Structural Transformations in Solid Nitrogen at High Pressure

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The Andersen-Parrinello-Rahman constant-pressure molecular-dynamics technique has been generalized to study molecular crystals. The method, which appears to have wide applicability, is used to study structural transformations in solid nitrogen at high pressures.

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The constant-pressure computer-simulation technique proposed by Andersen[1] for the study of liquids and elegantly generalized by Parrinello and Rahman,[2] in order to discuss the relationship of crystal structure to pair potentials in atomic systems, has been further extended to handle the case of molecular solids and liquids. As a pedagogical example we discuss structural transformations that we observe upon isobarically quenching a model solid-nitrogen crystal initially held at room temperature and high pressure. In particular, at a pressure of 70 kbar and $T = 140$ K we observe a spontaneous shear distortion of the nitrogen crystal that transforms the structure from cubic to trigonal. This distortion is accompanied by preferential alignment of certain of the molecules with the trigonal axis. The results of our calculations will likely have important implications for the interpretation of high-pressure experiments that can now be carried out with diamond anvil cells.[3,4]

It has been known for some time that depending upon the conditions of temperature and pressure solid nitrogen can exist in different crystal structures.[5] The relative stability of the phases at lower pressures depends upon fine details of the intermolecular potentials such as the balance between the short-range forces that are responsible for the shape of the molecule and the longer-ranged electrostatic interactions that occur between the quadrupole moments.[6-8] Recent investigations, using diamond anvil cells to generate the required high pressure, have revealed that at room temperature solid nitrogen exists in a cubic plastic crystal phase, with eight molecules per unit cell. This $Pm3n$ crystal structure is akin to the famous $A15$ structure of high-temperature superconductors.[4] In the case of solid nitrogen there are chains of disklike, orientationally disordered molecules along the cube directions (D_{2d} sites) together with an interpenetrated bcc lattice of more spherically disordered molecules (T_d sites). Previous computer-simulation studies of this structure[9] have confirmed that the disorder is dynamic and not static and this in turn is consistent with the intramolecular Raman spectrum which consists of two distinct lines.[3]

At room temperature solid nitrogen is therefore isomorphous with the high-temperature low-pressure structure of solid oxygen.[10] The analogy is even more striking when one notes that the ratio of intermolecular separation to bond length is virtually identical in these two solids. Since it is known that in solid oxygen the electrostatic quadrupole-quadrupole interaction is unimportant it is perhaps reasonable to conclude that at the pressures generated in the diamond anvil cell, the same situation pertains in solid nitrogen. Accordingly, one should then be able to model the intermolecular interactions by simple atom-atom potentials and this what we have done here.

When the $Pm3n$ phase of solid oxygen is cooled it transforms into a rhombohedral structure, $R\bar{3}m$, appropriate to the close packing of rodlike objects, namely two-dimensional rafts of close-packed molecules stacked in the fcc sequence *ABCABC...*, with all the molecular axes parallel to the stacking direction.[11] It is natural to ask whether or not the isobaric cooling of solid nitrogen from room temperature also generates the $R\bar{3}m$ structure found in solid oxygen and indeed recent static energy calculations have given support to this possibility.[12] However, unpublished experiments carried out at Los Alamos National Laboratory by the group of Mills and Schiferl show no evidence for such a transition.[13] In order to cast some light on this somewhat puzzling observation we have carried out a series of constant-pressure molecular-dynamics (MD) calculations for solid nitrogen at high pressure. Since in this method of calculation[2] the MD cell can change both its size and shape in response to the net imbalance between the thermally generated internal stresses and the externally applied pressure P_{ex}, it offers the possibility of studying isobaric structural transformations at finite temperatures.

Accordingly, we have in mind the study of the structure and dynamics of a system of rigid dumbbell molecules interacting through atom-atom potentials whose parameters are chosen to approximate solid nitrogen. The equations of motion for the system follow from the Lagrangian formulation of Parrinello and Rahman (PR) suitably augmented to allow for rotational motion. In particular, if $\underline{h}$ is the matrix formed by three time-dependent vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$ that specify the periodically replicated MD cell, then its volume $V = \det \underline{h} \equiv \vec{a} \cdot \vec{b} \times \vec{c}$. The position of molecule i in the cell is given by $\vec{r}_i = \underline{h}\,\vec{s}_i$ where the components of $\vec{s}$ range from 0 to 1. It then follows that $r_i^2 = \vec{s}_i{}'\underline{G}\,\vec{s}_i$, where $\underline{G} = \underline{h}'\underline{h}$ and the prime denotes a transposed quantity. We write the augmented PR Lagrangian as

