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Monte Carlo Calculations on the Beta–Delta Phase Transition in Nitrogen with a Generalized Free Energy Method

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Monte Carlo simulations that utilize an (N, P, T) ensemble with periodic deformable boundary conditions cannot describe phase transitions properly when a large potential barrier is involved. An alternative method is to calculate the Gibbs free energy difference between phases; the transition occurs when the difference is equal to zero. The Gibbs free-energy difference can be calculated using a generalized free-energy method. This method is used to determine the β–δ phase transition of solid nitrogen at room temperature. The Gibbs free-energy difference between the β and the δ phase was obtained at 4.0 GPa. The difference at other pressures could be determined with the equation of state. The transition pressure was found at about 6.2 GPa, 1.3 GPa above the experimental pressure.

KEY WORDS: Gibbs free energy; high pressure; Monte Carlo; nitrogen; phase transition.

1. INTRODUCTION

One of the many phase transitions that can occur in solid nitrogen is the β–δ phase transition (Fig. 1). The β phase has a hexagonal close-packed (hcp) structure in which the orientations of the nitrogen molecules are spherically disordered [1–7]. The structure of the δ phase (Pm3n) [8–10] is cubic, with eight molecules per unit cell. The molecules at the corners

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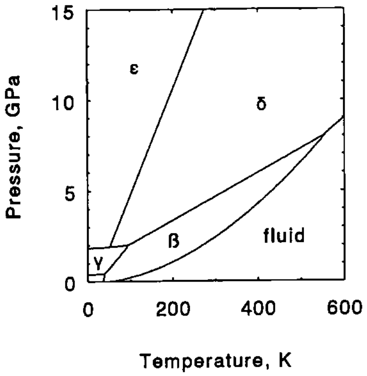

Fig. 1. Phase diagram of nitrogen.

and at the center of the cell are spherically disordered. The orientation of the molecules in the faces of the cell are disk-like disordered. The transition pressure at 300 K was found experimentally at about 4.9 GPa [10, 11]. Both phases could be observed within a region around the transition pressure. Belak et al. [12] performed Monte Carlo simulations on this system at 300 K using an (N, P, T) ensemble with a deformable box. It was found that both phases continued to exist beyond the experimental transition pressure, however no phase transition was found. We have determined the β–δ phase transition with Monte Carlo simulations using the generalized free-energy method.

2. METHOD

An equilibrium transition from phase i to phase j might occur when the difference in Gibbs free energy vanishes. This quantity can be calculated with a free-energy method [13, 14]. An artificial control parameter, λ, provides a reversible path from one phase to the other. The enthalpy is defined by

$$H(\lambda) = \lambda H_i + (1-\lambda) H_j \tag{1}$$

where H_i and H_j represent the enthalpies of phases i and j, respectively, and $0 \leqslant \lambda \leqslant 1$. Furthermore,

$$\partial G(\lambda)/\partial\lambda = \langle \partial H(\lambda)/\partial\lambda \rangle_\lambda = \langle H_i - H_j \rangle_\lambda \tag{2}$$

and the Gibbs free-energy difference between phase i and phase j is

$$\Delta G_{ij}(P) = G_i - G_j = \int_0^1 \langle \partial H(\lambda)/\partial\lambda \rangle_\lambda \, d\lambda \tag{3}$$

where the averages are taken over the Boltzman distribution $\exp[-H(\lambda)/k_B T]$. The averages $\langle H_i \rangle_\lambda$ and $\langle H_j \rangle_\lambda$ can be determined by using the same set of Monte Carlo configurations in the (N, P, T) ensemble, even when the states (i, j) have different structures. Symmetry transformations are then performed on the 5N molecular coordinates and the vectors defining the Monte Carlo unit cell from state i to state j. However, no suitable symmetry transformation is known between the β and the δ phase.

To solve this problem a model system is introduced under the following constraints. It should be possible to calculate the free energy of this model system easily and there should be a reversible path from the model system to the real system. To accomplish this we used a model system with the molecules at the same lattice positions as the real system and with harmonic forces between the nearest neighbors. The Gibbs free energy of the harmonic system can be calculated by

$$G_h = F_h + PV_h \tag{4}$$

With Eqs. (3) and (4) the Gibbs free energy of the real system can be calculated. In this way the Gibbs free energy of the β as well as of the δ phase was determined separately with the corresponding model system. By calculating the Gibbs free-energy difference between the β and the δ phase at various pressures, the transition pressure P_t is obtained from

$$\Delta G_{\beta\delta}(P_t) = 0 \tag{5}$$

The Gibbs free-energy difference at various pressures can be calculated with the free energy method for each pressure.

