Molecular Dynamics Simulation of Solid α-Nitrogen

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The present paper reports on Molecular Dynamics simulation of solid α-Nitrogen, using an atom-atom Lennard-Jones potential together with a point-quadrupolar interaction. Calculations were carried out at five temperatures up to 45 K; the addition of the quadrupolar term appears to improve the agreement with experiment, although this still remains rather unsatisfactory.

1. Introduction

In recent years there has been a considerable growth of interest in the properties of nitrogen, and a large amount of experimental data has been accumulated, especially for the three solid phases. On the theoretical side there have been numerous calculations of the lattice dynamical properties, using atom-atom or molecule-molecule potentials allowing for quadrupolar interactions [1–3]; much of this work was reviewed by Raich et al. who carried out self-consistent phonon calculations.

On the simulation side there have been extensive molecular dynamics calculations for both the solid and the liquid [4–8] as well as Monte-Carlo calculations [9, 10]. In all of these papers a Lennard-Jones atom-atom potential was used which, on the whole, does not seem to be very satisfactory for the solid. On the other hand, a model employing purely quadrupolar forces has also been investigated for the solid [11–15] and seems to yield better agreement with the $\alpha-\beta$ phase transition temperature as well as with the active Raman frequencies. However, neither the Lennard-Jones nor the quadrupole model seems to be completely satisfactory for a realistic description of nitrogen in the solid phase.

The present paper describes a molecular dynamics simulation of solid nitrogen using a Lennard-Jones atom-atom potential together with a point quadrupole-quadrupole interaction.

2. Model and Computational Details

The intermolecular potential for a pair of nitrogen molecules is defined by:

$$W_{ij} = \Phi_{ij} + \Psi_{ij}\,, \qquad (1)$$

where

$$\Phi_{ij} = \sum_{m=1}^{4} \varphi(r_m) \quad \text{and} \quad \varphi(r) = 4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (2)$$

and

$$\Psi_{ij} = \frac{3\,\theta^2}{4\,R^5}\left\{1 + 2\,C_{ij} - \frac{5}{R^2}\left(S_i^2 + S_j^2 + 4\,C_{ij}\,S_i\,S_j\right) + \frac{35}{R^4}\,S_i^2\,S_j^2\right\}, \qquad (3)$$

where

$$\boldsymbol{R} = \boldsymbol{R}_i - \boldsymbol{R}_j\,, \quad R = |\boldsymbol{R}|\,,$$
$$S_i = \boldsymbol{u}_i \cdot \boldsymbol{R}\,, \quad S_j = \boldsymbol{u}_j \cdot \boldsymbol{R}\,, \quad C_{ij} = \boldsymbol{u}_i \cdot \boldsymbol{u}_j\,. \qquad (4)$$

Here r_m is the distance between a pair of non-bonded atoms on molecules i and j, $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ are the coordinate vectors of their centres of mass, $\boldsymbol{u}_i$ and $\boldsymbol{u}_j$ are the unit vectors defining the molecular orientations and θ is the quadrupolar moment. The values used for the various parameters are listed in Table 1.

Table 1. Intermolecular potential parameters.

Lennard-Jones	ε	4.134 * 10^{-22} J
Lennard-Jones	σ	2.536 * 10^{-10} m
bond length	d_0	1.094 * 10^{-10} m (s. [4–6])
quadrupole moment	θ	1.30 * 10^{-26} esu cm^2 4.336 * 10^{-40} coulomb m^2

The parameters for the intermolecular potential were determined at first by fixing the quadrupolar moment to its recommended value [16] and fitting the energy and equilibrium condition for the lattice at 0 K; the values so obtained were found to give rise to a negative pressure at finite temperatures, and so they had to be adjusted by trial and error. The magnitude of the quadrupole moment falls within the range of values given in the literature [1, 16].

