Rotational Motion of the NH_4^+ Ion in Ammonium Chloride

Sadhana Pandey and S. K. Trikha

Department of Physics and Astrophysics,
University of Delhi, Delhi 110007, India.

Abstract

The rotational motion of the ammonium ion in NH_4Cl at low temperature under the influence of its nearest neighbours has been studied using a computer simulation technique. The Lennard Jones potential is used as the representative interaction between NH_4^+ and Cl^-. Three values of the time increment Δt occurring in the algorithm equation are taken to illustrate the three-dimensional effect on the rotational dynamics of the NH_4^+ ion. In each case we notice a well defined transition gap around $\langle E_{RK} \rangle = 1 \cdot 25$ separating phases II and III which are known from the literature. The libration frequency of the ammonium ion is found to be $\sim 170 \, cm^{-1}$, corresponding to the transition temperature of 242 K, which is in agreement with the Raman spectra study by Couzi *et al.* (1973).

1. Introduction

The discovery of the λ-type specific heat anomaly in ammonium chloride around 242 K by Simon (1922) led to a series of detailed experimental and theoretical investigations. The order of the phase transition at this temperature is still a matter of controversy because of the fact that it appears to be of first order from observations of the stepwise change of the lattice parameter, from thermal expansion measurements (Fredericks 1971), and from the piezoelectric effect (Mohler and Pitka 1974) in ammonium chloride. Following the work by Simon, heat capacity measurements in ammonium chloride were carried out by Klug and Johnson (1937) and Ziegler and Messer (1941). However, these measurements were not sufficiently closely spaced to reveal the shape of the heat capacity anomaly in the vicinity of 242 K. Using an improved experimental technique for heat capacity measurements, Schwartz (1971) and Chihara and Nakamura (1972) also predicted the λ-type phase transition around $242 \cdot 5$ K. More recently, Garland and Baloga (1977) reported the molar heat capacity of NH_4Cl near the transition with a high resolution a.c. calorimeter at one atmosphere pressure and detected the λ-type transition at $242 \cdot 6$ K. Slichter *et al.* (1971) put forward a phenomenological theory using the Ising model to explain the specific heat and the thermal expansion data of ammonium chloride near the λ-type transition. They noted that the agreement between experiment and theory was not very satisfactory near the transition temperature.

In various attempts to understand these phase transitions two hypotheses were put forward that either the motion (Pauling 1930) or the orientation (Frenkel 1935) of the ammonium ion plays a decisive role, and both hypotheses have now become well

established by subsequent studies. Many neutron scattering experiments have been performed in ammonium chloride below and above the transition temperature to study the rotational dynamics of the NH_4^+ ion. This type of measurement leads to the idea of hindered rotation of NH_4^+ at the lower temperature, previously thought to be of a librational character, whereas free rotation of NH_4^+ corresponds to the higher temperature. Woods et al. (1961) carried out neutron scattering experiments in NH_4Cl at 90, 208, 296 and 458 K and observed the change in the shape of the spectra. Using a beryllium detector spectrometer, Venkataraman et al. (1963) also performed inelastic neutron scattering experiments for NH_4Cl at 100, 300 and 400 K with a view to elucidate the nature of the specific heat anomaly. A change in the shape of the neutron spectrum was also noticed while going from 100 to 300 K, indicating a shift in the frequency of the rotational mode. Later Bajorek et al. (1965) carried out thermal neutron scattering experiments in crystals containing the NH_4^+ ion to correlate the connection between the scattering processes and the phase transitions. Neutron spectra in NH_4Cl were obtained at the temperatures 125, 140, 159, 186, 209, 224, 249 and 265 K, which indicated the occurrence of a phase transition around 242 K. More recently, Töpler et al. (1978) carried out quasi-elastic neutron scattering experiments near the order–disorder phase transition on a single NH_4Cl crystal in order to obtain information on the type of rotational motion of NH_4^+. Quasi-elastic spectra were measured for temperatures just above and below the phase transition with the Grenoble high resolution back scattering spectrometer. The neutron spectrum at 240 K was found to be relatively narrow compared with that at 246 K.

