Molecular Dynamics of the Phase Transition in Solid Deuterated Methane

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Abstract

The rotational dynamics of a single deuterated methane molecule in the presence of its twelve nearest neighbours has been studied by using a computer simulation technique. The three-dimensional motion of the tetrahedral molecule is described by the appropriate algorithm equations, as well as by the well known Lennard-Jones potential. The importance of the inverse-twelfth-power repulsive potential for the dynamics of the deuterated methane molecule is also highlighted. The second-nearest neighbour interactions contribute only 7% to the potential energy of the whole system and this hardly affects the dynamics of the central molecule. A detailed analysis of the direction cosine data reveals a change in the dynamical behaviour of the molecule around the transition temperature, which could be attributed to the singularity observed in the specific heat data. Corresponding to the Lennard-Jones potential, the period of oscillation of the central molecule comes out to be $0 \cdot 38 \times 10^{-12}$ s. Making use of the (dimensionless) average rotational kinetic energy at the transition, $\langle E_{RK} \rangle_{critical} = 6 \cdot 3$, and the period, the transition temperature is found to be $27 \cdot 7$ K, which is in quite good agreement with one of the λ-type transition temperatures reported by Clusius *et al.*

1. Introduction

Unlike the case of solid methane, Clusius *et al.* (1937) reported two λ-type transitions in the specific heat measurements of deuterated methane at $22 \cdot 1$ K and 27 K respectively. In spite of the fact that both the light (CH_4) and heavy (CD_4) methane molecules have spherically symmetrical gyrations, the splitting of the λ-type transition could not be understood properly. Surprisingly, no measurements of the specific heat of deuterated methane at such low temperatures appear to have been carried out with an improved experimental set-up since the work of Clusius *et al.*

Press (1972) studied the phase transitions in deuterated methane, obtained in the form of powder samples as well as in single crystals, by means of coherent neutron scattering. It was really astonishing to notice a drop in the neutron intensity at around 27 K, corresponding to reflection (531), and also at $22 \cdot 1$ K, for reflection (321). The drop in intensity around the transition temperature reveals the system to be a dynamical one. In addition, the neutron scattering study supports the existence of singularities at the transition temperatures.

James and Keenan (1959) developed a theory to account for this behaviour by considering interactions between CD_4 molecules residing at the sites of a static

face-centred cubic lattice in the classical molecular field approximation. Based upon their mathematical formulation, three phases were interpreted in terms of the various symmetries of deuterated methane, namely:

  (i) tetragonal symmetry, for temperatures less than 22 K;
  (ii) octahedral symmetry, for temperatures varying from 22 to 27 K; and
  (iii) 'missing symmetry', i.e. an orientationally disordered phase, for temperatures greater than 27 K.

Later O'Shea (1978) also predicted the existence of three phases, based on Monte Carlo calculations pertaining to a classical octopolar solid which could be taken as the physical analogue of CD_4. However in the analysis, the lower transition was predicted to occur at 20 K.

It is now a well established fact that the computer simulation technique offers a number of attractive and useful features that can enhance our understanding of the physical properties of condensed matter at low temperatures. In the present work we have studied the rotational dynamics of a single CD_4 molecule in the presence of its nearest neighbours and second-nearest neighbours by using the Lennard-Jones potential. The significance of the 'inverse-twelfth-power' repulsive potential on the dynamics of the deuterated methane molecule has also been considered. Although from the present study we are unable to predict the two λ-type singularities reported by Clusius *et al.*, the prediction of a transition temperature ($\approx$27.7 K) with the proposed model is quite remarkable. Further, the visualisation of three-dimensional motion of the molecule obtained from the detailed analysis of direction cosine data reveals a change in its dynamical behaviour at the transition which could be related to the singularities observed in the specific heat data over the temperature range 22–27 K.

2. Crystal Structure of Heavy Methane (CD_4) and Method

Apart from the crystal X-ray diffraction analysis of heavy methane, its crystal structure has also been studied extensively by neutron diffraction by Press *et al.* (1970). The structure was confirmed to be fcc with space group Fm3m. However, following an X-ray diffraction study, Bol'shutkin *et al.* (1971) pointed out the existence of a small tetragonal distortion for temperatures less than 20 K. The departure from the cubic lattice was found to be slight and the ratio of the two unequal sides came out to be quite small ($c/a \approx 1 \cdot 02$).

