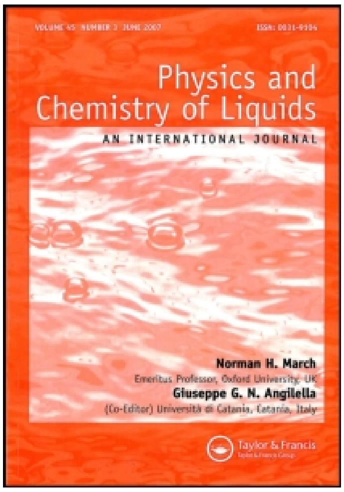

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# Study of Solid Phases of Cyclohexane by Molecular Dynamics Calculations

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# STUDY OF SOLID PHASES OF CYCLOHEXANE BY MOLECULAR DYNAMICS CALCULATIONS

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With an improved six-centre Lennard–Jones pair potential the recently started molecular dynamics (MD) investigation of rotator phases in cyclohexane was extended. The phase transition from the liquid to the plastic phase of fcc structure (solid I) could be more precisely determined and analyzed in terms of time correlation functions. The transition from the solid I to the low-temperature solid phase II could also be observed. Both transitions occur at thermodynamic conditions, which are in good agreement with experimental findings. This seems to be a good indication of the applicability of the present potential model. In order to study in detail the rotations around the symmetry-axes C2 and C3 of the molecules, suitable angle-distributions for nearest neighbour molecule pairs have been determined. The results show that relatively small changes of the rotational dynamics occur for the liquid-plastic transition, while the solid I–solid II transition is accompanied by strong alterations of the rotational behaviour. In particular, our findings contrast with accepted experimental evidence for the fact that rotations around the C3-axis are less hindered than those around the C2-axis in solid I phase.

KEY WORDS: Plastic phase, phase transition, rotational dynamics

## 1 INTRODUCTION

In recent work[1] we began an investigation of rotator phases of cyclohexane by molecular dynamics (MD) calculations using a six-centre Lennard-Jones pair potential and rigid model-molecules. We improved this potential model insofar as the experimental nearest neighbour separation is now exactly reproduced by the MD lattice[2] and the measured bond-angles between the basic C-atoms of cyclohexane are retained in the six-centre model molecule.

Using this optimized interaction model we determined the phase transitions of model cyclohexane in terms of the behaviour of the lower order reorientational time correlation functions, as described in[1]. The improvements were

i) maintenance of the fcc structure of the plastic phase
ii) study of the dynamic behaviour of the C2 and C3 symmetry-axes
iii) inclusion of a wide range of experimentally known thermodynamic states.

Moreover we determined suitable angle-distributions of nearest neighbour pairs of molecules to shed light on the molecular rotations with respect to the C2 and C3 symmetry-axes. The results are compared with those found from simple static model calculations and experimental investigations.

## 2 POTENTIAL, MD CALCULATIONS AND STATES

The potential model includes six-centre Lennard-Jones (LJ) pair interactions and a rigid molecule structure designed to reflect exactly the configuration of the basic C-atoms in cyclohexane. The H-atoms are only indirectly accounted for by an enlarged "bond-length" and a suitable $\sigma$-parameter of the LJ potential. LJ parameters, "bond-length" and "bond-angle" parameters are given in Table 1. It should be noted that the present potential model generates good thermodynamics and excellent transport coefficients of liquid cyclohexane. This comparison is made in a separate paper[3]. So the model is also usable for mimicking the liquid state of cyclohexane.

A few words to the MD computations are in order, although the computations have essentially been carried out in the manner described in[1]. To have sufficient statistical certainty for the average values of the time correlation functions and the angle-distributions, all the computations were done with 108 molecules and at least 10000 integration steps (see Table 2 for details). The evaluation of one angle-distribution required little more computer time than evaluation of a radial pair distribution function. For each chosen state, we started from a previous end-configuration and discarded the following 20000–30000 MD steps to ensure the new equilibrium. The course to equilibrium was recorded by calculating the radial pair correlation function and the mean square displacement of the molecules.

