib}} = E_{\text{hcp,cla}}^{\text{rot}} + E_{\text{vib}}^{\text{rot}}, \]
\[ E_{\text{vib}}^{\text{rot}} = V_0^{\text{hcp}} + E_{\text{vib}}^{\text{rot}} - \frac{N \theta^2}{4} \left[ \left( \frac{6 \tau_{5}^{\text{hcp}} + 7 \tau_{6}^{\text{hcp}}}{k_x^{\text{hcp}}} \right) + \frac{3 \gamma_{1}^{\text{hcp}}}{k_x^{\text{hcp}}} - \frac{2 \gamma_{2}^{\text{hcp}}}{k_x^{\text{hcp}} k_z^{\text{hcp}}} \right] \right]. \] (2.11)

In anharmonic approximation for FCC crystal [6, 7],

\[ E_{\text{fcc,an}}^{\text{vib}} = E_{\text{fcc,an}}^{\text{rot}} + E_{\text{vib}}^{\text{rot}}, \]
\[ E_{\text{vib}}^{\text{rot}} = N k_B \left[ 2 T \left\{ \ln \left( 4 \sinh \frac{\xi}{2 T} \right) \right\} - \frac{\xi}{2} \coth \frac{\xi}{2 T} - \frac{B}{2} - \frac{U_0 \eta^2}{2} \right] \]
\[ - k_B N T \frac{\partial}{\partial T} \left\{ 2 T \left\{ \ln \left( 4 \sinh \frac{\xi}{2 T} \right) \right\} - \frac{\xi}{2} \coth \frac{\xi}{2 T} - \frac{B}{2} - \frac{U_0 \eta^2}{2} \right\} \]
\[ \quad = \frac{k_B N}{2} \coth \frac{\xi}{2 T} \left( \xi \coth \frac{\xi}{2 T} + T \frac{\partial \xi}{\partial T} \right) \]
\[ - k_B N \left[ \frac{B}{2} + U_0 \eta \left( 1 - \frac{1}{2} - \frac{U_0 \eta}{T} \frac{\partial \eta}{\partial T} \right) \right] - \frac{k_B N}{4} \left( T \frac{\partial \xi}{\partial T} - \xi \right) \left( \frac{1}{T} \frac{\partial \xi}{\partial T} - \xi \right) \] (2.12)
and for HCP crystal [7, 8],

\[ E_{\text{hcp,an}}^{\text{vib}} = E_{\text{hcp,an}}^{\text{rot}} + E_{\text{vib}}^{\text{rot}}, E_{\text{vib}}^{\text{rot}} = V_0^{\text{hcp}} + E_{\text{vib}}^{\text{rot}}, \]
\[ \frac{-N \theta^2}{12} \left[ \left( \frac{6 \tau_{5}^{\text{hcp}} + 7 \tau_{6}^{\text{hcp}}}{k_x^{\text{hcp}}} \right) + \frac{3 \gamma_{1}^{\text{hcp}}}{k_x^{\text{hcp}}} \right] + \frac{1}{2} \left( 1 + Y_2^{\text{hcp}} + Y_2^{\text{hcp}} \right) \] (2.13)
2.1.3. Entropy

The entropy of molecular crystals of N\(_2\) type with FCC and HCP structures is the sum of the vibrational entropy and the rotational entropy. In harmonic approximation for FCC crystal [6, 7],

\[
S_{fcc,\text{har}} = \frac{E_{fcc,\text{har}}}{T} - \psi_{fcc,\text{har}} = S_{vib}^{fcc,\text{har}} + S_{rot}^{fcc,\text{har}},
\]

\[
S_{rot}^{fcc,\text{har}} = -\frac{N k_B U_0}{T} \left[ 1 - \frac{3B}{\xi} \coth \frac{\xi}{2T} \right] + \frac{N k_B U_0}{2} \left[ 1 - \frac{3B}{\xi} \coth \frac{\xi}{2T} \right]^2
\]

\[
\times \left\{ \frac{\xi}{2T^2} \left( \frac{T}{\partial \xi} - \xi \right) \left[ 1 - \coth^2 \frac{\xi}{2T} \right] - \frac{\partial \xi}{\partial T} \coth \frac{\xi}{2T} \right\} - \frac{k_B N}{T} \left[ 2T \ln \left( \frac{4 \sinh \frac{\xi}{2T}}{2 \sinh x_{fcc}} \right) - U_0 \eta + \frac{U_0 \eta^2}{2} \right]
\]

(2.14)

and for HCP crystal [7, 8],

\[
S_{hcp,\text{har}} = S_{vib}^{hcp,\text{har}} + S_{rot}^{hcp,\text{har}},
\]

\[
S_{vib}^{hcp,\text{har}} = N k_B \left\{ 2 \left[ X_{hcp} - \ln \left( 2 \sinh x_{hcp} \right) \right] + \left[ X_{Z_{hcp}} - \ln \left( 2 \sinh x_{Z_{hcp}} \right) \right] \right\}.
\]

