Monte-Carlo Simulation of Nitrogen

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The subject of the present paper is computer simulation of α-solid and liquid nitrogen, using a Lennard-Jones atom-atom potential and the isothermal-isobaric Monte-Carlo method. Two sets of calculations were performed, both at the same pressure (1 atm) and temperatures (α-solid at 25 and 35.6 K, liquid at 63.15 and 77.35 K). In the first set the molecules are assumed to be rigid, whereas in the second they are allowed to vibrate; the molecular vibration is treated classically and assumed to be harmonic. Comparison are mode between the two models and with experiment.

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 and molecule-molecule potentials allowing for quadrupolar interactions. Much of this work has been reviewed in recent papers by Raich et al.[1, 2] who carried out self-consistent phonon calculations using an atom-atom potential, but obtained only qualitative agreement with experiment.

On the simulation side there have been extensive molecular dynamics calculations both for the solid and the liquid[3–7] as well as Monte Carlo simulation of the compressed solid by Gibbons and Klein[8]. In all these papers a Lennard-Jones atom-atom potential was used which, on the whole, does not seem to be very satisfactory, at least for the solid. On the other hand, a model employing purely quadrupolar forces has also been investigated for the solid[9–13] and seems to yield a better agreement with the $\alpha-\beta$ phase transition temperature as well as with Raman active frequencies. However neither the Lennard-Jones nor the quadrupolar model seems wholly satisfactory for the lattice dynamical properties.

In all previous simulation work the molecules have been assumed to be rigid; the object of the present paper is a Monte Carlo simulation of α-solid and liquid nitrogen using a Lennard-Jones atom-atom potential. Two sets of calculations were carried out, both assuming the same intermolecular potential: in the first model the molecules were assumed to be rigid, whereas in the second they were allowed to vibrate. This allowed a test of the parameters for the atom-atom potential with respect to thermodynamical properties and, by comparison between the two models, to assess the effect of molecular vibrations on thermodynamic properties, which might be expected to be small.

2. Model and Computational Details

The Lennard-Jones atom-atom potential used here was the same as in Quentrec's calculations[3–5]; the intramolecular potential was also treated classically and assumed to be harmonic, i. e.

$$G(d) = \tfrac{1}{2}\chi(d-d_0)^2, \qquad (1)$$

where d_0 is the equilibrium internuclear distance (bond length) and χ is the force constant for the bond. The values used for the various parameters are listed in Table 1.

Table 1. Potential energy parameters.

Lennard-Jones	ε	$6.067 \cdot 10^{-15}$ erg
Lennard-Jones	σ	3.341 Å
Bond length	d_0	1.094 Å
Force constant	χ	$2.297 \cdot 10^{-10}$ erg Å^{-2} (see[14])

The isothermal-isobaric (or $N p T$) Monte Carlo method was chosen here, in order to achieve a straightforward comparison between calculated and experimental quantities, which are usually measured at constant pressure rather than at constant volume.

In $N p T$ Monte Carlo calculations one deals with a sample consisting of N particles in a box (usually cubic) surrounded by a periodic replica of itself. Temperature T and pressure p are assigned, whereas the cell edge length and hence the interparticle sepa-

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rations are variable. At each step a particle is selected, either randomly or cyclically, and small random changes are imposed on its coordinates and to the cell edge length; by so doing the potential energy changes from U in the old configuration to U' in the trial configuration and the cell volume changes from V to V'. The pseudo-Boltzmann factor

$$\Delta = U' - U + p(V' - V) - N k T \ln(V'/V)\,, \qquad (2)$$

is calculated and if $\Delta \leqq 0$ the new configuration is accepted; if $\Delta > 0$, the new configuration is accepted with a probability equal to $\exp\{-\Delta/kT\}$. If the trial configuration is rejected, the old one is restored and in either case the current value of any function of coordinates is accumulated in order to evaluate its average.

In our case $N = 256$ and calculations were carried out for both models at $p = 1$ atm and at the following temperatures 25, 35.6 (experimental $\alpha-\beta$ transition temperature), 63.15 (liquid at the freezing point) and 77.35 K (liquid at the boiling point). In the solid phase ($T = 25$ and $T = 35.6$ K) calculations were started with a Pa3 lattice (see Table 2).