Density and temperature of the investigated states as well as the phase diagram of cyclohexane have been reported previously[4–5].

The most important thermodynamic conditions are summarized in Tables 3–4. These tables contain also MD pressures, which have been determined with only low

**Table 1** Potential model used for the description of the pair interaction in liquid and solid cyclohexane.

| | |
|---|---|
| Potential model | 6-center LJ |
| Shape of a molecule | chair form[1] |
| Separation between nearest LJ centers | 1.60E-10 m |
| Bond angles | 111.34 |
| Mass connected with one LJ center | 14.027 a.u. |
| LJ parameters: | |
| $\varepsilon/k$ | 78 K |
| $\sigma$ | 3.97E-10 m |

**Table 2** Technical details of the MD calculations.

| | |
|---|---|
| Number of molecules | 108 |
| Time step | 0.5E-14 s |
| Total number of integration steps | 10000<br>(for time correlation functions)<br>30000–70000<br>(for angle-distributions) |
| Computation time per 1000 steps | 150 s |
| Cutoff of the LJ potential | 3.2–3.25 $\sigma$ |

**Table 3** Thermodynamic states considered for the reorientational time correlation functions. The experimental temperature is constant. $T \approx 337.9$ K.

| *σ (g cm$^{-3}$)* | *p (bar)* | | *T (K)* |
|---|---|---|---|
| | *Exper.* | *MD* | |
| 0.7356 | 1 | −360 | 345 |
| 0.7467 | 100 | −275 | 344 |
| 0.7644 | 300 | −30 | 336 |
| 0.7720 | 400 | 210 | 341 |
| 0.7790 | 500 | 355 | 340 |
| 0.7856 | 600 | 415 | 340 |
| 0.7919 | 700 | 620 | 338 |
| 0.7974 | 800 | 820 | 339 |
| 0.8030 | 900 | 990 | 349 |
| 0.8082 | 1000 | 1120 | 343 |
| 0.8129 | 1100 | 1255 | 339 |
| 0.8495 | 1300 | 2875 | 342 |
| 0.8535 | 1400 | 3170 | 349 |
| 0.8568 | 1500 | 3400 | 349 |
| 0.8599 | 1600 | 3500 | 346 |
| 0.8627 | 1700 | 3700 | 348 |
| 0.8654 | 1800 | 3760 | 344 |
| 0.8680 | 1900 | 4000 | 342 |
| 0.8705 | 2000 | 4080 | 343 |
| 0.8731 | 2100 | 4210 | 342 |
| 0.8754 | 2200 | 4450 | 346 |
| 0.8779 | 2300 | 4530 | 340 |
| 0.8803 | 2400 | 4790 | 346 |
| 0.8846 | 2600 | 4960 | 344 |
| 0.8904 | 2900 | 5390 | 338 |

Experimental data from[5].

**Table 4** Thermodynamic states considered for the angle distributions.

| *state point* | *σ (g cm$^{-3}$)* | *T (K)* | *p (bar)* | *comment* |
|---|---|---|---|---|
| 1 | 0.8299 | 294 | 1200 | solid I |
| 2 | 0.8386 | 288 | 1440 | |
| 3 | 0.8452 | 273 | 1440 | |
| 4 | 0.8506 | 261 | 1480 | |
| 5 | 0.8568 | 249 | 1510 | |
| 6 | 0.8626 | 223 | 1210 | |
| 7 | 0.8691 | 222 | 1500 | |
| 8 | 0.8746 | 217 | 1650 | |
| 9 | 0.8794 | 198 | 90 | solid II |
| 10 | 0.8854 | 198 | 310 | |

The MD pressures have been obtained with short potential cut off.

accuracy. A more stringent comparison of MD pressure values and experimental data is presented in[3].