One can conclude from these neutron scattering experiments on NH_4Cl that the difference in the shape of the spectra around 242 K is caused by the change in the rotational behaviour of the NH_4^+ ion under the influence of its nearest neighbours. This forms the basis of our computer simulation study of the phase II $\leftrightarrow$ phase III transition at 242 K in NH_4Cl.

2. Crystal Structure of Ammonium Chloride

We confine ourselves to a single unit cell of NH_4Cl and the nearest neighbour interactions of chlorine atoms in order to avoid excessive computational work. We believe that the rotational behaviour of NH_4^+ in a unit cell is a reasonably accurate representation of the whole system of NH_4Cl, either in the powder or in the single crystal form. X-ray studies of NH_4Cl have shown the structure to be of CsCl type with a unit cell length of 0·386 nm. The nitrogen atom is taken at the origin, surrounded by the eight chlorine atoms situated at the vertices of a cubic unit cell. Neutron diffraction studies by Goldschmidt and Hurst (1951) have shown that the hydrogen atoms are arranged tetrahedrally about the nitrogen. The N–H bond length is taken to be 0·103 nm. The moment of inertia of NH_4^+ is $7·099 \times 10^{-47}$ kg m^2.

3. Interaction Potential

As reported earlier (Pandey and Trikha 1984) for ND_4Cl, the Lennard Jones (6–12) potential is more appropriate in predicting the phases II and III, compared with the repulsive potential, and we use the same potential here:

$$\phi(r) = 4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}, \tag{1}$$

where σ represents the distance of closest approach (≈ 0.35 nm). The relative effect of the electrostatic interaction on the phase transition has not been studied here. Also, the potential energy between NH_4^+ and Cl^- is a function of time because of the vibrational motion associated with the rotating NH_4^+ ion.

4. Mathematical Formulation of the Rotating Ammonium Ion

Let $l_1(t)$, $l_2(t)$ and $l_3(t)$ be the directions of the principal axes of the ammonium ion 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 Ω of the rotating NH_4^+ are written

$$W(t) = \omega_1(t)l_1(t) + \omega_2(t)l_2(t) + \omega_3(t)l_3(t), \tag{2}$$

$$\Omega(t) = I_1\,\omega_1(t)l_1(t) + I_2\,\omega_2(t)l_2(t) + I_3\,\omega_3(t)l_3(t), \tag{3}$$

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

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

$$\dot{l}_\alpha(t) = W(t) \times l_\alpha(t), \tag{4}$$

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

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

where $\alpha\ (=1, 2, 3)$ refers to the direction of the principal axes, τ is the torque exerted on the NH_4^+ ion by its nearest neighbours and $\mathbf{I}$ denotes the inertia tensor.

The computer program consists mainly of three parts: a routine to set up the initial position and orientation of the NH_4^+ ion obtained from the crystal structure, a routine to advance the time step with the help of an algorithm, and a routine to calculate the forces and torques exerted on the rotating NH_4^+ ion under the fixed field of the chlorine atoms. The algorithm here is very similar to that used for conventional studies of the molecular dynamics of liquids. The position $r(t)$, velocity $v(t)$ and acceleration $a(t)$ of a particle in the algorithm are replaced by the parameters $l_\alpha(t)$, $\dot{l}_\alpha(t)$ and $\ddot{l}_\alpha(t)$. The corresponding equations for the rotational motion of NH_4^+ are

$$l_\alpha(t+\Delta t) = l_\alpha(t) + \dot{l}_\alpha(t)\,\Delta t + \tfrac{1}{6}\{4\ddot{l}_\alpha(t) - \ddot{l}_\alpha(t-\Delta t)\}\Delta t^2, \tag{7}$$

$$\Omega(t+\Delta t) = \Omega(t) + \tfrac{1}{6}\{2\tau(t+\Delta t) + 5\tau(t) - \tau(t-\Delta t)\}\Delta t, \tag{8}$$

where $\dot{l}_\alpha(t)$ and $\ddot{l}_\alpha(t)$ are the first and second time derivatives of the direction cosine. We have the additional constraint that $l_\alpha(t)$ are orthogonal unit vectors.

