# Effect of Short-range Repulsive Interactions on the Dynamics of the Methane Molecule

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#### Abstract

Using a computer simulation technique, an attempt has been made to explain the  $\lambda$ -type transition in the specific heat of solid methane at around 20 K in terms of the changes in the dynamical behaviour of the methane molecule under the influence of its nearest neighbours. Different exponents of the short-range repulsive interaction occurring in the expression for the potential energy have been tried in order to select the appropriate value. The well known Lennard-Jones (6–12) and (6–15) potentials are found to reveal a phase transition in a well defined region. From an analysis of the direction cosine data, the three-dimensional motion of the central methane molecule has been visualised before and after the transition. Pertaining to the Lennard-Jones potential, the period of the torsional oscillation (libration) of the methane molecule comes out to be of the order of  $0.3 \times 10^{-12}$  s. From the computed critical rotational kinetic energy, the transition temperature is found to be 20.2 K which agrees well with experimental observations.

## 1. Introduction

It is a well known fact that the exponent of the short range repulsive interaction in the Lennard-Jones (6–12) potential is empirical in nature and is usually obtained from the analysis of virial coefficient data. In the case of methane, the value of 12 is taken from gaseous methane data for temperatures greater than 200 K. However, Byrne *et al.* (1968) mentioned that a (6–18) potential would be superior to the (6–12) form, on account of the fact that it was based upon the analysis of virial coefficient data pertaining to the temperature range 100–230 K.

Clusius (1929) noted the existence of a  $\lambda$ -type singularity in the specific heat of solid methane at around 20 K. Heberlein and Adams (1970) observed anomalous behaviour in their expansivity measurements around the same temperature ( $\approx$ 19.8 K). Later on, Kapulla and Gläser (1972) carried out high resolution inelastic neutron scattering experiments on solid methane at several temperatures between 1.4 and 21 K. They too observed a qualitative change of cross section in going from 19 to 21 K.

The various physical properties of condensed matter at low temperatures can be investigated by using the computer simulation technique. For such studies, one of the main requirements is the selection of an appropriate intermolecular potential. In the present work, we have studied the rotational dynamics of a single methane molecule in the presence of its nearest neighbours by using exponents of the short-range repulsive interaction varying from 9 to 18. Surprisingly, this computer simulation study reveals the occurrence of a phase transition in a well defined region. The visualisation of the three-dimensional motion of the molecule before and after the transition indicates a change in its dynamical behaviour which could be attributed to the  $\lambda$ -type singularity in the measurement of specific heat.

# 2. Crystal Structure of Light Solid Methane

The experimental determination of the structure of the different phases of methane has been difficult for several reasons. X-ray diffraction is unable to record the position of light hydrogen atoms in the lattice. However, no neutron diffraction study seems to have been carried out on solid methane. X-ray studies by Schallamach (1939) indicated the molecular lattice structure of solid methane to be face-centred cubic both above and below 20.4 K. Later structural investigations by Greer *et al.* (1969) and Herczeg and Stoner (1971) have also confirmed the basic structure of solid methane to be face-centred cubic down to liquid helium temperature.



Fig. 1. Structure of solid methane.

A molecule in solid methane has twelve nearest neighbour molecules around it. Hydrogen atoms are arranged tetrahedrally about a carbon atom, the C–H bonds being of length 1.09 Å (see Fig. 1). The side of the unit cell and the distance between nearest neighbour molecules in the solid state have been taken as 5.872 and 4.115 Å respectively. The moment of inertia of the methane molecule comes out to be  $7.94 \times 10^{-47}$  kg m<sup>2</sup>.

#### 3. Interaction Potential

In order to calculate the potential energy of the dynamical system, we have chosen to use a potential of the form

$$\phi(r) = 4\epsilon \left[ (\sigma/r)^n - (\sigma/r)^6 \right] \tag{1}$$

between the methane molecules, where  $\sigma$  and  $\epsilon$  are the characteristic parameters of the crystal. The term  $\epsilon$  corresponds to the depth of the potential well and  $\sigma$ (=3.796 Å) represents the distance of closest approach. For the Lennard-Jones potential the short-range repulsive power n is taken as 12.

From the larger size of the unit cell in solid methane (see Fig. 1), it appears that the electron cloud of the central methane molecule may not overlap with the electron clouds of neighbouring molecules; we are therefore led to believe that some different power of n may be appropriate. In the present analysis we have considered values for n of 9, 12, 15 and 18. It may be mentioned that the melting temperature of solid methane is around 89 K and the anomalous behaviour in the various physical properties is exhibited in the vicinity of 20 K. The value of n = 12 seems to be most appropriate in depicting the phase transition at low temperature.