## 3 RESULTS

### *3.1 Liquid-plastic phase transition*

Using the time decay of the two lower order reorientational correlation functions $C^1(t)$ and $C^2(t)$ we determined the phase transition from the high temperature plastic phase (solid I) to the liquid phase. The same technique as described in Ref. 1 was used; however, a larger number of thermodynamic states was considered. Results are plotted in Figures 1–2.

The noticeable sudden change in the slope of the plots indicates clearly the range of the phase transition, which is in good agreement with the experimentally determined region marked in Table 3 and visible in the plots by the gap, which

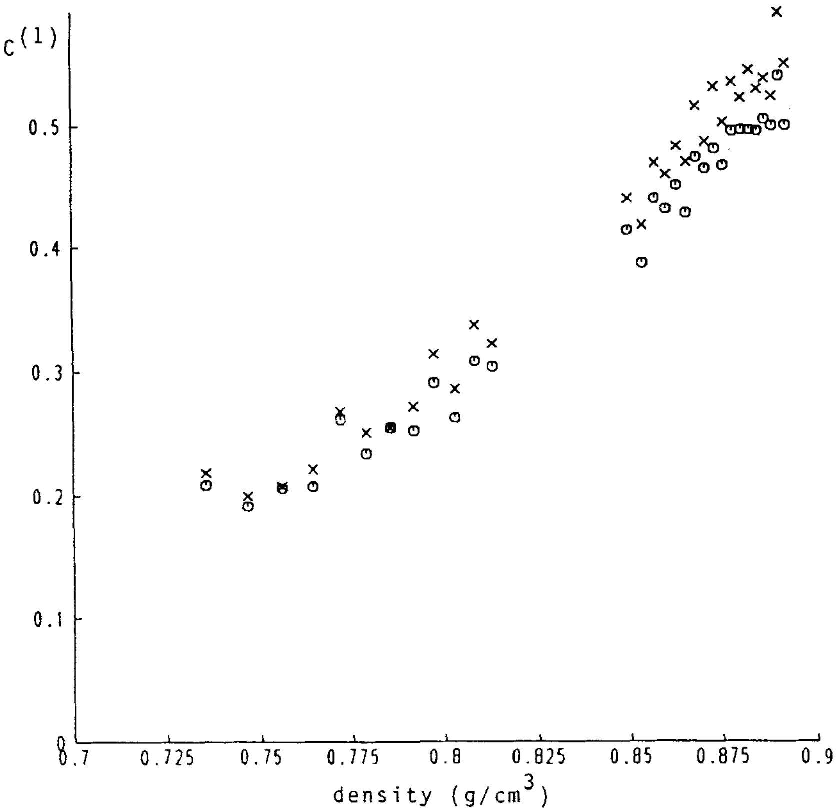

**Figure 1** Characteristic decay amplitudes (after 2 ps) of the first order normalized reorientational time correlation function for two symmetry axes as a function of density. The density gap indicates the experimental volume jump. T = 345 K. xxx rotation of the C2-axes; ooo rotation of the C3-axis.