Table 2. The elementary 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	$(0, 0, 0)$	$(1, 1, 1)$

The use of the NpT ensemble imposed a particular treatment of the atom-atom potential. The interaction energy between any two molecules i and j is given by

$$\Phi_{ij} = \sum_{a=1}^{4} v(\zeta_a)\,;\ v(\zeta_a) + 4\,\varepsilon \left[\left(\frac{\sigma}{\zeta_a}\right)^{12} - \left(\frac{\sigma}{\zeta_a}\right)^{6}\right], \qquad (3)$$

where ζ_a is the distance between a pair of nonbonded atoms on molecules i and j. Let $\boldsymbol{r}_i = (x_i, y_i, z_i \mid 0 \leqq x_i, y_i, z_i \leqq 1)$ be the dimensionless centre-of-mass coordinates of molecules, let $\boldsymbol{u}_i$ be the unit bond vectors defining their orientations, let d_i be their internuclear distances and finally let a be the cell edge length. For any real positive number n we have

$$\left(\frac{1}{\zeta_a}\right)^{2n} = [\boldsymbol{s}\cdot\boldsymbol{s}\,a^2 + a\,\boldsymbol{s}\cdot(\varrho_a d_i \boldsymbol{u}_i - \varrho_a' d_j \boldsymbol{u}_j) + \tfrac{1}{4}(\varrho_a d_i \boldsymbol{u}_i - \varrho_a' d_j \boldsymbol{u}_j)^2]^{-n}\,, \qquad (4)$$

$\boldsymbol{s} = \boldsymbol{r}_i - \boldsymbol{r}_j$; $\varrho_a, \varrho_a' = \pm 1$ (all possible combinations).

Let $b = 1/a$, then Eq. (4) becomes

$$\left(\frac{1}{\zeta_a}\right)^{2n} = b^{2n}\left[\boldsymbol{s}\cdot\boldsymbol{s} + b\,\boldsymbol{s}\cdot(\varrho_a d_i \boldsymbol{u}_i - \varrho_a' d_i \boldsymbol{u}_j) + \frac{b^2}{4}(\varrho_a d_i \boldsymbol{u}_i - \varrho_a' d_j \boldsymbol{u}_j)^2\right]^{-n}. \qquad (5)$$

The second factor in Eq. (5) is expanded as a Taylor-MacLaurin series, then we sum over α; in our case ($n = 3$ and $n = 6$) the series can be truncated at the fifth order term with sufficient accuracy; odd-order derivatives cancel out and we eventually obtain

$$\sum_{\alpha=1}^{4}\left(\frac{1}{\zeta_a}\right)^{2n} = b^{2n}\left\{\frac{1}{A^n} + \frac{b^2}{2!}\left[\frac{\Gamma(n+2)}{\Gamma(n)}\frac{B^2}{A^{n+2}} - 2\,\frac{\Gamma(n+1)}{\Gamma(n)}\frac{C}{A^{n+1}}\right]\right. \qquad (6)$$

$$\left. + \frac{b^4}{4!}\left[\frac{\Gamma(n+4)}{\Gamma(n)}\frac{B^4}{A^{n+4}} - 12\,\frac{\Gamma(n+3)}{\Gamma(n)}\frac{B^2 C}{A^{n+3}} + 12\,\frac{\Gamma(n+2)}{\Gamma(n)}\frac{C^2}{A^{n+2}}\right]\right\},$$

where $$A = \boldsymbol{s}\cdot\boldsymbol{s}\,;\quad B^2 = 4\,[(\boldsymbol{s}\cdot\boldsymbol{u}_i)^2 d_i^2 + (\boldsymbol{s}\cdot\boldsymbol{u}_j)^2 d_j^2]\,;\ C = d_i^2 + d_j^2\,, \qquad (7)$$

this kind of treatment for inverse-power atom-atom potentials was described by Goodings and Henkelman[15]. This manipulation gives the intermolecular potential as a sum of products of inverse powers of the cell edge length, each of them multiplied by a quantity which only depends on the various coordinates of particles. This implies that at each step the program just needs to calculate interactions between the selected particle and all others and perform an appropriate scaling. On the other hand, if Eq. (5) is used, then at each step all pair interactions must be recalculated, which is quite impracticable; with the vibrating model, of course, at each step the internuclear distance is also given a small random change. A detailed discussion of the NpT method is available elsewhere[16, 17]; for another example of manipulation of the intermolecular potential in connection with NpT Monte Carlo calculations see reference [18].