$$L = \tfrac{1}{2}\sum_i m_i \dot{\vec{s}}_i{}'\underline{G}\dot{\vec{s}}_i - \sum_i \sum_{j>i} \varphi(r_{ij}, \vec{\alpha}_i, \vec{\alpha}_j) + \tfrac{1}{2} W \operatorname{Tr}(\dot{\underline{h}}'\dot{\underline{h}}) + \tfrac{1}{2}\sum_i \vec{\omega}_i \underline{I}_i \vec{\omega}_i - P_{\mathrm{ex}} V,$$

where $\vec{\omega}_i$ and $\underline{I}_i$ are the angular velocity and inertia tensor of molecule i whose mass is m_i. The potential energy, which depends upon the orientations $\vec{\alpha}$, is assumed to be the sum of interactions between site k on molecule i and site l on molecule j, separated by the distance $R_{ij}{}^{kl}$, thus

$$\varphi(r_{ij}, \vec{\alpha}_i, \vec{\alpha}_j) \equiv \varphi_{ij} = \textstyle\sum_{kl} \varphi_{ij}{}^{kl}.$$

The equations of motion for the scaled center-of-mass coordinates are then formally identical to those of PR, namely

$$\ddot{\vec{s}}_i = \underline{h}^{-1}\vec{f}_i / m_i - \underline{G}^{-1}\dot{\underline{G}}\dot{\vec{s}}_i.$$

Here $\vec{f}_i$ is the net force acting on molecule i, which in turn is the sum of all the forces acting on its individual interaction sites, k:

$$\vec{f}_i = \sum_k \vec{f}_i{}^k = \sum_{j \neq i} \sum_{kl} -(\partial\varphi_{ij}{}^{kl} / \partial\vec{R}_{ij}{}^{kl}).$$

The equations of motion for the angular coordinates are identical to those in the usual constant-volume MD method and follow by relating the time rate of change of the angular momentum $\vec{M}_i = \underline{I}_i \vec{\omega}_i$ to the torque; thus we have

$$\dot{\vec{M}}_i = \textstyle\sum_k \vec{d}_i{}^k \times \vec{f}_i{}^k,$$

where $\vec{d}_i{}^k$ is the position vector of site k relative to the center of mass. In our application we have rewritten the above equations to describe the motion of the intramolecular bond vector.

Finally, the equations governing the dynamics of the unit cell are also similar to those of PR, namely

$$W\ddot{\underline{h}} = (\underline{\pi} - P_{\mathrm{ex}})\underline{\sigma},$$

where $\underline{\pi}$ is a stress tensor and the matrix $\underline{\sigma} \equiv V\underline{h}'^{-1}$.

We give only brief technical details of the calculations because the method and more extensive applications will be presented elsewhere. The centers of mass of 64 rigid nitrogen molecules, interacting through a simple Lennard-Jones atom-atom potential $\varphi(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$ with $\epsilon = 37.3$ K and $\sigma = 3.31$ Å and fixed half bond length $d = 0.1646\sigma$, were initially arranged in the observed high-pressure room-temperature *Pm*3*n* structure with appropriate, randomly chosen, orientations.[9] A MD calculation was carried out at constant volume with use of a time step of 0.005 ps and the equations of motion were integrated with a fifth-order algorithm for the translational coordinates, $\vec{s}_i$, and a fourth-order one for angular coordinates, $\vec{\alpha}_i$. This initial calculation confirmed the results of an earlier study of this crystal by conventional MD methods.[9] The condition of constant volume was then replaced by the constraint of constant pressure, which in our case was fixed by $P_{\mathrm{ex}} \sim 70$ kbar, and the calculation continued. Since the MD cell is now free to undergo volume and shear fluctuations we were able to examine whether or not the initial *Pm*3*n* configuration is at least locally stable for our adopted potential.

The left-most panel in Fig. 1 shows the evolution of the room-temperature high-pressure MD run for 2500 time steps. Also shown is the evolution of the lengths of the MD cell vectors and the angles between them. Although there are considerable fluctuations in both of these quantities, which are related to the elastic compliances of the crystal,[14] there is no evidence for any deviation from a cubic unit cell. More detailed investigation of the behavior of individual molecules confirmed the *Pm*3*n* structure. In particular, the disklike and spherical disordered molecules retained their identities.