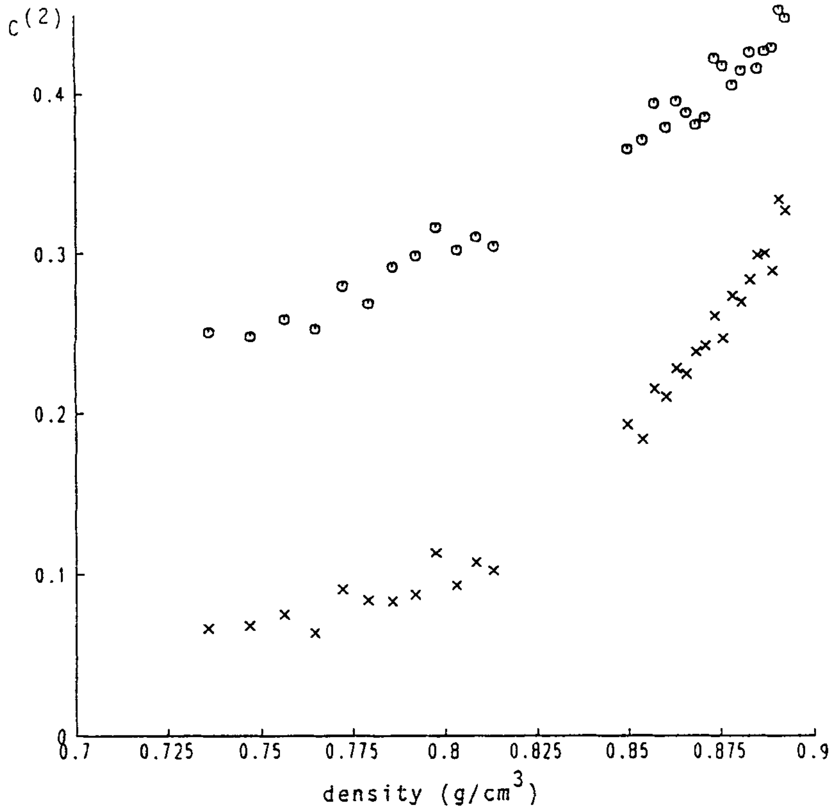

**Figure 2** As in Figure 1, but for the second order reorientational time correlation function.

corresponds to the experimental volume jump. Comparison of Figures 1 and 2 shows furthermore that the higher order reorientational TCF $C^2(t)$ is better suited for the indication of the phase transition. The $C^2(t)$-function displays also lower decay rates for rotations of the C3-axis around the C2-axis than for rotations of the C2 symmetry axis. This is intuitively expected due to the stronger hindrance of the molecules for rotations around the C2 symmetry axis.

In order to investigate the molecule motion of nearest neighbours in the rotator phase, we computed the angle-distribution of nearest neighbour pairs with respect to their symmetry axes C2 and C3. The average values for these distributions were thereby formed with at least 10000 events. Hence the statistical uncertainty can be estimated to a few percent. We have plotted examples of distributions of a near-liquid and a far-from-liquid state of the solid I phase for the C2 and C3 axes in Figure 3. The distributions are normalized by that of a completely disordered low density state of model-cyclohexane.

While the distributions are nearly uniform for the orientations of the C3-axis, distributions for the C2-axes show a dependence on temperature and density. For the C2-axes, the angle-distribution is uniform at higher temperatures and lower

