PHYSICAL REVIEW B VOLUME 45, NUMBER 9 1 MARCH 1992-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Method for calculating solid-solid phase transitions at high temperature: An application to N_2O

B. Kuchta and R. D. Etters

Department of Physics, Colorado State University, Fort Collins, Colorado 80523

(Received 26 July 1991)

Two similar techniques for calculating solid-solid phase transitions at high temperatures are developed, where the contribution of the entropy may be a decisive factor. They utilize an artificial reversible path from one phase to another by application of a control parameter. Thermodynamic averages are calculated using constant-volume and constant-pressure Monte Carlo techniques. An application to N_2O at room temperature shows that the cubic *Pa*3 to orthorhombic *Cmca* transition occurs near 4.9-GPa pressure, very close to the value calculated at very low temperatures. These results support experimental evidence that the transition pressure is virtually independent of temperature.

Recent calculations on solid N_2O have predicted a transition from the cubic *Pa*3 structure into an orthorhombic *Cmca* phase at $P_t = 4.75$ GPa pressure.[1,2] It was established by comparing enthalpies of the competing phases in the limit of zero temperature. In concert, x-ray-diffraction measurements[3] have confirmed this transition at 4.85 GPa for temperatures $T = 100$ and 300 K. The above results are consistent with earlier Raman-scattering data[4] that showed distinct changes in the libron frequencies near this pressure, although the structure could not be established. Thus, it appears that the transition pressure is virtually temperature independent.

The purpose of this work is to devise a method for calculating the pressure of solid-solid phase transitions at high temperature, with the objective of determining P_t at room temperature for N_2O. This is quite difficult[5] because the entropy must be accurately calculated to evaluate the Gibbs free energy *G*, which establishes the thermodynamic stability of a system. In fact, the condition for a transition is that the difference in free energy between two phases satisfies

$$\Delta G = 0 . \qquad (1)$$

The methods used here employ an artificial control parameter to provide a reversible path from one phase to another. Similar procedures have been used to calculate melting temperatures and transitions in model systems.[6–8] This is an application of the technique to a solid-solid transition in a real system; in this case solid N_2O at 300 K, and we use constant pressure ensembles with deformable, periodic boundary conditions.

The first procedure is to construct an energy

$$U_i(\lambda) = \lambda U_i + (1-\lambda)U_m , \qquad (2)$$

where $0 \leq \lambda \leq 1$ is a control parameter and U_m represents the energy of a model system of noninteracting local harmonic oscillators, three translational and two orientational. U_i is the energy of the physical system, either cubic or orthorhombic in this case. U_i for N_2O is given by the sum of interactions between all pairs of molecules within a distance of 9 Å, with continuum corrections beyond. The overlap-dispersion contribution is represented using three force centers along each molecular axis. The electric-multipole interactions are represented by three point charges, distributed to reproduce the first four known moments. This potential has had considerable success[1,2] in predicting most known properties of condensed N_2O and, as mentioned, also predicting a high-pressure transition into the *Cmca* phase, recently confirmed by experiment.[3] Monte Carlo calculations are conducted on the system defined by Eq. (2) using an (N,V,T) ensemble, where the Einstein oscillators of the model system are localized on the lattice sites of the physical system at each volume *V*. The number of molecules in the system is *N*. The orientational and translational force constants for the model were determined by evaluating the appropriate second derivatives of the N_2O potential at the equilibrium lattice sites of the physical system. In principal, any set of force constants will suffice, but, as briefly described in the summary, there is a practical advantage in choosing them close to those of the physical system. The following exact thermodynamic relationships apply:

$$\delta F_i(\lambda)/\delta\lambda = \langle \delta U_i(\lambda)/\delta\lambda \rangle = \langle U_i - U_m \rangle_\lambda , \qquad (3)$$

$$F_i(V) = F_m(V) + \int_0^1 \langle \delta U_i(\lambda)/\delta\lambda \rangle d\lambda , \qquad (4)$$