The next panels in Fig. 1 show the effect of sequentially quenching the room-temperature solid-nitrogen structure in steps of 50 K down to 100 K while maintaining $P_{\mathrm{ex}} = 70$ kbar. The volume is seen to decrease systematically as the temperature is lowered and the three MD cell vectors remain equal in length, within the statistical un-

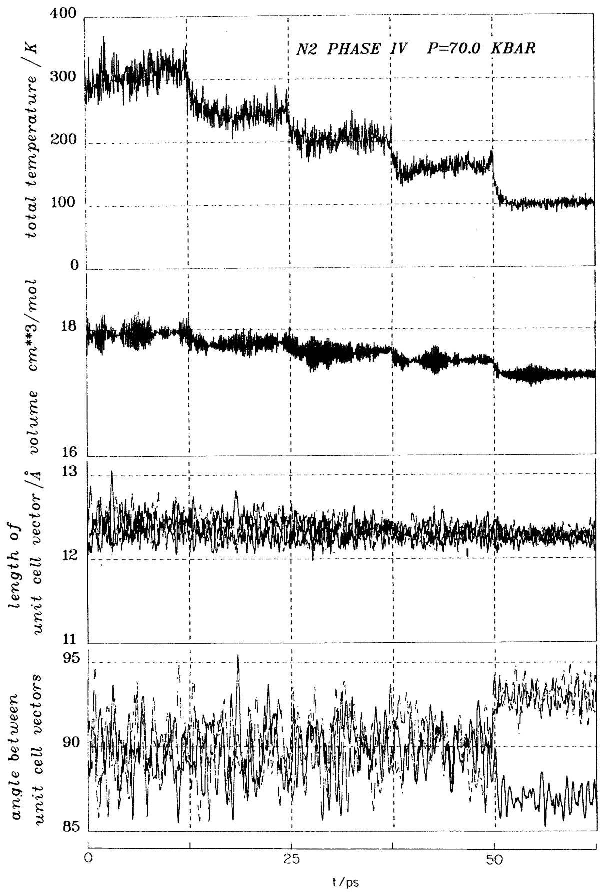

FIG. 1. Time evolution of quantities characterizing the basic molecular-dynamics cell used for solid nitrogen at 70 kbar. The left-most panel of the figure refers to $T = 300$ K and displays results for 2500 time steps, the first 500 of which are used to scale the temperature of the system. Subsequent panels contain similar information but for temperatures sequentially lowered by about 50 K. The last panel, which refers to $T = 100$ K, clearly reveals the trigonal distortion that takes the crystal from $Pm3n$ to $R3c$ (see text).

certainties. However, below 150 K the MD cell angles are no longer 90°; the system has undergone a spontaneous shear distortion of 3°. An inspection of the structure so generated reveals that the spherically disordered molecules are now all aligned along the trigonal direction, the crystal having $R3c$ symmetry, but not the $R\bar{3}m$ structure of solid O_2. At the pressure set in the MD calculation (70 kbar) the experimental molar volume is about 1 $cm^3\ mol^{-1}$ less than that found in the simulation.[4] This discrepancy could probably be rectified by examining a more realistic intermolecular potential.[11] However, the aim of this study was not simply to obtain a quantitative modeling of solid nitrogen; it was intended also to provide a demonstration of the elegance and utility of constant-pressure MD calculations. Additional calculations using a potential model that included a quadrupole-quadrupole interaction yield essentially the same result, confirming our earlier discussion. Careful heating and cooling of the crystal reveals little hysteresis and locates the shearing transition at 140 K. These studies also show that this transition is proceeded, at about 230 K, by the alignment of the disklike molecules parallel to a cube axis. Both transformations involve small volume changes, certainly less than 0.1 $cm^3\ mol^{-1}$.

In summary, we have reported computer-simulation calculations on the effect of isobaric cooling of a nitrogen crystal. At 70 kbar we observe cubic ($Pm3n$, $z = 8$) → cubic($I2_13$, $z = 64$) → trigonal ($R3c$, $z = 64$) phase transformations at around $T = 230$ K and $T = 140$ K, respectively. Our prediction of a trigonal distortion at low temperatures agrees with two recent energy minimization calculations.[15,16] It will be of considerable interest to see if our calculation is consistent with structural and spectroscopic measurements on high-pressure nitrogen crystals.

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