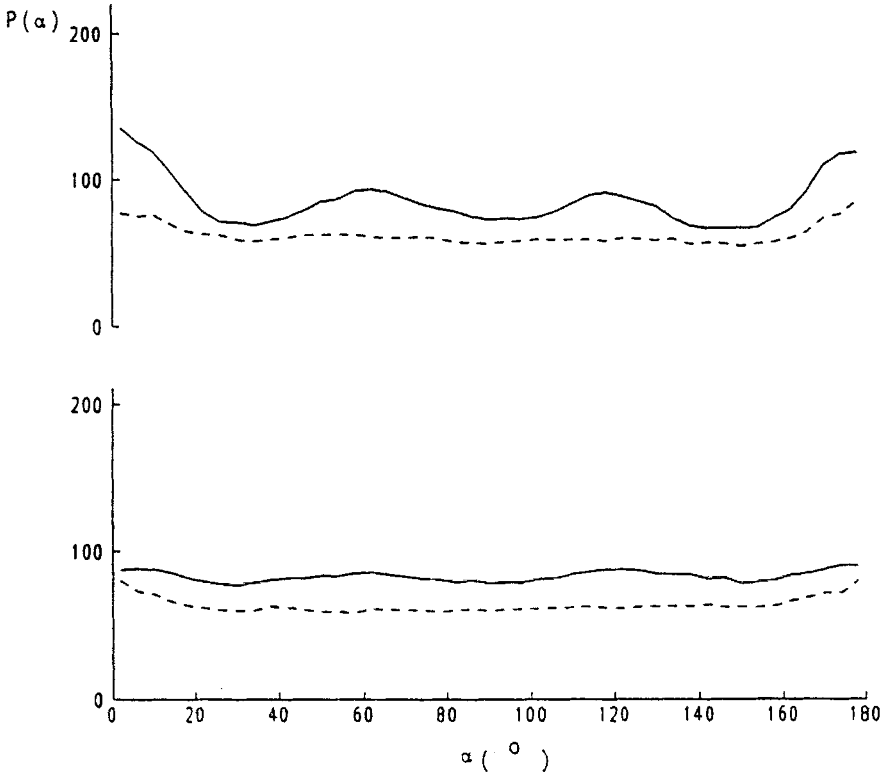

**Figure 3** Reduced angle-distributions of pairs of molecules concerning the C2 and C3-axes for solid I. *y*-axis in arbitrary units. —— C2-axis; --- C3-axis (upper curves: state 7, lower curves: state 1).

densities, but shows a significant favouring of multiples of 60 degree orientations at lower temperatures and higher densities.

This result contrasts with current model assumptions used to explain experimental findings[6–7]. Two types of models have been applied in the past (i) isotropic rotational motion (ii) discrete number of possible orientations. In case of model (i) there is no preference of any angle, neither between C2-axes nor between C3-axes of neighbouring molecules. For model (ii), which gives better agreement with X-ray investigations, one of the authors has recently performed static calculations taking into account a certain number of pair-configurations[7]. The least number of overlaps was found for molecules oriented with their C3-axes parallel to the [111] direction and equivalent directions of the elementary cell. This corresponds to an angle of 109.5 or 70.5 degrees between adjacent molecules. The present calculations do not indicate any preference of angles between the C3-axes of molecule-pairs, but indicate a discrete angle-distribution for the C2-axes. An explanation of this disagreement may be the fact that the present interaction model has not directly accounted for the H-atoms of cyclohexane. We return to this point in the discussion.