From equation (6), the components of $W(t)$ are

$$\omega_1(t) = \Omega(t).l_1(t)/I_1, \quad \omega_2(t) = \Omega(t).l_2(t)/I_2, \quad \omega_3(t) = \Omega(t).l_3(t)/I_3. \tag{9}$$

The first derivatives of the direction cosine can be written as

$$\dot{l}_1(t) = \omega_3(t)l_2(t) - \omega_2(t)l_3(t), \tag{10a}$$

$$\dot{l}_2(t) = \omega_1(t)\,l_3(t) - \omega_3(t)\,l_1(t), \tag{10b}$$

$$\dot{l}_3(t) = \omega_2(t)\,l_1(t) - \omega_1(t)\,l_2(t). \tag{10c}$$

From equations (9) we get

$$\dot{\omega}_1(t) = \{\tau(t)\cdot l_1(t) + \omega_2(t)\,\omega_3(t)(I_2 - I_3)\}/I_1, \tag{11a}$$

$$\dot{\omega}_2(t) = \{\tau(t)\cdot l_2(t) + \omega_3(t)\,\omega_1(t)(I_3 - I_1)\}/I_2, \tag{11b}$$

$$\dot{\omega}_3(t) = \{\tau(t)\cdot l_3(t) + \omega_1(t)\,\omega_2(t)(I_1 - I_2)\}/I_3. \tag{11c}$$

Differentiating equations (10a) and (10b) we obtain

$$\ddot{l}_1(t) = -\{\omega_2^2(t) + \omega_3^2(t)\}l_1(t)$$

$$+ I_3^{-1}\{\tau(t)\cdot l_3(t) + \omega_1(t)\,\omega_2(t)(I_1 - I_2 + I_3)\}l_2(t)$$

$$- I_2^{-1}\{\tau(t)\cdot l_2(t) - \omega_1(t)\,\omega_3(t)(I_1 + I_2 - I_3)\}l_3(t), \tag{12a}$$

$$\ddot{l}_2(t) = -\{\omega_3^2(t) + \omega_1^2(t)\}l_2(t)$$

$$+ I_1^{-1}\{\tau(t)\cdot l_1(t) + \omega_2(t)\,\omega_3(t)(I_2 - I_3 + I_1)\}l_3(t)$$

$$- I_3^{-1}\{\tau(t)\cdot l_3(t) - \omega_2(t)\,\omega_1(t)(I_2 + I_3 - I_1)\}l_1(t), \tag{12b}$$

with a similar expression for $\ddot{l}_3(t)$. The torque experienced by the NH_4^+ ion is given by

$$\tau(t) = \sum_{i=1}^{4} \{r_i(t) - r_{cm}(t)\} \times F_i(t), \tag{13}$$

where the $r_i(t)$ correspond to the positions of the four hydrogen atoms arranged tetrahedrally about the nitrogen atom. In the present analysis the centre of mass can be assumed to be time independent because of the low temperature of the system. The force F_i can be obtained from the space derivative of $\phi(r)$ using equation (1). The positions of the hydrogen atoms change in time, whereas the nitrogen atom remains fixed.