#### 4. Mathematical Formulation of the Model

Let  $\ell_1(t)$ ,  $\ell_2(t)$  and  $\ell_3(t)$  be the directions of the principal axes of the methane molecule at time t and  $I_1$ ,  $I_2$  and  $I_3$  be the principal moments of inertia (see Pandey and Trikha 1984). The angular velocity W and the angular momentum  $\Omega$  of the rotating methane molecule are written as:

$$W(t) = \omega_1(t) \ell_1(t) + \omega_2(t) \ell_2(t) + \omega_3(t) \ell_3(t), \qquad (2)$$

$$\boldsymbol{\Omega}(t) = I_1 \,\omega_1(t) \,\boldsymbol{\ell}_1(t) + I_2 \,\omega_2(t) \,\boldsymbol{\ell}_2(t) + I_3(t) \,\omega_3(t) \boldsymbol{\ell}_3(t) \,, \tag{3}$$

where  $\omega_1(t)$ ,  $\omega_2(t)$  and  $\omega_3(t)$  are the components of the angular velocity  $\boldsymbol{W}(t)$ .

A feature of the solution is the use of axes fixed in space. The classical equations of motion are written as

$$\boldsymbol{\ell}_{\alpha}(t) = \boldsymbol{W}(t) \times \boldsymbol{\ell}_{\alpha}(t), \qquad (4)$$

$$\dot{\boldsymbol{\Omega}}(t) = \boldsymbol{\tau}(t), \qquad (5)$$

$$\boldsymbol{W}(t) = \mathbf{I}^{-1} \boldsymbol{.} \boldsymbol{\Omega}(t) , \qquad (6)$$

where  $\alpha$  (=1, 2, 3) refers to the direction of the principal axes,  $\tau$  is the torque exerted on the methane molecule by its nearest neighbours and I denotes the inertia tensor.

The computer program consists mainly of three parts:

- (i) a routine to set up the initial position and orientation of the central methane molecule as obtained from the crystal structure,
- (ii) a routine to advance the time step with the help of an algorithm, and

(iii) a routine to calculate the forces and torques exerted on the rotating methane molecule under the fixed field of twelve methane molecules located on the mid-points of the sides of the cubic unit cell.

The algorithm used here is very similar to that used for conventional studies of the molecular dynamics of liquids. The position  $\mathbf{r}(t)$ , velocity  $\mathbf{v}(t)$  and acceleration  $\mathbf{a}(t)$  of a particle in the algorithm are replaced by the parameters  $\boldsymbol{\ell}_{\alpha}(t)$ ,  $\dot{\boldsymbol{\ell}}_{\alpha}(t)$  and  $\ddot{\boldsymbol{\ell}}_{\alpha}(t)$ . The corresponding equations for the rotational motion of the central methane molecule are

$$\boldsymbol{\ell}_{\alpha}(t+\Delta t) = \boldsymbol{\ell}_{\alpha}(t) + \boldsymbol{\ell}_{\alpha}(t) \Delta t + \frac{1}{6} \left[ 4 \boldsymbol{\ell}_{\alpha}(t) - \boldsymbol{\ell}_{\alpha}(t-\Delta t) \right] \Delta t^{2}, \qquad (7)$$

$$\boldsymbol{\Omega}(t+\Delta t) = \boldsymbol{\Omega}(t) + \frac{1}{6} \left[ 2\boldsymbol{\tau}(t+\Delta t) + 5\boldsymbol{\tau}(t) - \boldsymbol{\tau}(t-\Delta t) \right] \Delta t , \qquad (8)$$

where  $\dot{\ell}_{\alpha}(t)$  and  $\ddot{\ell}_{\alpha}(t)$  are the first and second time derivatives of the direction cosine. We have the additional constraints that  $\ell_{\alpha}(t)$  are orthogonal unit vectors. Also,  $\Delta t$  is the time increment and is of the order of  $10^{-13}$  s. The mathematical details of the calculations are similar to those given by Pandey and Trikha (1984) for the NH<sub>4</sub>Cl system.

The torque experienced by the central methane molecule is given by

$$\boldsymbol{\tau}(t) = \sum_{i=1}^{4} \left[ \boldsymbol{r}_i(t) - \boldsymbol{r}_{\rm cm}(t) \right] \times \boldsymbol{F}_i(t) \,, \tag{9}$$

where the  $\mathbf{r}_i(t)$  correspond to the positions of the four hydrogen atoms arranged tetrahedrally about the carbon atom. In the present analysis the position of the centre of mass can be assumed to be time-independent because of the low temperature of the solid methane. The  $\mathbf{F}_i(t)$  can be obtained from the space derivative of  $\phi(r)$  using equation (1). The positions of the hydrogen atoms change in time whereas the carbon atom remains fixed.