In the present work, we consider the same size of the cubic unit cell ($=5 \cdot 872$ Å) and the same nearest-neighbour distance ($=4 \cdot 115$ Å) as were used in our earlier study of light methane (Kansal and Trikha 1993). The hydrogen atoms are replaced by deuterium atoms. Regarding the structure of the unit cell of CD_4, one can refer to the earlier paper. The deuterium atoms are arranged tetrahedrally about the carbon atom, the C–D bonds being of length $1 \cdot 09$ Å. The central molecule is surrounded by twelve neighbour molecules situated at the mid-points of the sides of the cube. The moment of inertia of deuterated methane is taken to be $15 \cdot 88 \times 10^{-47}$ kg m^2. The mathematical formalism and method of solution used are those reported in our previous studies of the low-temperature rotational dynamics of ammonium chloride (NH$_4$Cl, Pandey and Trikha 1984) and light methane (Kansal and Trikha 1993). In order to compute the potential energy

and interatomic forces in the dynamical system, we have considered two forms
for the potential between the CD_4 molecules:

$$\phi_1(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{1}$$

$$\phi_2(r) = 4\varepsilon\left(\frac{\sigma}{r}\right)^{12}. \tag{2}$$

The second potential, $\phi_2(r)$, although hypothetical, is considered in order to
investigate the importance of the short-range repulsive potential where we have
ignored the contribution of the attractive term $(\sigma/r)^6$. The terms σ and ε are
the characteristic parameters of the crystal and correspond to the distance of
closest approach ($=3\cdot796$ Å) and the depth of the potential well respectively.

3. Results and Discussion

In the present study the angular momentum of the central CD_4 molecule
was gradually increased to examine its rotational motion under the influence
of its twelve nearest neighbour molecules. The increasing value of the angular
momentum (expressed in reduced units $\equiv 10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}$) of the central molecule
corresponds to the rising temperature of the system. For both the potentials used,
the rotational kinetic energy along with the potential energy of the system were
computed for different values of the angular momentum varying from $1\cdot0$ to $20\cdot0$.

We have also calculated the energies of the system incorporating the second-
nearest neighbour interactions. These neighbours, six in number, are located at
the centres of the cubes surrounding the original one. The distance between the
central and the second-nearest neighbours is equal to the dimension of the unit
cell ($5\cdot872$ Å).

The rotational behaviour of the CD_4 molecule was followed up to 10,000 time
steps. An optimum value of the duration of the time step used, as well as the
total number of time steps, must be chosen, taking into account the truncation
errors in the computation. In the present work we have considered three different
time-step values, namely $\Delta t = 0\cdot001$, $0\cdot01$ and $0\cdot1$, for calculating the energies
of the system. We notice that the values of the average energy $\langle E \rangle$ (the sum
of the rotational kinetic energy and potential energy) and the average rotational
kinetic energy $\langle E_{\mathrm{RK}} \rangle$ so computed are nearly same for $\Delta t = 0\cdot001$ and $0\cdot01$.
However, a large discrepancy is noticed at $\Delta t = 0\cdot1$ which seems to violate the
energy conservation condition. For the present work we have used the value of
$\Delta t = 0\cdot001$ which is quite reasonable.