The second difference algorithm [17] was used for integration of the translational equations of motion; the rotational motion was also treated by a second

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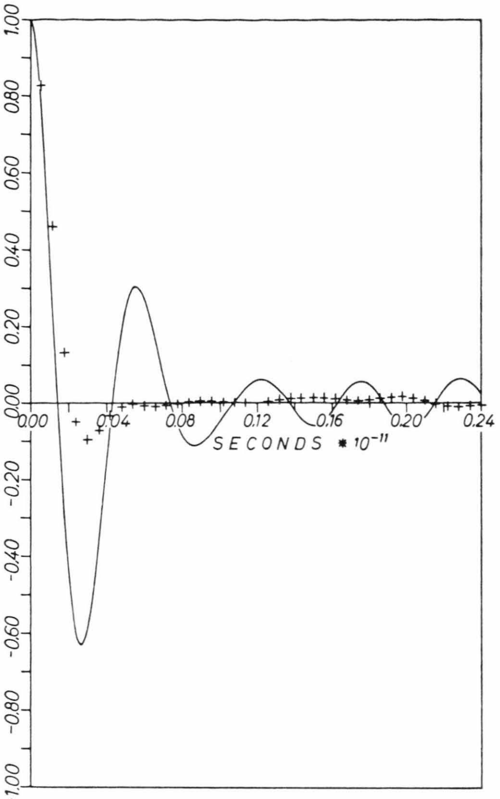

Fig. 1. Angular momentum self-correlation function at 36 K (continuous line) and 45 K (crosses).

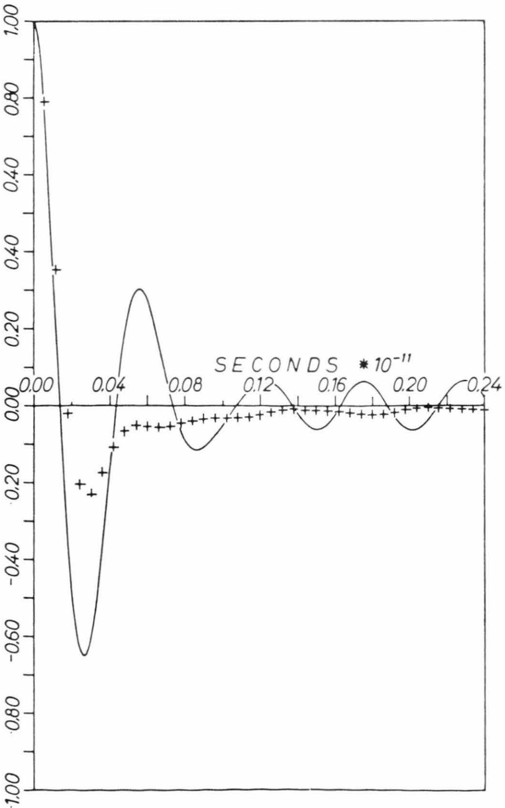

Fig. 2. Self-correlation function for the time derivative of the bond vector at 36 K (continuous line) and 45 K (crosses).

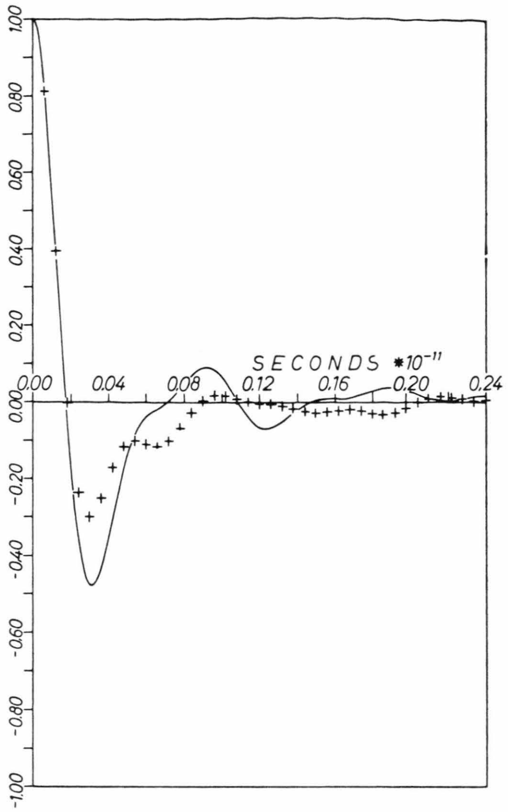

Fig. 3. Centre-of-mass velocity self-correlation function at 36 K (continuous line) and 45 K (crosses).