Further, one can write

$$r_i(t) - r_{cm} = U_{1i}\,l_1(t) + U_{2i}\,l_2(t) + U_{3i}\,l_3(t), \tag{14}$$

where the U refer to relative distances. Finally, one gets the expression for $\tau(t)$ used in the calculations:

$$\tau(t) = \sum_{i=1}^{4} \{U_{1i}\,l_1(t) \times F_i(t) + U_{2i}\,l_2(t) \times F_i(t) + U_{3i}\,l_3(t) \times F_i(t)\}. \tag{15}$$

The components of torque used in the expressions for $\ddot{l}_\alpha(t)$ are

$$\tau(t) \cdot l_1(t) = \sum_{i=1}^{4} [U_{2i}\{l_3(t) \cdot F_i(t)\} - U_{3i}\{l_2(t) \cdot F_i(t)\}], \qquad (16a)$$

$$\tau(t) \cdot l_2(t) = \sum_{i=1}^{4} [U_{3i}\{l_1(t) \cdot F_i(t)\} - U_{1i}\{l_3(t) \cdot F_i(t)\}], \qquad (16b)$$

with a similar expression for $\tau(t) \cdot l_3(t)$.

The algorithm given has been found to give both excellent stability and energy conservation over long periods of time, which are the necessary conditions for this type of computation.
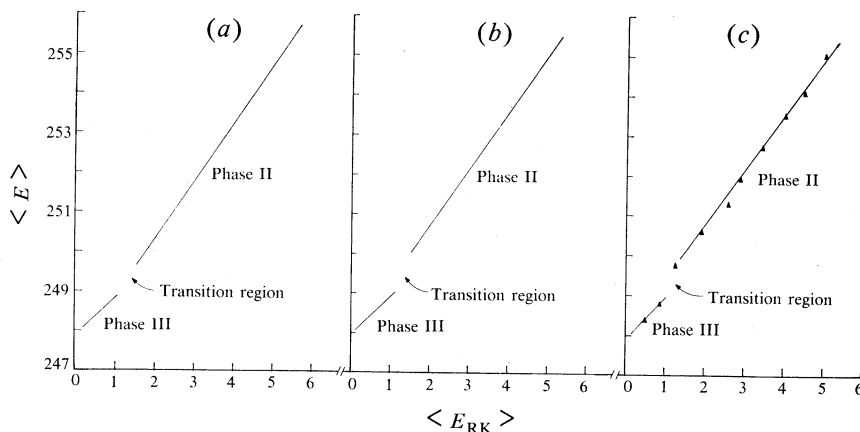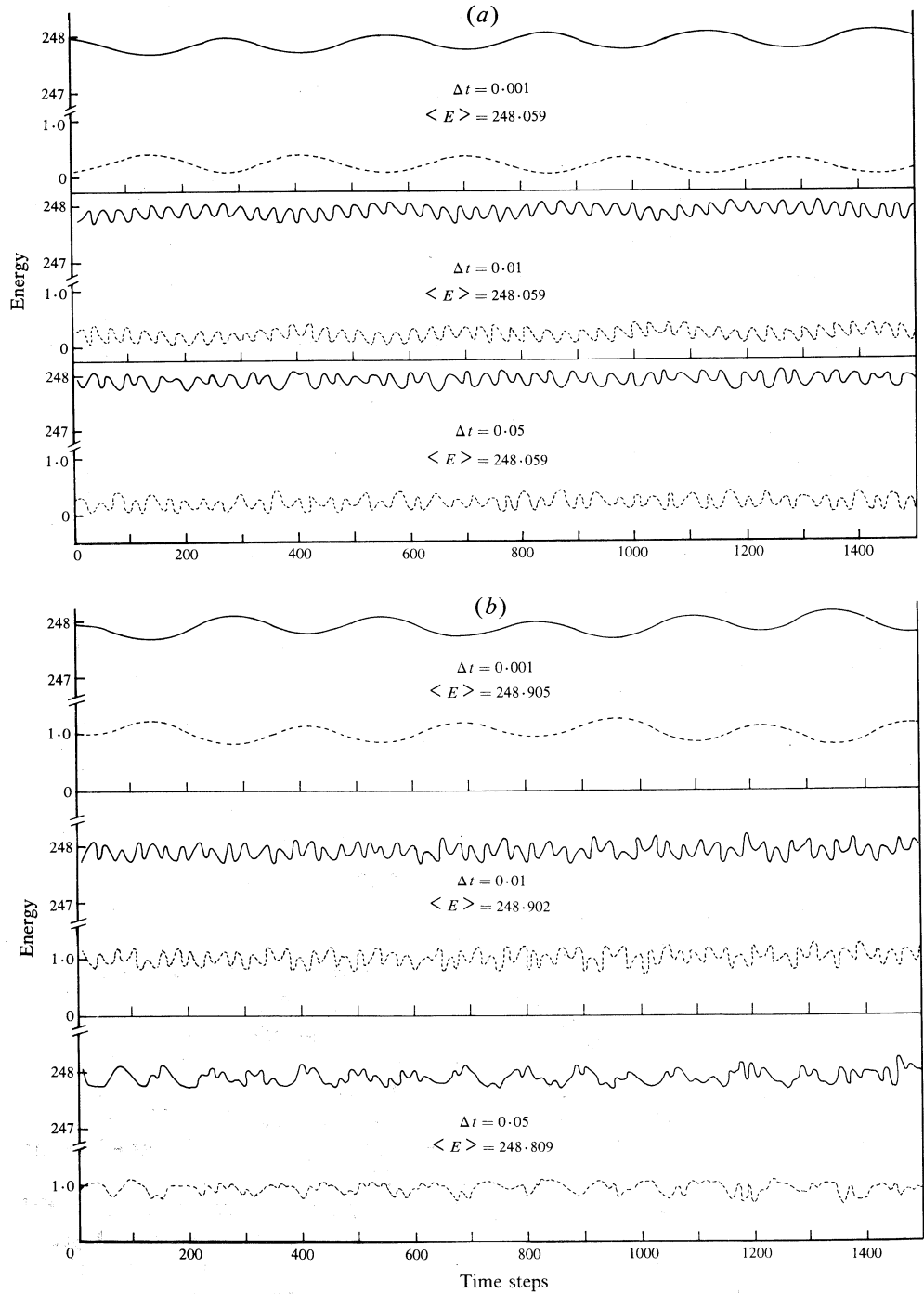