In Fig. 1 the variation of $\langle E \rangle$ against $\langle E_{\mathrm{RK}} \rangle$ is shown for the Lennard-Jones
potential and r^{-12} repulsive potential respectively. The calculations reveal two
distinct lines with different slopes which are referred to two phases of the solid
deuterated methane for both the potentials. Unlike the case for light methane,
the present transition is quite sharp in the case of the Lennard-Jones potential.
The magnitude of the potential energy corresponding to the r^{-12} repulsive
potential is increased due to the absence of the attractive r^{-6} term. However,
the magnitude of $\langle E_{\mathrm{RK}} \rangle$ is found to be the same for both potentials. The value
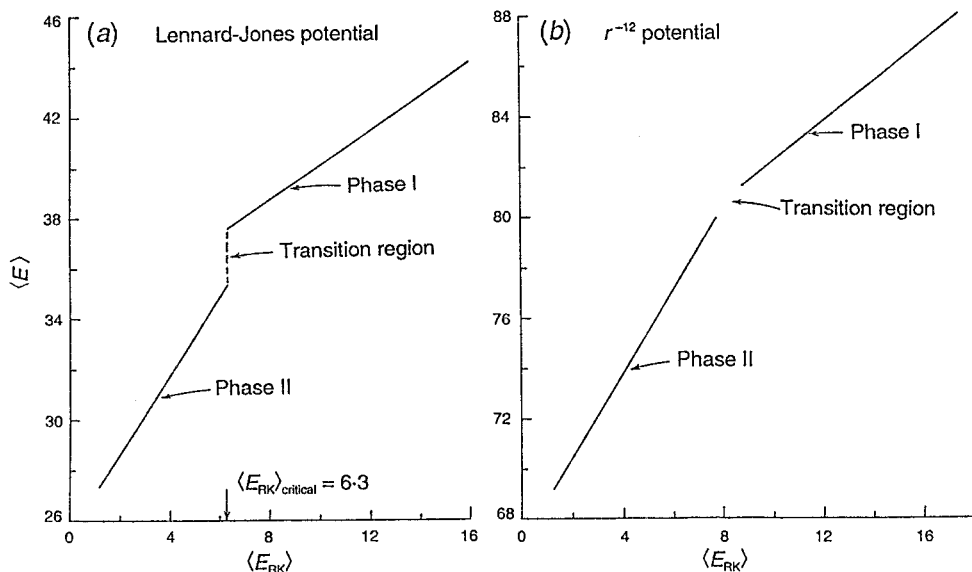
Fig. 1. Average total energy $\langle E \rangle$ versus average rotational kinetic energy $\langle E_{RK} \rangle$ (in reduced units) for the central CD_4 molecule subject to (a) the Lennard-Jones potential and (b) the r^{-12} repulsive potential.

of $\langle E_{RK} \rangle = 6 \cdot 3$ reduced units ($\equiv 6 \cdot 3 \times 10^{-21} \, \mathrm{kg \, m^2 \, s^{-2}}$), the so-called critical value, indicates the onset of the phase transition corresponding to the Lennard-Jones potential.

It should be stated that the existing model does not incorporate the structural change of the unit cell taking place around the transition temperature; this is done simply to avoid the complexity of the computation. Moreover, the structural change is not appreciable. Since in the calculations only one transition region is depicted, we consider phase II as relating to lower values of $\langle E \rangle$ and $\langle E_{RK} \rangle$ just before the transition, where the angular momentum imparted to the central molecule varies from 1 to 12. Corresponding to angular momentum varying from 13 to 15, the value of $\langle E_{RK} \rangle$ is more or less of the same magnitude, but $\langle E \rangle$ goes on increasing vertically (see Fig. 1a). This indicates a sudden increase in the potential energy of the system in what may be called the transition region. Phase I corresponds to higher values of $\langle E \rangle$ and $\langle E_{RK} \rangle$ just after the transition. Both the potentials give rise to discontinuities in the $\langle E \rangle$ versus $\langle E_{RK} \rangle$ curve which indicates a quite substantial contribution of the repulsive part of the Lennard-Jones potential in governing the dynamics of the system. Consequently we have carried out a detailed analysis of the dynamics of the central molecule under the influence of its nearest neighbours for both cases.