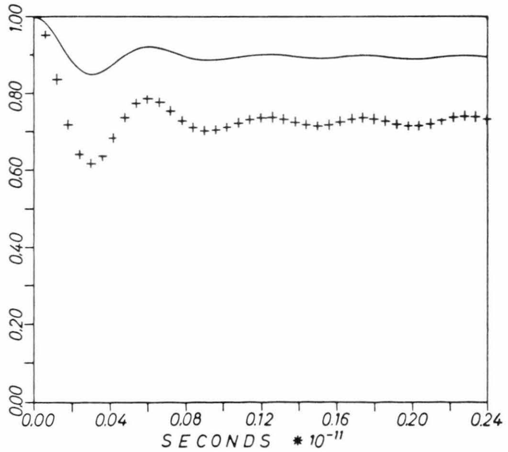

Fig. 4. ${}_1F_u$ (continuous line) and ${}_2F_u$ (crosses) at 36 K.

Table 2. The unit cell in a Pa3 lattice.

Particle	Coordinates	Orientation
1	$(\frac{1}{2}, \frac{1}{2}, 0)$	$(1, -1, -1)$
2	$(\frac{1}{2}, 0, \frac{1}{2})$	$(-1, -1, 1)$
3	$(0, \frac{1}{2}, \frac{1}{2})$	$(-1, 1, -1)$
4	$(0, 0, 0)$	$(1, 1, 1)$

difference algorithm outlined in Ref. [18] and fully developed in Reference [28]. The sample consisted of 256 particles; with a time step of $0.25 * 10^{-14}$ s, the energy was conserved to within 0.01%. The results are based on runs of 3000 steps, after 2400 steps for equilibriation. Calculations were carried out at five different temperatures and the input molar volumes correspond to the experimental values at the same temperatures and atmospheric pressure [19, 20]. Calculations were started from a configuration where particles are arranged in the Pa3 lattice (see Table 2).

3. Results and Discussion

Our results for equilibrium properties are listed in Table 3 and Quentrec's [6] are given on Table 4 for comparison. The order parameters are defined by (6),

$$O_t = \frac{1}{N}\left\langle \sum_{i=1}^{N} \cos(\boldsymbol{q}\cdot\boldsymbol{R}_i) \right\rangle$$

$$\cdot\ O_r = \frac{1}{2N}\left\{ 3\left\langle \sum_{i=1}^{N} (\boldsymbol{u}_i\cdot\boldsymbol{e}_i)^2 \right\rangle - N \right\}, \qquad (5)$$

where O_t refers to translational and O_r to rotational order, $\boldsymbol{q}$ is the vector $4\pi/a\ (1, 1, 1)$, a is the unit cell edge length and $\boldsymbol{e}_i$ is the unit vector defining the orientation of particle i in the Pa3 lattice. The addition of the quadrupolar term appears to improve the agreement between calculated and experimental energies and pressures, although this still remains rather unsatisfactory; rotational order is, in agreement with experiment- preserved to a higher temperature than with the purely diatomic potential model: our rotational order parameter is 0.83 at 36 K and falls to zero at 45 K, Quentrec's value is already zero at 25 K and the experimental $\alpha-\beta$ transition temperature is 35.6 K [19, 20]. Self-correlation functions were calculated both at 36 and 45 K for centre-of-mass velocity ($F_{\dot{x}}$), time derivative of the bond vector ($F_{\dot{u}}$), angular momentum (F_J), and the bond vector, i. e., ${}_1F_u = \langle P_1[\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)]\rangle$ and ${}_2F_u = \langle P_2[\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)]\rangle$, where P_1 and P_2 are first and second Legendre polynomials, and they were found to be broadly similar to Quentrec's [6]. At 36 K both $F_{\dot{u}}$ und F_J show an oscillating behaviour which is suppressed at 45 K, whereas their negative part is retained; at 45 K we found by least-square fitting the following long-time behaviour for ${}_1F_u$:

$${}_1F_u(t) = \exp\left(-\sum_{m=0}^{2} b_m t^m\right) \text{for } t \geqq 0.6 * 10^{-12}\,\text{s}, \quad (6)$$