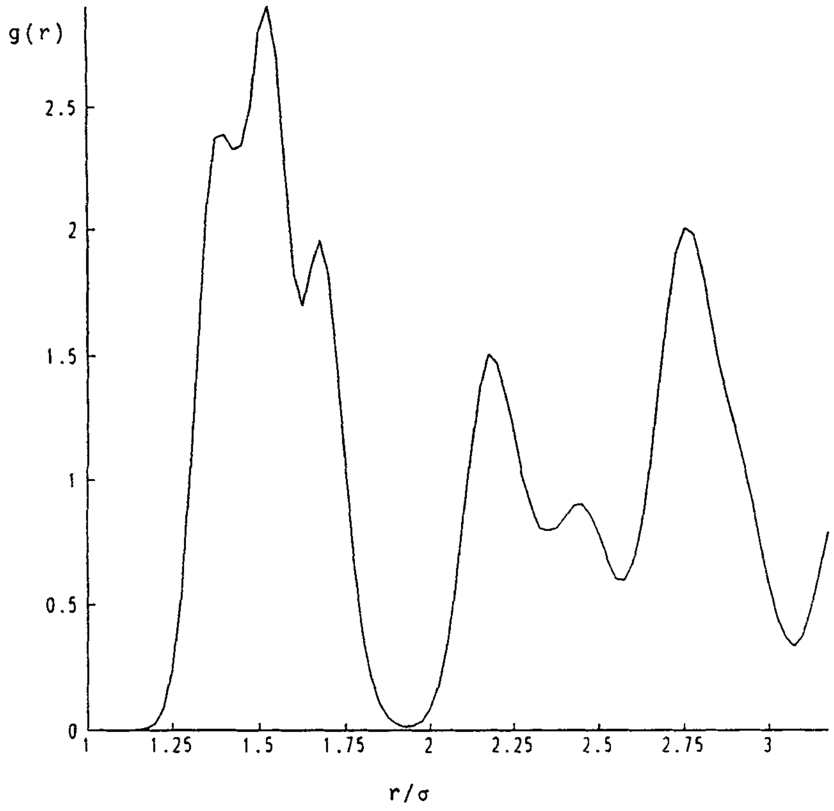

**Figure 4** Pair correlation function for the low-temperature non rotator crystalline phase, solid II. State 10.

### *3.2 Plastic-nonplastic (solid) phase transition*

Going to still higher densities and lower temperatures, the experimentally found transition to the low-temperature crystalline phase (solid II) is well reproduced by our model calculations. The pair correlation function (PCF) changes significantly. Its first and second peak split into several subpeaks, which show that the fcc structure of the lattice has been transformed. Figure 4 illustrates the PCF of the new structure of model cyclohexane. Whether this new lattice is of monoclinic structure could not yet be confirmed.

Nevertheless we found this transition in both directions, that is, starting from the plastic phase and rising the density or starting from solid II and lowering the density. Only a small hysteresis effect could be noticed.

This phase transition is well indicated by the nearest neighbour angle distributions. We plot here, for example, the angle distributions for the C2 and C3-axes in the solid II phase in Figure 5.

Evidently, for both symmetry axes, a favouring of about 60 degree configurations

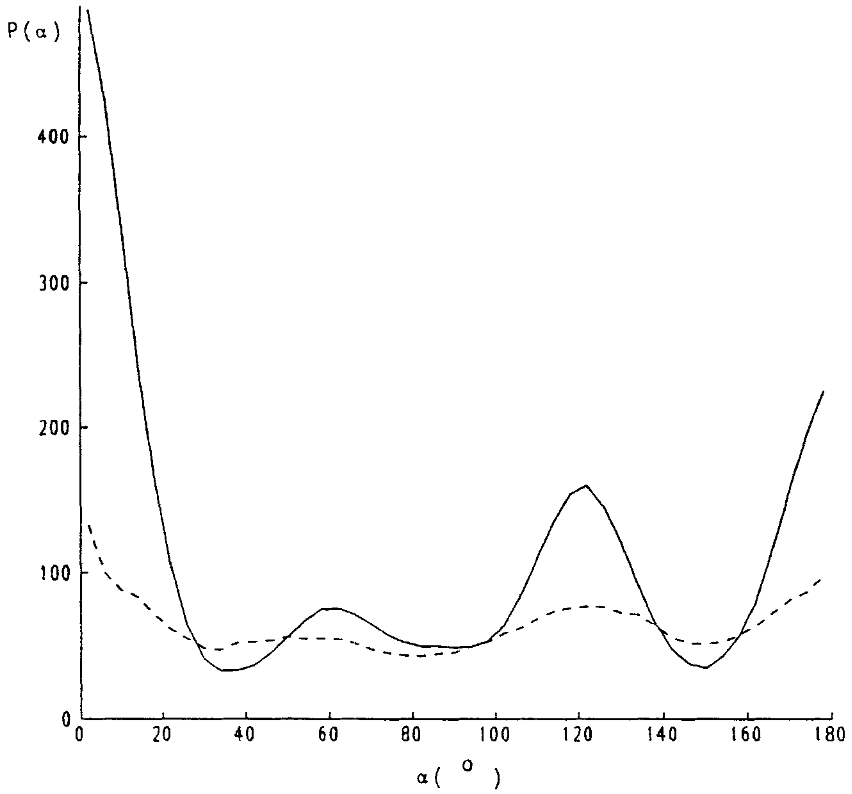

Figure 5 As in Figure 3, but for the low-temperature nonrotator phase, solid II. State 10.

is supported. This confirms that the rotational mobility of the molecules has decreased to a minimum in agreement with experimental findings.