Regarding the Lennard-Jones potential, for $\Delta t = 0 \cdot 001$, we have shown in Fig. 2 the average potential energy and the average rotational kinetic energy as a function of the angular momentum imparted to the central molecule for the nearest and the second-nearest neighbour approximations. The average potential energy so obtained in the case of second-nearest neighbour interactions contributes only 7%. The average rotational kinetic energy increases with an increase in angular momentum; this contribution is of more or less the same magnitude in
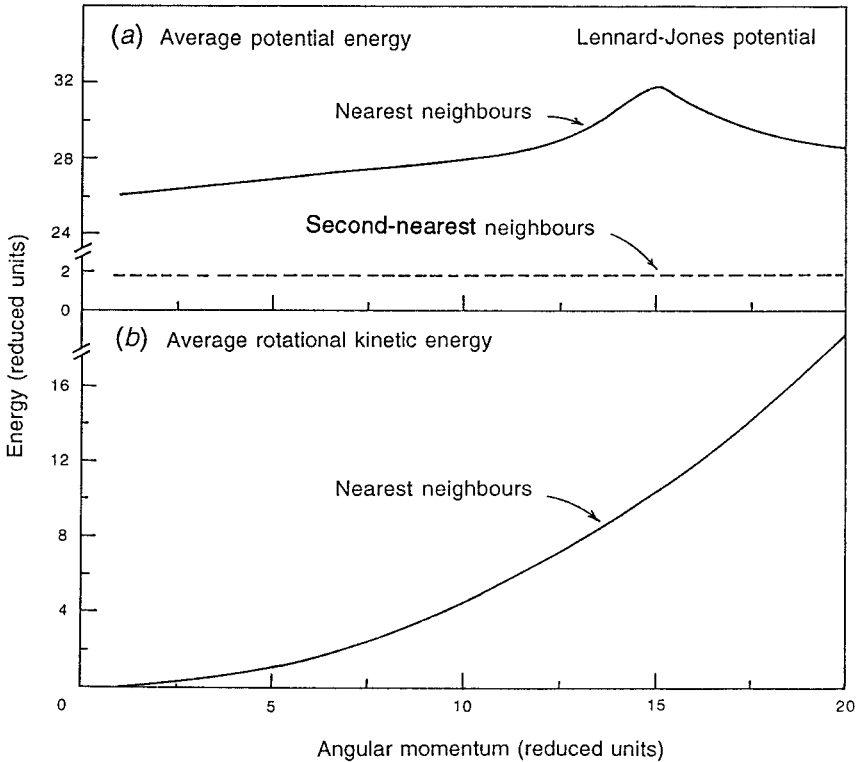
Fig. 2. Average potential energy and average rotational kinetic energy (in reduced units) versus angular momentum for (a) nearest and second-nearest neighbours, and (b) nearest neighbours, respectively, subject to the Lennard-Jones potential.

both the approximations. The hump depicted in the average potential energy curve (nearest neighbours) in Fig. 2a represents the transition region.

In Figs 3a and 3b we have plotted the potential energy (solid curves) and rotational kinetic energy (dashed curves) of the system as a function of time for angular momenta of 4·0 and 8·0 reduced units imparted to the central molecule about the z-axis, for the Lennard-Jones potential. In Figs 3c and 3d we plot the potential and rotational kinetic energy for the same angular momenta (4·0 and 8·0) pertaining to the repulsive potential. We observe that the variation of energy with time is more or less of the same nature. The fluctuations of the potential energy values for both the potentials are within the same limits (±2 units) although their magnitudes differ. All these energy curves refer to phase II of the system.