Fig. 1. Average total energy against average rotational kinetic energy (in reduced units) for the NH$_4^+$ ion for (a) $\Delta t = 0 \cdot 001$, (b) $\Delta t = 0 \cdot 01$ and (c) $\Delta t = 0 \cdot 05$. The triangles are for the calculation by Trikha and Jain (1975) with a maximum time step of 5000.

5. Discussion and Results

Here we study the effect of considering $\Delta t = 0 \cdot 001$, $0 \cdot 01$ and $0 \cdot 05$ on the rotational dynamics of the NH$_4^+$ ion (under the influence of the eight chlorine atoms fixed at the vertices of the unit cell). (The time increment is expressed in reduced units and is of the order of $\sim 10^{-13}$ s.) We find that in each case we get a well defined transition gap starting around $\langle E_{RK} \rangle = 1 \cdot 25$, separating phases II and III. The rotational behaviour of NH$_4^+$ is followed up to 10^4 time steps. The rotational kinetic energy of the system is computed for values of the angular momentum imparted to the NH$_4^+$ ion about the z-axis in the range $1 \cdot 0$ to $8 \cdot 0$ (in reduced units).

In Fig. 1 the variation of the average total energy $\langle E \rangle$ (the sum of the potential and rotational kinetic energies) is shown as a function of $\langle E_{RK} \rangle$ of the NH$_4$Cl system for the Lennard Jones potential. In each case, the two solid lines of different slopes correspond to the phases II and III, which are well separated by a transition gap. Computed values of $\langle E \rangle$ and $\langle E_{RK} \rangle$ from phase III come out to be nearly the same irrespective of the choice of Δt, whereas slight deviations in the values are observed for phase II. For a given value of the total time step ($\sim 10^4$ here) a small value of Δt (see Fig. 1a) indicates fewer rotations of NH$_4^+$ compared with a higher value.

Fig. 2. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the NH_4^+ ion as a function of time step for angular momentum (a) $1 \cdot 0$ and (b) $3 \cdot 0$ corresponding to $\Delta t = 0.001$, $0 \cdot 01$ and $0 \cdot 05$.