(2.15)

In classical approximation for FCC crystal [6, 7],

\[
S_{fcc,\text{cla}} = S_{vib}^{fcc,\text{cla}} + S_{rot}^{cla},
\]

\[
S_{vib}^{fcc,\text{cla}} = 3N k_B \left[ 1 - \ln \left( 2 \sinh x_{fcc} \right) \right] + \frac{6N k_B \theta}{k_{\text{fcl}}} \left( \gamma_1^{fcc} - \gamma_2^{fcc} \right), x_{fcc} \approx 0.283,
\]

\[
S_{rot}^{cla} = S_{0rot}^{\text{cla}} + \frac{k_B N U_0}{2T} \left[ \frac{\eta}{2} - 1 \right] + \frac{k_B N U_0}{2 \partial \eta} (1 - 2\eta) - 2k_B N \left( \frac{T}{\partial \eta} - 1 \right)
\]

\[
- \frac{k_B N}{2T} \left[ -U_0 \eta + \frac{U_0 \eta^2}{2} + 2T \ln \left( \frac{\sqrt{6B U_0 \eta}}{T} \right) \right]
\]

(2.16)

and for HCP crystal [7, 8],

\[
S_{hcp,\text{cla}} = S_{vib}^{hcp,\text{cla}} + S_{rot}^{cla},
\]

\[
S_{vib}^{hcp,\text{cla}} = S_{0vib}^{\text{hcp}} + \frac{N k_B \theta}{2} \left( \frac{6\tau_1^{hcp} + \tau_0^{hcp}}{k_{\text{hcp}}^2} \right) - \frac{3\tau_1^{hcp}}{k_{\text{hcp}}^2 k_{\text{hcp}}} - \frac{2\tau_2^{hcp}}{k_{\text{hcp}} k_{\text{hcp}}} \right\}.
\]

(2.17)

In anharmonic approximation for FCC crystal [6, 7],

\[
S_{fcc,\text{anh}} = S_{vib}^{fcc,\text{anh}} + S_{rot}^{\text{anh}},
\]

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\[ S_{\text{vib}}^{\text{fcc, anh}} = 3Nk_B \left[ X^{\text{fcc}} - \ln \left( 2 \sinh x^{\text{fcc}} \right) \right] + \frac{3Nk_B\theta}{k_{\text{vib}}^2} \left[ \frac{\gamma^{\text{fcc}}}{3} \left( 4 + X^{\text{fcc}} + Y^{\text{fcc}} \right) - 2\gamma^{\text{fcc}} X^{\text{fcc}} Y^{\text{fcc}} \right], \]

\[ S_{\text{rot}}^{\text{anh}} = \frac{k_B N}{2T} \coth \frac{\xi}{2T} \left( \xi \coth \frac{\xi}{2T} + T \frac{\partial \xi}{\partial T} \right) \]

\[ - \frac{k_B N}{T} \left[ \frac{B}{2} + U_0 \eta \left( \frac{1}{2} - T \frac{\partial \eta}{\partial T} \right) \right] \]

\[ \left\{ 2T \ln \left[ \frac{4 \sinh \frac{\xi}{2T}}{2} \right] - \frac{\xi}{2} \coth^2 \frac{\xi}{2T} - \frac{B}{2} - \frac{U_0 \eta^2}{2} \right\} \]

(2.18)

and for HCP crystal [7, 8],

\[ S_{\text{vib}}^{\text{hcp, anh}} = S_{\text{vib}}^{\text{anh}} + S_{\text{vib}}^{\text{anh}} \]

\[ S_{\text{vib}}^{\text{anh}} = \frac{N k_B \theta}{12} \left[ \frac{6\tau_5^{\text{hcp}} + \tau_6^{\text{hcp}}}{k_x^{\text{hcp}} k_z^{\text{hcp}}} \left( 4 + X^{\text{hcp}} + Y^{\text{hcp}2} \right) \right] \]

\[ + \frac{3\tau_1^{\text{hcp}}}{k_z^{\text{hcp}2}} \left( 4 + X_z^{\text{hcp}} + Y_z^{\text{hcp}2} \right) + \frac{\tau_2^{\text{hcp}}}{k_x^{\text{hcp}2} k_z^{\text{hcp}}} \left( 8 + X^{\text{hcp}} + Y^{\text{hcp}2} + X_z^{\text{hcp}} + Y_z^{\text{hcp}2} \right) \].