Fig. 4 shows the energy pattern curves for an angular momentum of 15·0 (representing the transition region) corresponding to the Lennard-Jones and repulsive potentials. In both the cases the system is quite perturbed. For the Lennard-Jones potential, the fluctuations are within the limits of ±6 and for the repulsive potential, these are within the limits of ±4 units.
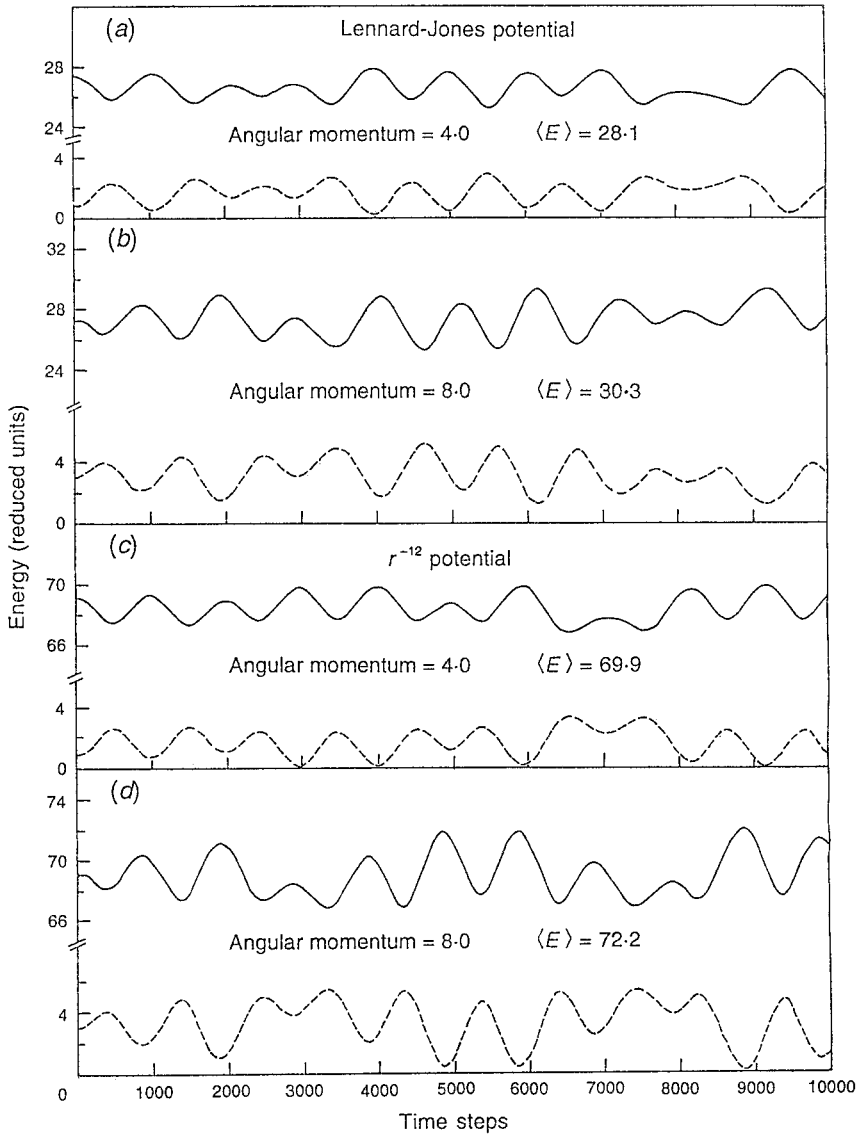
Fig. 3. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central CD_4 molecule as functions of time for angular momentum values of (a) $4 \cdot 0$ and (b) $8 \cdot 0$, subject to the Lennard-Jones potential, and (c) $4 \cdot 0$ and (d) $8 \cdot 0$, subject to the r^{-12} repulsive potential.

Fig. 5 shows the energy curves for angular momenta of $18 \cdot 0$, $20 \cdot 0$ and $25 \cdot 0$ for the Lennard-Jones potential. This situation corresponds to phase I. The potential energy and rotational kinetic energy pertaining to the angular momentum $25 \cdot 0$ are nearly equal and they intermix at some time steps (400, 760, 1560, 1920, 2720 etc.). Further, we note that the intermixing occurs at regular time step intervals.
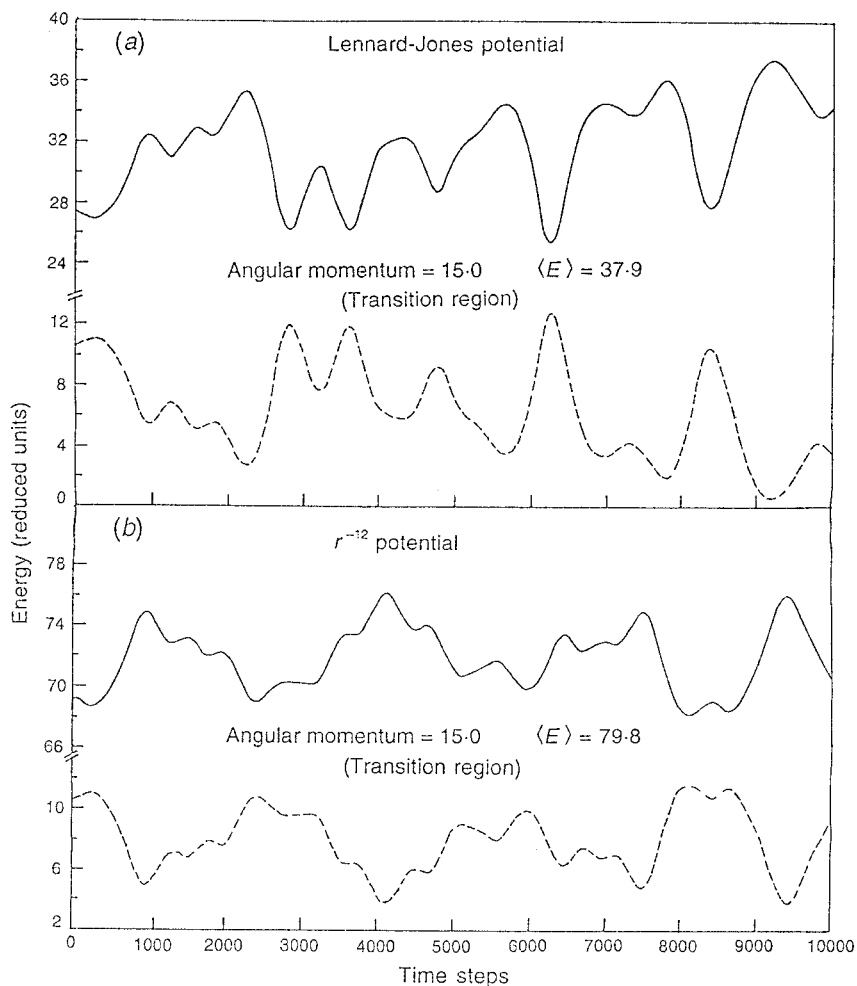
Fig. 4. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central CD$_4$ molecule as functions of time for an angular momentum value of 15·0 subject to (a) the Lennard-Jones potential, and (b) the r^{-12} repulsive potential.