For this type of calculation an optimum value of Δt and of the total time step must be chosen taking into account the truncational errors in the computations. Earlier, Trikha and Jain (1975) reported a similar calculation for NH_4Cl with $\Delta t = 0\cdot05$ and with a total time step of 5000 (see the triangles in Fig. 1c). However, the lower transition region was overlooked by these authors as their calculations were not sufficiently detailed.

In Fig. 2a we have plotted the potential energy (solid curves) and rotational kinetic energy (dashed curves) of the system as a function of time step for angular momentum $1\cdot0$ for three values of Δt. The potential energy is found to dominate, in agreement with the work of Gerling and Hüller (1983) on NH_4Cl. There are small oscillations for both the potential energy and rotational kinetic energy, while for $\Delta t = 0\cdot001$ the curves are relatively smooth. In Fig. 2b we have plotted the energy for angular momentum $3\cdot0$, and we see that the magnitude of the rotational kinetic energy has increased with an increase in angular momentum. A comparison of Figs 2a and 2b shows that the variation of energies with respect to the time step is of similar type indicating the ordered motion of NH_4^+ under the influence of the fixed chlorine atoms, and this corresponds to phase III of NH_4Cl.

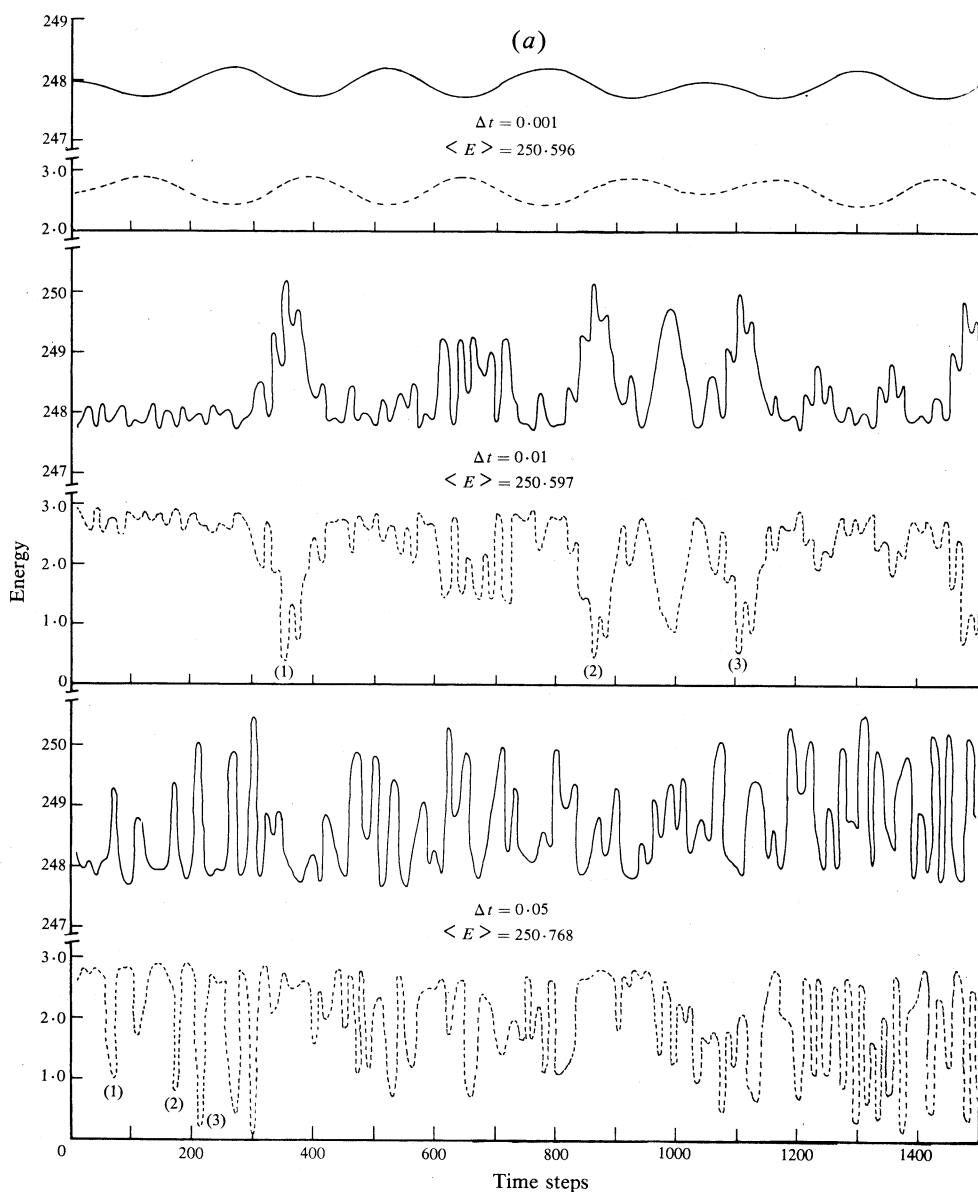Fig. 3a shows the results for angular momentum $5\cdot0$ for $\Delta t = 0\cdot001$, $0\cdot01$ and $0\cdot05$. For $\Delta t = 0\cdot01$ and $0\cdot05$, we see rapid fluctuations in the potential energy and rotational kinetic energy. Prominent dips are evident in the rotational kinetic energy at time steps 70, 170, 220 for $\Delta t = 0\cdot05$ and are also seen at time steps 350, 860 and 1100 for $\Delta t = 0\cdot01$. These large variations are not observed for the much smaller time increment $\Delta t = 0\cdot001$. In Fig. 3b we have increased the angular momentum to $6\cdot0$ and again with $\Delta t = 0\cdot001$ we notice that the variation of energy is quite smooth. The prominent dips in the rotational kinetic energy of NH_4^+ ion occur at time steps of 55, 100 and 215 for $\Delta t = 0\cdot05$ and are also visible at time steps of 250, 400 and 1000 for $\Delta t = 0\cdot01$. Since each energy curve is different for different angular momentum, this situation corresponds to phase II. The large fluctuations in the energy curves correspond to the vibrational motion associated with the rotating NH_4^+ ion.