The results quoted here are averages over 200000 configurations together with a similar number for equilibration; the statistical errors were calculated from subaverages over 50000 configurations. The computations are rather time-consuming: the program used in the present work generates 45 configurations per second on the CDC 6600 at the University of London Computer Centre.

3. Results and Discussion

The calculated thermodynamic quantities include the Lennard-Jones potential energy $W = \sum_{i=1}^{N} \sum_{j>i} \varphi_{ij}$, the vibrational energy $E = \sum_{i=1}^{N} G(d_i)$ and the enthalpy, which is defined by

$$H = W + pV + \tfrac{5}{2} NkT, \qquad (8)$$

for rigid molecules and by

$$H = W + E + pV + 3NkT, \qquad (9)$$

for vibrating molecules.

In the NpT ensemble the mean value of a function $f(\tau, V)$ of coordinates and volume is defined by

$$\langle f \rangle = \frac{\int_0^\infty \exp\{-\beta p V\} V^N \int f \exp\{-\beta U\} \, \mathrm{d}\tau \, \mathrm{d}V}{\int_0^\infty \exp\{-\beta p V\} V^N \int \exp\{-\beta U\} \, \mathrm{d}\tau \, \mathrm{d}V}, \qquad (10)$$

where $\beta = 1/kT$, U is the potential energy (i.e. $U = W$ or $U = W + E$) and $\int \ldots \mathrm{d}\tau$ indicates integration over all coordinates. From Eq. (10) we find

$$\left(\frac{\partial \langle f \rangle}{\partial T}\right)_p = \frac{\beta}{T} \left[\langle f(U + pV) \rangle - \langle f \rangle \langle U + pV \rangle\right], \qquad (11)$$

and

$$\left(\frac{\partial \langle f \rangle}{\partial p}\right)_T = \beta \left[\langle f \rangle \langle V \rangle - \langle f V \rangle\right]. \qquad (12)$$

Isothermal compressibility, isobaric expansivity and specific heat were calculated from Eqs. (11) and (12). Compresibilities and expansivities calculated for the two models were found to agree broadly with each other and with available experimental data (21, 23) within a rather large statistical error (5 – 10%). As for the specific heat, the agreement with experiment is rather poor for both models (see Table 7). On the whole, both models agree reasonably well with experiment for molar volume (within 4%), although the agreement is rather worse for enthalpy, where discrepancies may be as large

Table 3. Lennard-Jones energy.

	$-\langle W \rangle/J$ mole^{-1}	
T/K	Rigid model	Vibrating model
25	8257 ± 19	8246 ± 18
35.6	7969 ± 6	8024 ± 13
63.15	6933 ± 31	6807 ± 19
77.35	6473 ± 22	6449 ± 26

Table 4. Vibrational energy.

T/K	$\langle E \rangle/J$ mole^{-1}	$2\langle E \rangle/RT$	$10^4 \langle (d-d_0)^2 \rangle/\text{Å}^2$
25	110 ± 1	1.04	0.16
35.6	151 ± 2	1.02	0.22
63.15	273 ± 4	1.04	0.39
77.35	341 ± 1	1.06	0.48

Table 5. Molar volumes.

T/K	$\langle V \rangle/\mathrm{cm}^3$ mole^{-1}		
	Rigid model	Vibrating model	Expt. [21–23]
25	27.99 ± 0.04	28.01 ± 0.04	27.23
35.6	28.70 ± 0.02	28.56 ± 0.03	27.68
63.15	31.82 ± 0.10	32.22 ± 0.07	32.22
77.35	33.51 ± 0.08	33.57 ± 0.11	34.67

Table 6. Enthalpies.

T/K	$-\langle H \rangle/J$ mole^{-1}		
	Rigid model	Vibrating model	Expt. [21, 23]
25	7734 ± 19	7510 ± 18	6766 (20 K), 6401 (30 K)
35.6	7226 ± 6	6982 ± 11	6284
63.15	5618 ± 31	4956 ± 19	4187
77.35	4862 ± 22	4175 ± 26	3378

Table 7. Specific heats.