In Fig. 6 we plot the energy curves for the r^{-12} repulsive potential for angular momenta of 18·0 and 20·0. Since the values of rotational kinetic energy and potential energy differ significantly in magnitude, in order to equalise the energies, a large value of the angular momentum has to be imparted to the central molecule. Such a system would correspond to a temperature approaching the melting temperature of deuterated solid methane ($\approx$90 K).

In Fig. 7 the variation of the angle θ_z between the fixed axis (z-axis) and the moving z'-axis associated with the rotating central molecule is shown as a function of time for both the phases as well as for the transition region in the field of the Lennard-Jones potential. The angle θ_z varies from 31° to 68° for angular momentum 8·0 (phase II). However, the range of θ_z is greatest for angular momentum 15·0 (transition region), varying from 40° to 160°. Suprisingly, the smallest variation in θ_z (45°–60°) is found for angular momentum 20·0

(phase I). By interpreting the variation of θ_z as a function of time, one can infer that the central CD_4 molecule (under the influence of its nearest neighbours) experiences the maximum nutational motion in the transition region. As a consequence the potential energy of the system increases abruptly as indicated by the hump in Fig. 2a.
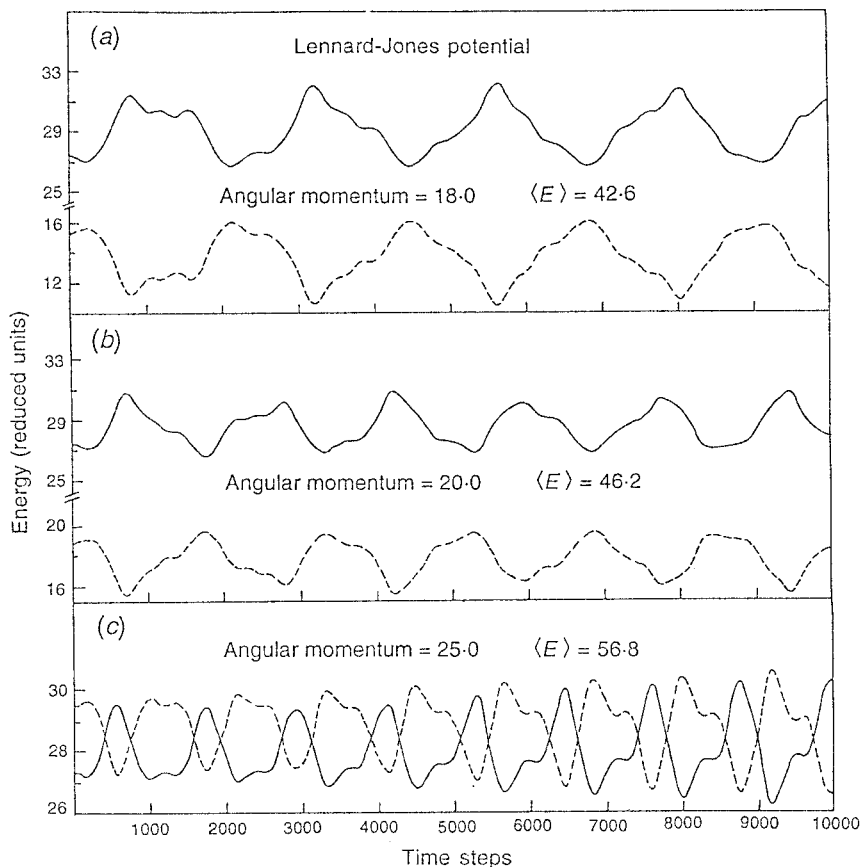