$$b_0 = 0.1260;\quad b_1 = 0.8266 * 10^{12};$$
$$b_2 = 0.1181 * 10^{24}; \qquad (7)$$

at $T = 29$ K Quentrec finds that ${}_1F_u(t)$ decays exponentially for $t \geqq 0.8 * 10^{-12}$ s. The frequency spectrum (6) was calculated by Fourier-transforming $F_{\dot{x}}$ and $F_{\dot{u}}$: (8)

$$D(\omega) = \frac{1}{20\pi}\int_0^\infty \{3\,F_{\dot{x}}(t) + 2\,F_{\dot{u}}(t)\}\cos(\omega t)\,\mathrm{d}t\,.$$

Table 3. Results for equilibrium properties.

T/K	V/cm^3 mole^{-1}	$-\langle U\rangle$/J mole^{-1}	$\langle p\rangle$/atm	O_r	O_t	expt $-H$/J mole^{-1} (s. [19])
12	27.09	6806	30	0.98	0.98	7065 (10 K)
19.5	27.23	6484	218	0.97	0.97	7044 (20 K)
26.7	27.68	6159	176	0.96	0.96	6679 (30 K)
36	28.86	5583	66	0.85	0.93	6462 (35.6 K)
45	29.56	4704	429	0.00	0.81	6065 (40 K) β-phase
						5669 (50 K) β-phase

Table 4. Quentrec's results for equilibrium properties [6].

ϱ^*	T^*	V/cm^3 mole	T/K	$-\langle U\rangle$/J mole^{-1}	$\langle p\rangle$/atm	O_r	O_t
0.841	0.16	26.70	7	8927	180	0.97	0.99
0.841	0.47	26.70	20.7	8569	1014	0.67	0.95
0.841	0.66	26.70	29	8306	1635	0.00	0.86
0.817	0.39	27.49	17.2	8653	−33	0.82	0.97
0.817	0.43	27.49	18.9	8521	229	0.21	0.92
0.817	0.57	27.49	25.1	8375	556	0.00	0.84

ϱ^* and T^* are reduced density and temperature, as defined in the original paper.

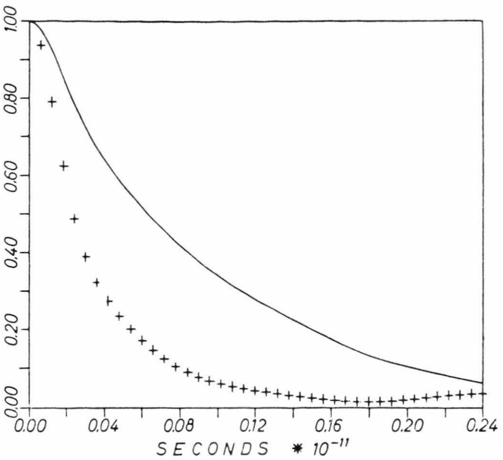

Fig. 5. $_1F_u$ (continuous line) and $_2F_u$ (crosses) at 45 K.

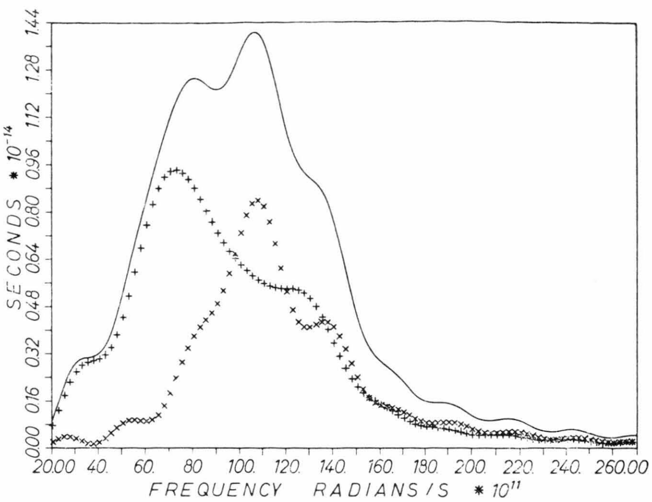

Fig. 6. Frequency spectrum at 36 K: total (continuous line), translational (+) and rotational contribution (×).

