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Monte Carlo simulation of nitrogen crystalline atomic phase

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The molecular-atomic crystal transition is one of the fundamental phase transitions in the physics of condensed matter. Search of this transition in solid nitrogen has gained a stimulus in view of the considerable progress in experimental methods at high and superhigh pressures.

The possibility of an atomic phase of crystalline nitrogen to exist was first assessed by McMahan and LeSar [1] and Martin and Needs [2]. As it follows from their calculations, several atomic structures possess at high pressures a lower energy, as compared to the molecular ones. Martin and Needs [2] have established that the most stable structure in the atomic phase is the arsenic structure *A*7. A phase transition to an atomic phase in solid nitrogen has been predicted [1,2] to occur at zero temperature with an evaluated transition pressure of 1 Mbar and a volume jump of 1.7 Å^3 per atom.

This phase transition was not experimentally observed at low temperatures, which is likely to be a consequence of the large energy barrier between the phases. However, Nellis and collaborators has found a first-order phase transition in shock-compressed nitrogen fluid at higher temperatures [3]. The corresponding temperature measurements [4] provided evidence of a phase transition with a molar volume jump of 1.5 or 2 cm^2/mole. There were several attempts [5–7] to explain the physical nature of this transition. In particular, it was assumed [7] that both transitions, in the solid as well as in the liquid phases, are of the same origin. It was supposed that the transition is accompanied by a rupture of the triple chemical bond in the diatomic and a formation of three simple bonds with the three nearest atoms in the *A*7 lattice. Starting from this model, the *P–T* line of this transition has been calculated [8] for the high temperature region. To evaluate the free energy of both phases, the equation of state for the classical crystal was utilized [9]. The Monte Carlo method was used [10] to investigate the properties of the nitrogen atomic phase, the internal energy and the pressure were calculated along the $T = 1\,500$ K (1.5 kK) isotherm. A good agreement between theoretical and simulation results was recognized.

The aim of this report is to continue the investigation of the atomic nitrogen crystal using the Monte Carlo method. We did calculations on the $V = 40a_0^3$ per atom ($a_0 = 0.529 \cdot 10^{-10}$ m is the Bohr radius) for six temperatures ($T =$ 0.5, 1, 1.5, 2, 2.5, and 3 kK). Interest to the simulation of the atomic crystal at fixed volume can be understood from the following considerations. The main contribution to the variation of the properties on an isotherm comes from the energy of the static lattice. By contrast, variations with temperature of the same properties of the crystal on an isochore are mainly determined by the vibrations of the atoms in the lattice. Moreover, here one is able, in particular, to monitor relatively small variations of the pressure and the internal energy that are caused by thermal motion.

We made use of the same crystal model as previously [8], the interaction between atoms was taken as central and consisting of two components, an additive one, $\Phi(R) = AR^{-13/2}$, which describes the repulsion of the electron shells of the atoms, and a nonadditive one, $U(R) = -B \exp(-bR)$, which contributes to the formation of chemical bonds. The latter was applied only to the interaction with the three nearest neighbors. As previously [8,10], we took the following values: $A/k = 3.86 \cdot 10^5$ K, $B/k = 6.6 \cdot 10^5$ K, $b = 1.52\ \text{Å}^{-1}$.

The crystal was modeled in the following way. Initially, all the 512 atoms in the mesh were placed at sites of a simple cubic lattice whose lattice parameter was determined by the volume preset. The extra «chemical» contribution to the interaction $U(R)$ was assigned to neighboring atoms so as to form layers oriented normal to direction [111]. Then one of the fcc sublattices was shifted along direction [111] until a minimum of the total lattice energy was reached. This minimum corresponded to the *A*7 structure. Then all the atoms were given small (within 10^{-4} Å) random displacements and the process of shifting individual atoms began. These shifts were performed according to the known algorithm of Metropolis [11]. Setting a certain limit (about 0.1 Å) for atomic displacements along an axis of the Cartesian frame during one step, we chose at random one among the atoms as well as its displacements along every of the axes within the limit indicated above. We calculated the energy of interaction of the atom with all the other ones in the initial configuration, E_0, and in another configuration that arose after displacement, E. In case when either $E < E_0$ or $\exp((E_0 - E)/kT) > r$ (where r is a random value uniformly distributed within the interval (0,1)), the displacement was treated as having occurred, otherwise the atoms were restored to their initial positions and the try was repeated anew. In energy calculations we employed periodic boundary conditions. The cubic lattice under consideration was surrounded from all sides by another 26 similar cells, in which image atoms were simultaneously displaced. We took into account the interaction of the chosen atom with all the atoms in the cell plus with the images at distances less than 5 Å. In addition, to eliminate nonphysical configurations appearing at high temperatures, in which chemically bonded atoms are separated by considerable distances, we imposed a restriction on allowable distances between bonded atoms (not larger than 2 Å). At the same time, we did not impose any special conditions to guarantee preservation of the initial crystal structure.