Fig. 5. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central CD_4 molecule as functions of time for angular momentum values of (a) $18\cdot0$, (b) $20\cdot0$ and (c) $25\cdot0$, subject to the Lennard-Jones potential.

4. Analysis of the Direction Cosine Data

A detailed analysis of the direction cosine data pertaining to the Lennard-Jones potential, recorded at each time step, reveals the following interesting features:

    (i) Corresponding to phase II, the central molecule performs torsional oscillations in the x–y plane which are hindered. As a consequence the period of the oscillations is not well defined. One may ascribe this behaviour of the oscillations to the small values of angular momentum imparted to the central molecule which is unable to overcome the potential barriers.
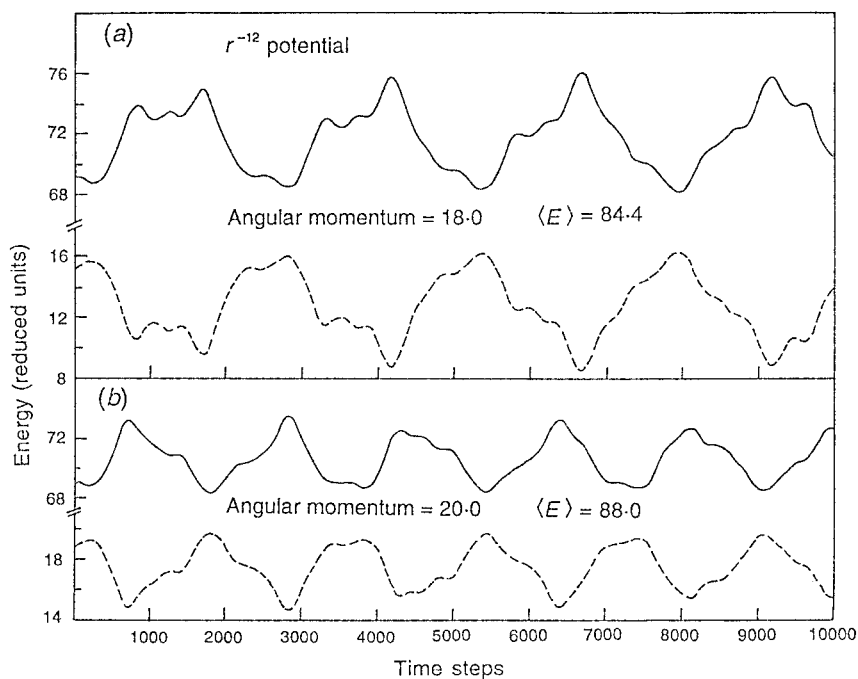
Fig. 6. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central CD_4 molecule as functions of time for angular momentum values of (a) $18 \cdot 0$ and (b) $20 \cdot 0$, subject to the r^{-12} repulsive potential.
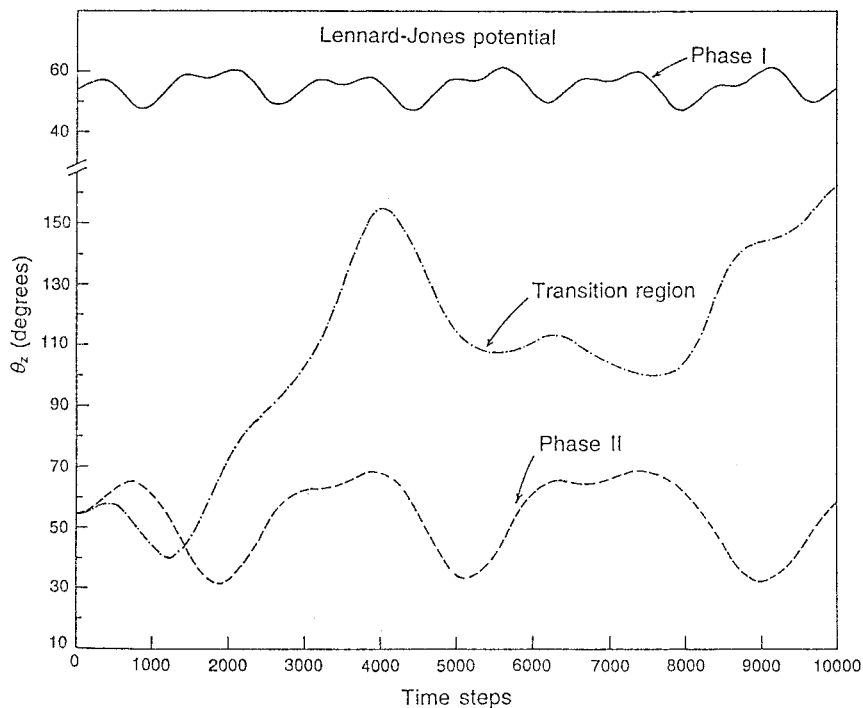