## 4 DISCUSSION AND CONCLUDING REMARKS

Our MD computations have shown that the present 6-centre LJ potential model works well for discerning fluid, plastic and nonrotator solid phases in cyclohexane. We have furthermore shown that certain orientations of pairs of molecules predominate in the plastic phase on approaching the lower solid I–solid II transition. This indicates that the rotation of the molecules is strongly restricted in the rotator phase at lower temperatures.

Somewhat surprising results were found for the high temperature plastic phase. While experiments and simple static model calculations point to a stronger hindrance of rotations around the C2 symmetry axes compared with that around the C3-axis, the present MD computations support the inverse behaviour resulting in an appreciable preference of certain configurations with respect to rotations around the C2-axes.

We have checked, whether this latter result could be a consequence of the moments of inertia around the different symmetry axes, which are not in agreement with the experimental ones. However, the ratio of the moments of inertia of the model molecule concerning the different symmetry axes deviates only about 5 percent from that of the cyclohexane molecule. We show results of the angle distributions for model molecules that have the correct ratio of the moments of inertia in Figure 6. Apparently, there is no significant change of the results in comparison with those displayed in Figure 3. So the influence of the slightly altered moments of intertia of our model-molecules on the rotational properties of the system is small and cannot explain the occurring discrepancies.

Consequently in our future work we shall consider additionally a further more sophisticated cyclohexane model to ensure that the observed rotational motion in the plastic phase is not an artefact of the present six-centre model.

Moreover, we prepare MD computations in the NPT ensemble[8] to allow a more realistic comparison with experimental measurements also with respect to the

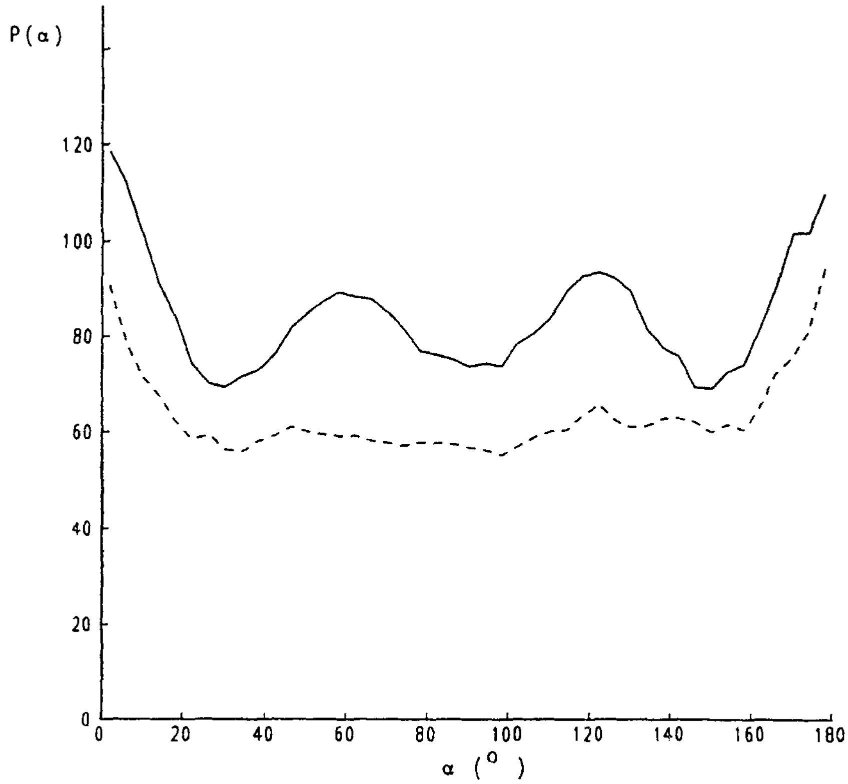

**Figure 6** As in Figure 3, but for altered moments of inertia of the model molecule. The ratio of the moments of inertia around the C2 and C3 symmetry axes corresponds here to that of the cyclohexane molecule.

pressure-induced phase transitions[4,9], which were performed at constant pressure rather than constant volume.

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