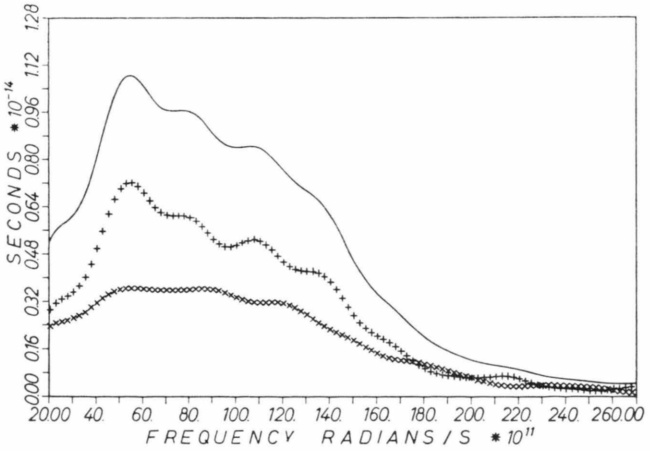

Fig. 7. Frequency spectrum at 45 K: total (continuous line), translational (+) and rotational contribution (×).

At $T = 36$ K the translational part of $D(\omega)$ exhibits a broad maximum at 38.5 cm^{-1} and the rotational contribution has a broad maximum at 57 cm^{-1}. Although no straightforward comparison is possible with phonon frequencies at zero wave-vector [6], these values roughly correspond to known translational (49 cm^{-1} at 30 K) [21] and rotational modes (62 cm^{-1} at 18 K) [22, 23]; at temperatures around 20 K Quentrec finds broad maxima at about 37 cm^{-1} for the rotational contribution and 79 cm^{-1} for the translational one.

Mean square force and torque were also calculated from $F_{\dot{x}}$ and F_J; one has

$$\langle \boldsymbol{F}(0)\cdot\boldsymbol{F}(t)\rangle = -\frac{1}{3\,k\,T\,m}\,\frac{\mathrm{d}^2}{\mathrm{d}t^2}\,F_{\dot{x}} \quad \text{and}$$

$$\langle \mathbf{Q}(0)\cdot\mathbf{Q}(t)\rangle = -\frac{1}{2\,k\,T\,I}\,\frac{\mathrm{d}^2}{\mathrm{d}t^2}\,F_J \qquad (9)$$

thus

$$\langle \boldsymbol{F}\cdot\boldsymbol{F}\rangle = -\frac{1}{3\,k\,T\,m}\left|\frac{\mathrm{d}^2}{\mathrm{d}t^2}\,F_{\dot{x}}\right|_{t=0}$$

and

$$\langle \mathbf{Q}\cdot\mathbf{Q}\rangle = -\frac{1}{2\,k\,T\,I}\left|\frac{\mathrm{d}^2}{\mathrm{d}t^2}\,F_J\right|_{t=0}, \qquad (10)$$

where m is the molecular mass and I is the moment of inertia. Mean square forces and torques were also used to calculate the vapour pressure isotopic separation factor, which does not seem to have been measured for the solid so far. The vapour pressure isotopic separation factor is defined by [24, 25]

$$\alpha = \left[\frac{N_A}{N_B}\right]_v \left[\frac{N_B}{N_A}\right]_c, \qquad (11)$$

Table 5

	$T = 36$ K	$T = 45$ K	
$\langle \boldsymbol{F}\cdot\boldsymbol{F}\rangle$	4.73 * 10^{-21}	6.08 * 10^{-21}	Newton [2]
$\langle \boldsymbol{Q}\cdot\boldsymbol{Q}\rangle$	4.68 * 10^{-42}	1.64 * 10^{-41}	Joule [2]
$\ln \alpha - {}^{14}\mathrm{N}\,{}^{15}\mathrm{N}$	1.95 * 10^{-2}	2.23 * 10^{-2}	
$\ln \alpha - {}^{15}\mathrm{N}_2$	4.00 * 10^{-2}	4.52 * 10^{-2}	
	$T = 66.66$ K	$T = 73.30$ K	
$\ln \alpha - {}^{14}\mathrm{N}\,{}^{15}\mathrm{N}$	5 * 10^{-3}	4.9 * 10^{-3}	Calculated in Ref. [29]
$\ln \alpha - {}^{15}\mathrm{N}_2$	1.05 * 10^{-2}	9.79 * 10^{-3}	
$\ln \alpha - {}^{14}\mathrm{N}\,{}^{15}\mathrm{N}$	5.9 * 10^{-3}	4.6 * 10^{-3}	Expt. results Ref. [25]
$\ln \alpha - {}^{15}\mathrm{N}_2$	1.16 * 10^{-2}	9.2 * 10^{-3}	