Fig. 7. Variation of the angle θ_z between the fixed z-axis and the moving z'-axis associated with the rotating central CD_4 molecule, as a function of time for angular momentum values of $8 \cdot 0$, $15 \cdot 0$ and $20 \cdot 0$ reduced units (lower, middle and upper curves respectively), subject to the Lennard-Jones potential.

(ii) In the transition region, the system seems to be quite perturbed. This is associated with a large-amplitude nutational motion. A change in the plane of oscillation, also occurs which could be identified as the inversion phenomenon.

(iii) In phase I, the analysis reveals that the wide fluctuations settle down to a minimum value. The system acquires sufficient energy (due to its large angular momentum) to overcome the potential barriers and starts performing well-behaved and smooth torsional oscillations. The period of these oscillations is found to be 0.38×10^{-12} s. Using this result and the critical value of $\langle E_{RK} \rangle$, we calculate the transition temperature of the deuterated methane system to be 27.7 K, in good agreement with one of the transition temperatures reported by Clusius et al.

5. Conclusions

A computer simulation technique has been used to study the dynamics of the deuterated methane molecule near the transition temperature. Although the r^{-12} repulsive potential is hypothetical in nature, it reveals very interesting features in depicting the transition in the $\langle E \rangle$ versus $\langle E_{RK} \rangle$ curves. Therefore the short-range repulsive term in the expression for the Lennard-Jones potential is quite significant.

The explanation of the λ–type transition in CH_4 as well as in CD_4 in terms of an order–disorder transformation seems to be quite vague. It appears to be a difficult task to classify different phases in terms of molecular orientations. In the present case there are twelve possible orientations, depending upon the positions of the twelve nearest neighbours situated at the mid-points of the sides of the cubic unit cell. However, the interpretation of the λ–type transition in NH_4Cl occurring near 242 K in terms of the order–disorder transformations seems to be simple and quite reasonable (the N–H bond of the tetrahedral NH_4^+ ion in a unit cell of NH_4Cl can point towards Cl^- ions situated at the corners of the cubic cell in two possible orientations). This type of situation does not arise in the case of the CH_4 and CD_4 systems.

In the present analysis we have classified different phases in heavy methane resulting from the detailed analysis of direction cosine data. The dynamical behaviour of the central molecule is controlled by the intermolecular forces of its nearest neighbours as well as by the algorithm equations. Moreover the rotational behaviour of the central molecule in a single unit cell is a fairly true representation of the whole system. The contribution to the potential energy of the system due to the second-nearest-neighbour interactions is barely 7%, so that one is justified in considering the nearest-neighbours-only approximation. In our opinion the contribution of next-nearest-neighbour interactions would not affect the dynamics of the central molecule.

In further investigations we plan to incorporate the structural changes (i.e. cubic to tetragonal) in computations around the transition temperature. We are hopeful that this will throw some light on the splitting of the λ–type transition, especially in deuterated methane.

to Dr D. S. Mann, the Principal of Sri Aurobindo College, Delhi University, for encouraging him and providing him the time to pursue the research work at the Department of Physics and Astrophysics, Delhi University.

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