It is also possible to calculate this quantity with the free-energy method for just one pressure to determine the free energy at other pressures with the equation

$$F(V) = F(V_0) - \int_{V0}^{V} P(V)\, dV \tag{6}$$

The harmonic model system with the structure of the β phase (hcp) has 12 nearest neighbors. In the case of the δ phase, the lattice positions corresponding to the spherically disordered molecules will have 12 disk-like disordered neighbors and the lattice positions corresponding to the disk-like disordered molecules will have 4 spherically disordered and 10 disk-like disordered neighbors. The energy between two lattice sides is given by

$$E_{ij} = \tfrac{1}{2} k (r_{ij} - Rr0_{ij})^2 \tag{7}$$

where $r0_{ij}$ is the distance between the molecules when they are at the lattice positions of the initial volume, V^0. To obtain a smooth curve, required for the evaluation of the integral of Eq. (3), the values of k and R are determined at each state point in such a way that the energy and volume of the harmonic model system is the same as the corresponding real system. The free energy of the harmonic system is calculated by making the approximation of a decoupled harmonic system with the nearest neighbors at the lattice positions. If the deviation from the equilibrium position is small, denoting the position and the equilibrium position of particle i by r_i and $r0_i$, respectively, and summing over all nearest neighbors, Eq. (7) gives

$$E_i = \tfrac{1}{2}k'(r_i - r0_i)^2 + E_{0i} \tag{8}$$

for the β phase and the spherically disordered molecules of the δ phase, and

$$E_i = \tfrac{1}{2}k'_x(x - x0)^2 + \tfrac{1}{2}k'_y(y - y0)^2 + \tfrac{1}{2}k'_z(z - z0)^2 + E_{0i} \tag{9}$$

for the disk-like disordered molecules of the δ phase.

The energy E_{0i} is given by

$$E_{0i} = \sum_{j=1}^{n.n.} \tfrac{1}{2}k(R_{ij} - Rr0_{ij})^2 \tag{10}$$

where R_{ij} is the distance between the molecules when they are at the lattice positions of the equilibrium volume. The free energy per particle in units of K for the harmonic system corresponding with the β phase will be

$$F = -\tfrac{3}{2}T\ln[4\pi T/V^{2/3}k'] + \tfrac{1}{2}E_0 \tag{11}$$

and for the harmonic system corresponding to the δ phase,

$$F = -\tfrac{3}{2}T\ln[(4\pi T/V^{2/3})(k'k'_xk'_yk'_z)^{-1/4}] + \tfrac{1}{8}(E_{OS} + 3E_{OD}) \tag{12}$$

where V is the equilibrium volume and E_{OS} is the E_0 for the spherically disordered and E_{OD} for the disk-like disordered particles.

The values of k', k'_x, k'_y, k'_z, E_0, E_{OS}, and E_{OD} can be determined by displacing one particle in the harmonic system with the equilibrium volume, while keeping the other particles fixed.

The calculations were performed at $T = 300$ K with an (N, P, T) ensemble. The site–site potential derived by Etters et al. [15] was used between a pair of N_2 molecules. With this potential a wide range of properties of nitrogen can be accurately described. The Monte Carlo cell of the δ phase consisted of 64 molecules. The unit cell for the β phase was taken rectangular and contained four molecules; the total Monte Carlo cell consisted of 108 molecules. After an equilibration run of 10^4 Monte Carlo steps, the thermodynamic averages were taken through another 10^4 steps. Each step consisted of a random move of the position and the orientation of each molecule and a change in the size of the Monte Carlo cell. To do better statistics on the volume of the harmonic ($\lambda = 0$) and the physical ($\lambda = 1$) systems, we used an equilibration run of 5×10^4 MC steps followed by a production run of 10^5 steps. The integral in Eq. (3) was calculated with the extended Simpson's rule over the interval $0 \leqslant \lambda \leqslant 1$ in steps of 0.05.