The algorithm used in the present study has been found to give both excellent stability and long time energy conservation which are necessary conditions for this type of computation.

## 5. Discussion and Results

In the present study, the angular momentum of the central methane molecule was gradually increased to investigate the effect of various powers of the short-range repulsive term in the potential energy expression on its rotational dynamics. This methane molecule is subjected to the interatomic forces of the twelve nearest neighbours (see Fig. 1). The rise in the temperature of the system is incorporated through the increase of angular momentum of the central methane molecule.

It may be mentioned here that we have confined ourselves to a single unit cell and the nearest-neighbour interactions. In reality one must consider all possible interactions between methane molecules situated at different unit cells. However, we feel that the rotational dynamics of the central methane molecule in a single unit cell is a fairly true representation of the whole system of solid methane.

The different values of the angular momentum imparted to the central molecule were in the range 1.0 to 20.0, expressed in reduced units. In all cases the time increment  $\Delta t = 0.001$  (in reduced units) was utilised in the algorithm equations as mentioned earlier. The rotational behaviour of the methane molecule was followed up to 10,000 time steps. An optimum value of  $\Delta t$  (which is of the order of  $10^{-13}$  s) and of the total number of time steps must be chosen taking into account the truncation errors in the computation. The rotational kinetic energy as well as the potential energy was computed at each time step corresponding to different values of the angular momentum.

In Fig. 2 the variation of average total energy  $\langle E \rangle$  (which is the sum of the rotational kinetic and potential energies) is shown as a function of the average



**Fig. 2.** Average total energy  $\langle E \rangle$  versus average rotational kinetic energy  $\langle E_{\rm RK} \rangle$  (in reduced units) for the central methane molecule subject to various potentials: (a) (6–9); (b) (6–12); (c) (6–15); (d) (6–18).

rotational kinetic energy  $\langle E_{\rm RK} \rangle$  of the system pertaining to various powers of the short-range repulsive interaction. Except in Fig. 2*d* we notice that two distinct lines, having different slopes, are separated by a transition region. One can identify these slopes with two different phases of solid methane, known as phases I and II in the literature. In our text, we refer to phase II as corresponding to lower values of  $\langle E \rangle$  and  $\langle E_{\rm RK} \rangle$  just before the transition and phase I corresponding to higher values of  $\langle E \rangle$  and  $\langle E_{\rm RK} \rangle$ . Further, it may be mentioned that we have not considered any structural change occurring in the unit cell of solid methane around the transition region in our computer simulation study—this is supported by the experimental observation of Schallamach (1939). Our calculations reveal that the rotational dynamics of the central molecule changes at the transition region.

With increasing exponent of the short-range repulsive interaction, we find that the total energy of the system increases in magnitude, whereas the average rotational kinetic energy remains of the same order. The discontinuity in the  $\langle E \rangle$  versus  $\langle E_{\rm RK} \rangle$  curve corresponding to n = 9 appears at ~2.4 reduced units. Further, we notice that the well known Lennard-Jones (6–12) potential as well as the (6–15) potential exhibit discontinuities in the  $\langle E \rangle$  versus  $\langle E_{\rm RK} \rangle$  curves at around the same value ( $\approx 6.8$  reduced units), although their slopes are different. Surprisingly, the discontinuity disappears altogether for the (6–18) potential. The



Fig. 3. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central methane molecule as functions of time for angular momentum values of (a)  $6 \cdot 0$  and (b)  $8 \cdot 0$  reduced units, subject to the (6-12) potential.

present calculations reveal that the short-range repulsive exponent n = 18 is not appropriate for depicting the transition. Earlier, Singh and Trikha (1984) also arrived at the same conclusion in solid methane using this power.

One can correlate the discontinuity exhibited in the present calculations to the  $\lambda$ -type transition observed in the specific heat data of solid methane at around 20 K by Clusius (1929). In the  $\langle E \rangle$  versus  $\langle E_{\rm RK} \rangle$  curves as shown in Figs 2a-c, we find that the temperature derivative ( $\approx \partial \langle E \rangle / \partial T$ ) corresponds to the specific heat of the system and the  $\langle E_{\rm RK} \rangle$  is a function of the angular momentum, which is nothing but the representative of temperature. Hence there appears to be a close similarity in the experimental and computed specific heat curves, both showing the anomalous behaviour.