where N are numbers of molecules, the subscripts v and c refer to the vapour and condensed phase respectively, A refers to the lighter isotopic species and B to the heavier one; a was calculated applying the treatment given by Gordon [26]. The vibrational frequencies needed in connection with it were taken from Refs. [22] and [27], and the force constant was assumed to be isotope independent [29]. Results are given in Table 5, together with the results for the liquid calculated by Thompson, Tildesley and Streett [29] using a purely diatomic potential model.

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[1] J. C. Raich, N. S. Gillis, and A. B. Anderson, J. Chem. Phys. **61,** 1399 [1974].

[2] J. C. Raich, N. S. Gillis, and T. R. Koehler, J. Chem. Phys. **61,** 1411 [1974].

[3] E. Huler and A. Zunger, Phys. Rev. B **12,** 5878 [1975].

[4] J. Barojas, D. Levesque, and B. Quentrec, Phys. Rev. A **7,** 1092 [1973].

[5] B. Quentrec and C. Brot, Phys. Rev. A **12,** 272 [1975].

[6] B. Quentrec, Phys. Rev. A **12,** 282 [1975].

[7] J. J. Weis and M. L. Klein, J. Chem. Phys. **63,** 2869 [1975].

[8] P. S. Y. Cheung and J. G. Powles, Mol. Phys. **30,** 921 [1975].

[9] T. G. Gibbons and M. L. Klein, Chem. Phys. Lett. **29,** 463 [1974].

[10] S. Romano, Z. Naturforsch. **31 a,** 1108 [1976].

[11] M. Mandel, J. Chem. Phys. **60,** 1432 [1974].

[12] M. Mandel, J. Chem. Phys. **60,** 4880 [1974].

[13] S. Romano, Z. Naturforsch. **29 a,** 1631 [1974].

[14] J. C. Raich and R. D. Etters, J. Low. Temp. Phys. **7,** 449 [1972].

[15] J. C. Raich, J. Chem. Phys. **56,** 2395 [1973].

[16] D. E. Stogryn and A. P. Stogryn, Mol. Phys. **11,** 371 [1966].

[17] L. Verlet, Phys. Rev. **159,** 98 [1967].

[18] E. M. Gosling and K. Singer, Chem. Phys. Lett. **39,** 361 [1976].

[19] F. Din, Thermodynamic Functions of Gases, Vol. 3, Butterworth, London 1961.

[20] D. C. Heberlein, E. D. Adams, and T. A. Scott, J. Low. Temp. Phys. **2,** 449 [1970].

[21] R. V. St. Louis and O. Schnepp, J. Chem. Phys. **50,** 5177 [1969].

[22] A. Anderson, T. S. Sun, and M. C. A. Donkersloot, Can. J. Phys. **48,** 2265 [1970].

[23] F. D. Medina and W. B. Daniels, Phys. Rev. Lett. **32,** 167 [1976].

[24] E. Ancona, G. Boato, and G. Casanova, Nuovo Cimento **24,** 111 [1962].

[25] G. Jancso and W. A. van Hook, Chem. Rev. **74,** 689 [1974].

[26] R. G. Gordon, J. Chem. Phys. **44,** 576 [1976].

[27] International Tables of Selected Constants. Spectroscopic data relative to Diatomic Molecules. Pergamon Press, 1970.

[28] K. Singer, A. J. Taylor, and J. Singer, to be published.

[29] S. M. Thompson, D. J. Tildesley, and W. B. Street, Mol. Phys. **32,** 711 [1976].