3. RESULTS

The results are summarized in Tables I, II, and III. The parameters of the harmonic systems are determined at 4.0 GPa, resulting in a volume and energy identical to that of the corresponding real system. The free energy of the harmonic system was calculated with Eqs. (11) and (12) and the ΔG between the harmonic and the real system was determined by evaluating the integral of Eq. (3) (Table I). Next, the Gibbs free energy and free energy of the β and δ phase could be calculated at 4.0 GPa. To determine the Gibbs free energy of the β and δ phase at 5.0, 6.0, 7.0, and 8.0 GPa, Eq. (6) was used, where the expression for $P(V)$ was obtained by a fit through the (P, V) data (Tables II and III). The difference in Gibbs free energy between the β and the δ phase is plotted in Fig. 2. The transition is

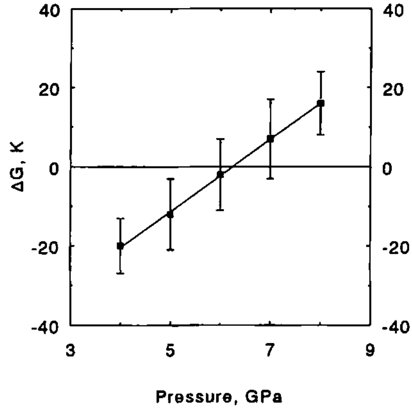

Fig. 2. The calculated Gibbs free-energy difference between the β and the δ phase of nitrogen, $G_\beta - G_\delta$, at room temperature. The line is a guide to the eye.

Table I. The Parameters, Volume, Free Energy, and Gibbs Free-Energy Difference of the Harmonic Systems at 4.0 GPa

β phase

$V^0 = 18.79\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
$V_\mathrm{h} = 18.789(3)\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
$\Delta G = -945(5)\ \mathrm{K}$
$F_\mathrm{h} = 2188(2)\ \mathrm{K}$
$k = 36{,}000\ \mathrm{K} \cdot \text{Å}^{-2}$
$R = 1.0105$
$k' = 35{,}330(60)\ \mathrm{K} \cdot \text{Å}^{-2}$
$E_0 = 298(3)\ \mathrm{K}$

δ phase

$V^0 = 18.72\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
$V_\mathrm{h} = 18.718(3)\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
$\Delta G = -857(4)\ \mathrm{K}$
$F_\mathrm{h} = 2154(2)\ \mathrm{K}$
$k = 30{,}000\ \mathrm{K}$
$R = 1.0105$
$k'_x = 36{,}310(30)\ \mathrm{K} \cdot \text{Å}^{-2}$
$k'_y = 36{,}310(30)\ \mathrm{K} \cdot \text{Å}^{-2}$
$k'_z = 30{,}250(30)\ \mathrm{K} \cdot \text{Å}^{-2}$
$k' = 29{,}340(30)\ \mathrm{K} \cdot \text{Å}^{-2}$
$E_\mathrm{OD} = 247(3)\ \mathrm{K}$
$E_\mathrm{OS} = 313(3)\ \mathrm{K}$

Table II. Calculated Volume and Free Energy for the β and δ Phase at Various Pressures

	β phase		δ phase	
Pressure (GPa)	Volume ($\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$)	Free energy (K)	Volume ($\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$)	Free energy (K)
4.0	18.783(7)	1246(6)	18.712(5)	1300(5)
5.0	17.929(5)	1704(6)	17.862(4)	1756(5)
6.0	17.260(5)	2145(6)	17.184(4)	2202(5)
7.0	16.711(4)	2573(6)	16.626(6)	2638(5)
8.0	16.246(2)	2992(6)	16.155(3)	3063(5)

Table III. Calculated Gibbs Free Energy and Difference Gibbs Free Energy for the β and δ Phase at Various Pressures

	Gibbs free energy (K)		
Pressure (GPa)	β phase (K)	δ phase (K)	Difference Gibbs free energy (K)
4.0	10277(5)	10297(5)	−20(7)
5.0	12479(7)	12491(5)	−12(9)
6.0	14593(7)	14595(6)	−2(9)
7.0	16634(7)	16627(7)	7(10)
8.0	18614(6)	18598(6)	16(8)

found at about 6.2 ± 1.0 GPa, which is 1.3 GPa off in pressure compared with the experimental value. A possible reason for this difference could be the approximation made to calculate the free energy of the harmonic system. To verify this, simulations have to be performed to calculate the Gibbs free energy at different pressures by evaluating the integral of Eq. (3). The results should be compared with the results obtained with the equation of state. In conclusion, with the free-energy method it is possible to calculate the β–δ transition in nitrogen in good agreement with experiment.

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