(2.19)

2.1.4. Heat capacity at constant volume

The heat capacity at constant volume of molecular crystals of N\(_2\) type with FCC and HCP structures is the sum of the vibrational heat capacity at constant volume and the rotational heat capacity at constant volume. In harmonic approximation for FCC crystal [6, 7],

\[ C_{\text{V, vib}}^{\text{fcc, har}} = -T \left( \frac{\partial^2 \psi_{\text{fcc, har}}}{\partial T^2} \right)_V = C_{\text{V, vib}}^{\text{fcc, har}} + C_{\text{V, rot}}^{\text{har}}, \]

\[ C_{\text{V, vib}}^{\text{fcc, har}} = 3Nk_B Y^{\text{fcc}2}, \]

\[ C_{\text{V, rot}}^{\text{har}} = \frac{N k_B}{2} \left( \frac{\xi}{\sinh^2 \frac{\xi}{2T}} \right)^2 \left( 1 - T \frac{\partial \xi}{\partial T} \right) \]

(2.20)

and for HCP crystal [7, 8],

\[ C_{\text{V, vib}}^{\text{hcp, har}} = C_{\text{V, vib}}^{\text{hcp, har}} + C_{\text{V, rot}}^{\text{har}}, \]

\[ C_{\text{V, vib}}^{\text{hcp, har}} = N k_B \left( 2Y^{\text{hcp}2} + Y_z^{\text{hcp}2} \right). \]

(2.21)

In classical approximation for FCC crystal [6, 7],

\[ C_{\text{V, vib}}^{\text{fcc, cla}} = C_{\text{V, vib}}^{\text{cla}} + C_{\text{V, rot}}^{\text{cla}} + C_{\text{V, vib}}^{\text{fccccla}} = 3Nk_B \left[ 1 + \frac{2\theta}{k_{\text{vib}}^2} \left( \gamma_1^{\text{fcc}} - \gamma_2^{\text{fcc}} \right) \right], \]

\[ C_{\text{V, rot}}^{\text{cla}} = C_{\text{V, rot}}^{\text{cla}} + k_B N U_0 (\eta - 1) \frac{\partial \eta}{\partial T} + \frac{k_B N U_0}{2} \left[ (1 - 2\eta) \left( \frac{\partial \eta}{\partial T} + T \frac{\partial^2 \eta}{\partial T^2} \right) - 2T \left( \frac{\partial \eta}{\partial T} \right)^2 \right] \]

\[ - 2k_B N \left\{ \frac{T}{2} \eta \left( \frac{\partial \eta}{\partial T} - 1 \right) + \frac{T}{2\eta^2} \left[ \eta \left( \frac{\partial \eta}{\partial T} - T \frac{\partial^2 \eta}{\partial T^2} \right) - T \left( \frac{\partial \eta}{\partial T} \right)^2 \right] \right\} \]

(2.22)
and for HCP crystal [7, 8],

$$C_{V,cla}^{hcp} = C_{V,vib}^{hcp} + C_{V,rot}^{hcp}, C_{V,vib}^{hcp} = \frac{1}{2} \left( 6 \tau_5^{hcp} + \tau_6^{hcp} \right) + \frac{3 \tau_1^{hcp}}{k_x^{hcp}} + \frac{2 \tau_2^{hcp}}{k_x^{hcp} k_z^{hcp}} \right) \right).$$

(2.23)

In anharmonic approximation for FCC crystal [6, 7],

$$C_{V,anh}^{fcc} = C_{V,vib}^{fcc} + C_{V,rot}^{anh},$$

$$C_{V,vib}^{fcc} = 3Nk_B \left( 2Y fcc + \gamma fcc \left( 2\gamma fcc + \gamma fcc \right) \right)$$

$$+ \frac{2\gamma fcc}{3} - \gamma fcc \left( Y fcc + 2X fcc \gamma fcc \right) \right) \right)$$

(2.24)

$$C_{V,rot}^{anh} = \frac{Nk_B}{2} \left( \coth \frac{\xi}{2T} + \frac{\xi}{2T} + \frac{1}{2T} \sinh \frac{\xi}{2T} \left( T \frac{\xi}{2T} - \frac{1}{2T} \right) \right)$$

and for HCP crystal [7, 8],

$$C_{V,anh}^{hcp} = C_{V,vib}^{hcp} + C_{V,rot}^{anh},$$

$$C_{V,vib}^{hcp} = \frac{1}{2} \left( 2Y^{hcp} + Y^{hcp} \right) - \frac{6 \tau_5^{hcp} + \tau_6^{hcp}}{k_x^{hcp} k_z^{hcp}} \left( 2 + X^{hcp} Y^{hcp} \right)$$

$$+ \frac{3 \tau_1^{hcp}}{k_x^{hcp}} \left( 2 + X^{hcp} Y^{hcp} \right) + \frac{\tau_2^{hcp}}{k_x^{hcp} k_z^{hcp}} \left( 4 + X^{hcp} Y^{hcp} + X^{hcp} Y^{hcp} \right) \right) \right).$$

(2.25)

3. Conclusion

In this paper, we derive analytic expressions of thermodynamic quantities such as the free energy, the energy, the entropy and the heat capacity at constant volume of molecular cryocrystals of nitrogen type with FCC and HCP structures in harmonic, classical and anharmonic approximations based on combining the SMM and SCFM.

In the next paper, we shall use theoretical results of this paper to calculate numerically the thermodynamic properties for molecular cryocrystals of nitrogen type.
REFERENCES