After a certain number of steps (roughly 3 displacements on the average per every atom) we calculated the internal energy and the pressure using the virial theorem. The relaxation period over, the calculated values underwent only random oscillations around some average values, which were taken as the equilibrium values of E and P. The number of steps needed for the system to relax depends but slightly on temperature. Both the pressure and energy became stable after approximately 30,000 steps. Then we performed another 50 to 70 thousand steps to find the mean values. The time necessary for the entire calculation cycle to complete using an IBM PC 486-DX2/66 computer varied from 2 hours at high temperatures to approximately 20 hours at low temperatures. The magnitude of the most probable error for these vales was estimated against r.m.s. deviations of the individual values of temperature and pressure during a simulation run from the above-mentioned averages [10].

Calculated values of the pressure and the internal energy are summarized in Table 1 and plotted as solid rhombs in Fig. 1, borrowed from the review of Ref. 12. As one can see, the internal energy is virtually a linear function of temperature with a slope that is well consistent with the Dulong—Petit law. At the same time, the $P(T)$ dependence along the isochore studied has a tendency to flatten out into a plateau, deviating substantially from the predicted linear dependence.

Table

Monte Carlo simulation data at $V = 40a_0^3$ per atom

T, kK	P, GPa	Probable MC error, GPa	E/k, kK	Probable MC error, kK
0.5	36.12	0.31	−47.66	0.07
1.0	37.10	0.29	−46.68	0.08
1.5	37.08	0.39	−44.96	0.09
2.0	37.36	0.43	−43.32	0.12
2.5	38.74	0.49	−41.57	0.07
3.0	39.81	0.54	−39.78	0.11

These deviations are small in absolute magnitude and hence become noticeable only at fixed volume when the static-lattice contribution to the pressure is constant. The peculiarity indicated here can be observed close to the melting line of the atomic crystal, as predicted in Ref. 10. Yet, it should not be identified as melting, since the $A7$ structure survives. This is clearly demonstrated in Fig. 2, where the radial distribution function of atoms is compared at different temperatures with the arrangement of coordinate spheres of the static lattice (the vertical dashes duly scaled). As one can see, even at possibly high temperatures the long-range order survives in the system. Therefore, this anomaly can be, most likely, treated as a change of sign of the thermal expansion within a certain temperature range. This question needs further investigation.

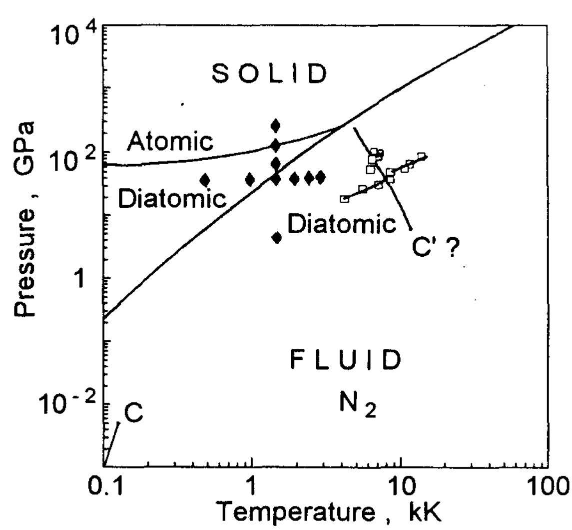

Fig. 1. A hypothetical phase diagram of nitrogen at high pressures. The solid rhombs are calculations of this paper and data of Ref. 10; the open squares are experiment by Nellis et al. [4] in the liquid. The «atomic-molecular crystal» equilibrium line as well as the melting line are plotted according to data of Ref. 8. C is the vapor-liquid critical point; C' is the hypothetical transition point «molecular fluid — polymer» [7].

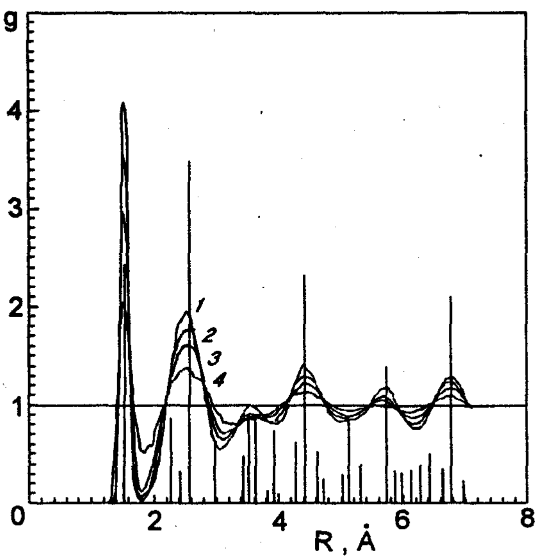

Fig. 2. Radial distribution function of atoms in the crystal at different temperatures *T* (in kK): 0.5 (*1*), 1.0 (*2*), 1.5 (*3*), and 3.0 (4). The vertical lines are the coordinate spheres of the static lattice in arbitrary scale.

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