$$F_i(V) = F_i(V_0) - \int_0^V P_i(V) dV , \qquad (5)$$

where the brackets represent thermodynamic averages with respect to $U_i(\lambda)$. $F_i(V)$ and $F_m(V)$ are the Helmholtz free energies for the physical and model systems, respectively. The pressure of the system is $P_i(V)$. The subscript of the bracket of Eq. (3) is a reminder that the average depends on λ even though the argument does not. Equation (4) follows from Eq. (2) which shows that $U_i(\lambda)$ transforms continuously from that of the model system to the physical system as λ changes from zero to 1. Clearly, Eqs. (3)–(5) show that the free-energy difference between two phases can be determined if $\langle \delta U_i(\lambda, V)/d\lambda \rangle$ and $P_i(V)$ are evaluated at any temperature. The integrands in Eq. (4), and in the following Eq. (9), were evaluated for ten values of λ and the associated integrals were determined using a standard Gaussian integration routine. The former integrand is calculated in this work for both the cubic and orthorhombic phases of solid N_2O, using Monte Carlo methods, and $P(V)$ for each structure was previously determined.[1] Transforming these results to constant pressure, the difference in Gibbs free energy between the cubic and orthorhombic phases of N_2O is readily determined:

$$\Delta G(P) = \Delta F(P) + P\Delta V(P) , \tag{6}$$

where ΔF is the difference in Helmholtz free energies and similarly for ΔV. The phase-transition pressure is then defined by Eq. (1). Since the free energy of the model system can be determined exactly, so can that of the physical system, using Eqs. (3)–(5). This is a valuable feature.

The second method developed here defines a reversible path directly between the cubic and orthorhombic phases of N_2O. Note that the molecules of the *Pa*3 phase oscillate about equilibrium orientations along the body diagonals whereas, in the *Cmca* structure, they fluctuate about orientations in the *bc* plane, as shown on Figs. 1(a) and 1(b). These structures are related by a transformation T of the azimuthal symmetry coordinate ϕ that rotates each molecular orientation in the unit cell by 45° about the z axis, normal to the *ab* plane, as shown on Fig. 1(c). Formally, we define

$$H(\lambda) = \lambda H_c + (1-\lambda) H_0 , \tag{7}$$

where $H_0 = U_0 + PV_0$ and U_0 and V_0 are the energy and volume of the orthorhombic phase. An entirely similar relation obtains for H_c, representing the cubic phase. As before, the control parameter $0 \le \lambda \le 1$, and

$$\delta G(\lambda)/\delta\lambda = \langle \delta H(\lambda)/\delta\lambda \rangle_\lambda = \langle H_c - H_0 \rangle_\lambda , \tag{8}$$

so the difference in free energy between the two phases is

$$\Delta G(P) = \int_0^1 \langle \delta H(\lambda, P)/\delta\lambda \rangle_\lambda d\lambda \tag{9}$$

and

$$\Delta G(P) = \Delta G(P_0) + \Delta \int_{P_0}^{P} V(P) dP . \tag{10}$$

The integrand in Eq. (9) and $V(P)$ are calculated using a constant pressure Monte Carlo method with periodic, deformable boundary conditions. In this process Eq. (8) shows that the thermodynamic averages of both H_c and H_0 must be evaluated. The $5N$ coordinates $\{\mathbf{r}, \theta, \phi\}$ that define the mass-center positions and orientations of all molecules, and the six coordinates defining the unit cell, are randomly sampled along the Monte Carlo trajectories to evaluate these quantities. Note that H_c is a function of $\{\mathbf{r}, \theta, \phi\}$ and H_0 of $\{\mathbf{r}, \theta, T\phi\}$. The procedure described here is a straightforward generalization of that used by Moody, Ray, and Rahman[9] in model calculations of the fcc-hcp free-energy difference. The value of P for which Eq. (9) vanishes defines the transition pressure.

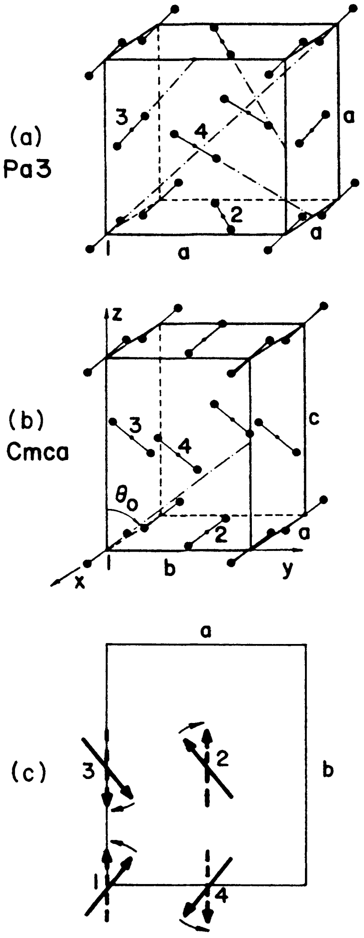

FIG. 1. The (a) cubic and (b) orthorhombic structure of solid N_2O. The solid and dashed arrows in (c) depict the projections of the equilibrium orientations onto the *ab* plane for the *Pa*3 and *Cmca* structures, respectively. The other arrows depict the rotation that carries one structure into the other.