Since both the Lennard-Jones (6–12) and the (6–15) potential exhibit discontinuities in the  $\langle E \rangle$  versus  $\langle E_{\rm RK} \rangle$  curves at nearly the same value, therefore we have carried out a detailed analysis of the dynamics of the central methane molecule under the influence of its nearest neighbours. In the preceding



**Fig. 4.** Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central methane molecule as functions of time for angular momentum values of (a) 6.0 and (b) 8.0 reduced units, subject to the (6–15) potential.

figures, we have shown the changes occurring in the values of the rotational as well as the potential energy of the system as the time advances by  $\Delta t$ .

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  $6 \cdot 0$  and  $8 \cdot 0$  (in reduced units imparted to the central methane molecule about the z-axis). A comparison of Figs 3a and 3b shows that the variation of energy with respect to the time is of similar type corresponding to the (6–12) potential. In Figs 4a and 4b we show the potential and rotational kinetic energies for angular momenta  $6 \cdot 0$  and  $8 \cdot 0$  of the system corresponding to the (6–15) potential. We notice that for the same angular momentum, the fluctuations in energies are more pronounced in the latter case as compared to



Fig. 5. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central methane molecule as functions of time for angular momentum values of (a) 16.0, (b) 17.0 and (c) 20.0 reduced units, subject to the (6–12) potential.



Fig. 6. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the central methane molecule as functions of time for angular momentum values of (a) 16.0 and (b) 20.0 reduced units, subject to the (6–15) potential.

the (6-12) potential. However, in both cases the potential energy of the system is dominant. This situation corresponds to phase II at temperatures less than the transition temperature.

In Figs 5a-c the energy pattern curves corresponding to angular momenta of  $16 \cdot 0$ ,  $17 \cdot 0$  and  $20 \cdot 0$  reduced units are shown. The potential energy and

rotational kinetic energy corresponding to angular momentum  $17 \cdot 0$  are nearly equal and they intermix at some time steps. For angular momentum greater than  $17 \cdot 0$ , we find that the rotational kinetic energy starts dominating the potential energy of the system, a situation which is not encountered in the case of the (6-15) potential (see Figs 6a, b). Even at angular momentum  $20 \cdot 0$ , the potential energy is still dominating the rotational kinetic energy. Since the energy patterns are quite different in each case, this situation therefore corresponds to phase I, pertaining to the temperatures greater than the transition temperature.

## 6. Analysis of the Direction Cosine Data

Analysis of the direction cosine data reveals that under the influence of its twelve nearest neighbours governed by (6-12) and (6-15) potentials, the central methane molecule performs hindered torsional oscillations corresponding to phase II. However, the period of oscillation is not well defined. It seems that the angular momentum imparted to the methane molecule is not sufficient to provide enough energy to enable full rotation.

With increasing values of the angular momentum, the central methane molecule starts performing well-behaved torsional oscillations. Even then it is unable to perform a full rotation of  $360^{\circ}$ . The period of oscillation corresponding to angular momentum  $12 \cdot 0$  (phase I) comes out to be nearly  $0.3 \times 10^{-12}$  s. The present analysis shows that the molecule has undergone a change in its dynamical behaviour on going from phase I to phase II and vice versa which could be attributed to the  $\lambda$ -type transition observed by experimentalists in their measurements of the specific heat of solid methane. However, detailed analysis of the data on the direction cosines and their derivatives at each time step is required to understand the complex motion of the methane molecule.

#### 7. Conclusions

The present computer simulation study of light solid methane reveals the occurrence of a phase transition at low temperature in a well defined region for both the Lennard-Jones (6-12) and (6-15) potentials. However, there is some indication of a phase transition occurring with the (6-9) potential too, but this is not very pronounced. Surprisingly, the phase transition disappears altogether with the (6-18) potential.

Further analysis of direction cosine data reveals that the well known Lennard-Jones (6–12) potential is much better in predicting the critical temperature ( $\approx 20$  K) because of the well behaved torsional oscillation which the central methane molecule performs in phase I, with a period of the order of  $0.3 \times 10^{-12}$  s. With the (6–15) potential, the critical temperature cannot be ascertained due to the varying time period of oscillation of the central methane molecule.

Later calculations revealed that the equalisation of rotational kinetic and potential energy occurs at a much higher value of angular momentum ( $\approx 33.0$ ) in the case of the (6–15) potential. Such a system would correspond to a temperature approaching the melting point of solid methane. Therefore, higher values of the angular momentum imparted to the central methane were not considered in the present work.

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