T/K	C_P/J mole^{-1} K^{-1}		
	Rigid model	Vibrating model	Expt. [21, 23]
25	33 ± 3	45 ± 8	27
35.6	34 ± 2	40 ± 2	48
63.15	34 ± 10	46 ± 10	56
77.35	35 ± 2	42 ± 5	58

Table 8. Quentrec's molecular dynamics results for thermodynamic properties [3–5].

T^*	ϱ^*	T/K	V/cm^3 mole^{-1}	$-\langle W\rangle/J$ mole^{-1}	$\langle p\rangle$/atm
0.57	0.817	25.05	27.49	8374	556
1.51	0.6964	66.40	32.25	6902	50
0.76	0.6964	77.35	32.25	6756	346

as 40%. However the vibrating model is in better accord with the observed enthalpy than the static model. Quentrec's results for our temperatures are given in Table 8, and seem to be in qualitative agreement with the results for the rigid model. We have converted our values of enthalpy and molar volume for the rigid model to Quentrec's pressures using the calculated values of

$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and $-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ and the relationship

$$\left(\frac{\partial H}{\partial p}\right)_T = V\left\{1 - T\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right\}, \qquad (13)$$

The two sets of results agree to within a few percent. As Tables 3 and 5 suggest, the vibrations have no effect on either the Lennard-Jones energy or the volume at 25 K, and this can be explained by the very small vibrational amplitude; at 77.35 K the vibrations again have no significant effect, but they have a small effect at the two intermediate temperatures. This might be caused by the model system being in the neighbourhood of phase transitions at these temperatures, which correspond to transitions for the real system. It is also to be noticed that at each temperature the vibrational energy is only a few percent higher than the value $RT/2$, corresponding to oscillations which do not affect the Lennard-Jones potential (see Eqs. (6) and (7)). The mean value of $(d-d_0)^2$ is about 10^{-5} Å^2, which is small in comparison with d_0^2; this justifies the harmonic approximation.

Rotational and translational order paratemers defined by [19, 20]

$$O_{\mathrm{t}} = \frac{1}{N}\left\langle\sum_{i=1}^{N}\cos(\boldsymbol{k}\cdot\boldsymbol{r}_i)\right\rangle; \quad O_{\mathrm{r}} = \frac{1}{N}\left\langle\sum_{i=1}^{N}(\boldsymbol{e}_i\cdot\boldsymbol{u}_i)\right\rangle \qquad (14)$$

were also calculated.

Here $\boldsymbol{k}$ is an arbitrary vector in the reciprocal space, for example $(2\pi/a)$ (1,1,1), and $\boldsymbol{e}_i$ is he unit vector defining the orientation of particle i in the Pa3 lattice. For the solid O_{t} is of the order unity, and is zero within $\pm N^{-\frac{1}{2}}$ when translational order is lost, as in a fluid. O_{r} has its maximum value 1 when the molecules are completely ordered. In agreement with Quentrec's results [4–6] in both models O_{r} is already zero at 25 K whereas O_{t} remains of the order of 0.8 at 25.6 K. Both O_{t} and O_{r} are zero in the liquid. Center-of-mass radial distribution functions were only calculated for the vibrating model and appear to be in broad agreement with Quentrec's results [4–6] (see Table 9).

Table 9. Centre-of-mass radial distribution function $g(r)$. All distances are given in Å; h is the closest approach distance; $R_1(R_2)$ is the position of the first (second) maximum; $r_1(r_2)$ is the position of the first (second) minimum; $M_1(M_2)$ is the height of the first (second) maximum. $n_{\mathrm{c}} = 4\pi\frac{(N-1)}{V}\int_0^{r_1} r^2 g(r)\,\mathrm{d}r$ is the coordination number.

T/K	h	R_1	M_1	r_1	n_{c}	R_2	M_2	r_2
25	3.34	4.00	7.49	4.90	12.0	5.70	1.50	6.25
35.6	3.35	4.00	6.04	4.90	12.0	5.75	1.14	6.35
63.15	3.10	4.05	2.88	5.50	12.7	7.05	1.31	9.15
77.35	3.05	4.05	2.58	5.55	12.6	7.25	1.36	9.20

Given the smallness of the effect of intramolecular vibrations on the thermodynamic properties, at present there seems to be not great need for including them; however there is a greater need for refining the parameters of the intermolecular potential and/or improving its analytical form.

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