The circles and squares in Fig. 2 show the calculated results for ΔG vs P at 300 K, for the first and second methods described herein, respectively. As prescribed by Eq. (1), the two methods predict the cubic to orthorhombic transition at $P_t = 4.91 \pm 0.2$ and 4.87 ± 0.15 GPa, respectively. This compares with the experimental value[3] of 4.85 GPa. The calculated entropy change on transition is $\Delta S(P_1) = \Delta H(P_1)/T = 0.28 \pm 0.08$ cal/K, compared to an estimated experimental value[3] of approximately 0.5 cal/K.

In summary, both techniques described in this work give virtually identical results for the transition pressure at 300 K, and agree closely with the experimental value[3] of 4.85 GPa. These results, and our previous calculations[1] at very low temperature, that gave $\lim_{T \to 0} P_t(T) = 4.75$

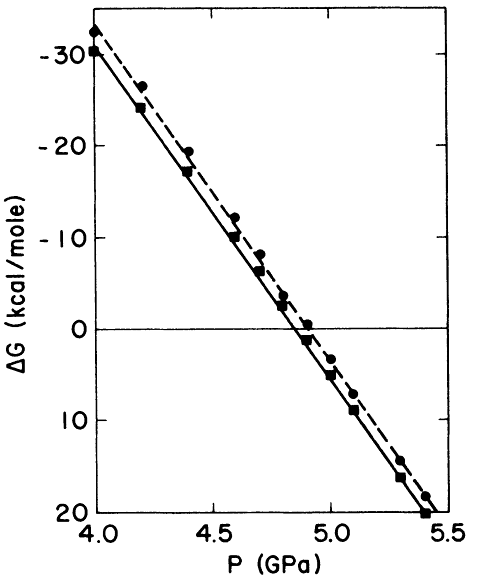

FIG. 2. The circles and squares show the calculated difference in Gibbs free energy between the cubic and orthorhombic phases using the two methods described in the text, respectively. The former utilizes the harmonic model reference system. The dashed and solid lines through the data are intended as aids to the eye.

GPa, show that the transition pressure is virtually independent of temperature. This is in complete accord with experimental evidence[3,4] and is gratifying support of the techniques developed in this work. As to which technique is best, it depends on the objectives of the calculation and the physical system in question. If the objective is to determine the absolute free energy of the system, the former method is required, since the model reference system can be analytically described. However, when a reversible path between two physical states can be found, such as for N_2O, calculated free-energy differences between them appear somewhat more accurate. Although there is a variety of possible approaches to this problem that are generically similar, it is too early to give a best strategy. Nevertheless, it is apparent that designing a tractable model system as similar to the physical state as possible is desirable. Also for methods that utilize the transition between two physical states, the maximum use of symmetry transformations that connect these states is helpful. In fact, the strategy is related to the nature of the transition itself.

We wish to thank Richard LeSar for discussions on this subject. The work was supported by Department of Energy Grant No. DE-FG02-86ER45238.

---

[1] B. Kuchta and R. D. Etters, J. Chem. Phys. **95**, 5399 (1991).

[2] B. Kuchta, R. D. Etters, and R. LeSar (unpublished).

[3] R. L. Mills, B. Olinger, D. T. Cromer, and R. LeSar, J. Chem. Phys. **95**, 5392 (1991).

[4] H. Olijnyk, H. Däufer, M. Rubly, H. Jodl, and H. D. Hochheimer, J. Chem. Phys. **93**, 45 (1990).

[5] D. Frenkel, in *Molecular Dynamics Simulations of Statistical Mechanical Systems*, edited by G. Ciccotti and W. G. Hoover (North-Holland, Amsterdam, 1986), p. 151.

[6] E. J. Meijer, D. Frenkel, R. LeSar, and A. J. Ladd, J. Chem. Phys. **92**, 7570 (1990).

[7] D. Frenkel, Phys. Rev. Lett. **56**, 858 (1986).

[8] D. Frenkel and A. J. Ladd, J. Chem. Phys. **81**, 3188 (1984).

[9] M. C. Moody, J. R. Ray, and A. Rahman, J. Chem. Phys. **84**, 1795 (1986).