In Fig. 4 we show the potential and rotational kinetic energies for angular momenta $1\cdot0$, $3\cdot0$, $5\cdot0$ and $6\cdot0$ with $\Delta t = 0\cdot001$ as a function of time step 1500 to 10000 to depict the overall variation experienced by the NH_4^+ ion in our calculations. For angular momenta $1\cdot0$ and $3\cdot0$, the variation in both the potential energy and kinetic energy is uniform and similar up to 10^4 time steps, whereas the large fluctuations for angular momenta $5\cdot0$ and $6\cdot0$ indicate the complex motion of the NH_4^+ ion. Prominent dips in the rotational kinetic energy occur at time steps 3500 and 8500 for angular momentum $5\cdot0$, whereas the first two dips are at 2250 and 3570 for angular momentum $6\cdot0$.

6. Conclusions

The following conclusions can be drawn from the present study:

(1) Similar to earlier work, the rotating model of the NH_4^+ ion supports the explanation by Pauling (1930) for the specific heat anomaly at 242 K in NH_4Cl. The transition phase II $\leftrightarrow$ phase III is explained in terms of the change in the rotational behaviour of NH_4^+.

Fig. 3. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the NH_4^+ ion as a function of time step for angular momentum (a) $5 \cdot 0$ and (b) $6 \cdot 0$ corresponding to $\Delta t = 0 \cdot 001$, $0 \cdot 01$ and $0 \cdot 05$.

(2)   In using the algorithm equation, a proper choice of the value of the time increment Δt must be made. Higher values of Δt sometimes lead to truncational errors in the computation. The value $\Delta t = 0 \cdot 05$ (in reduced units) has been found to be within the permissible range of errors.
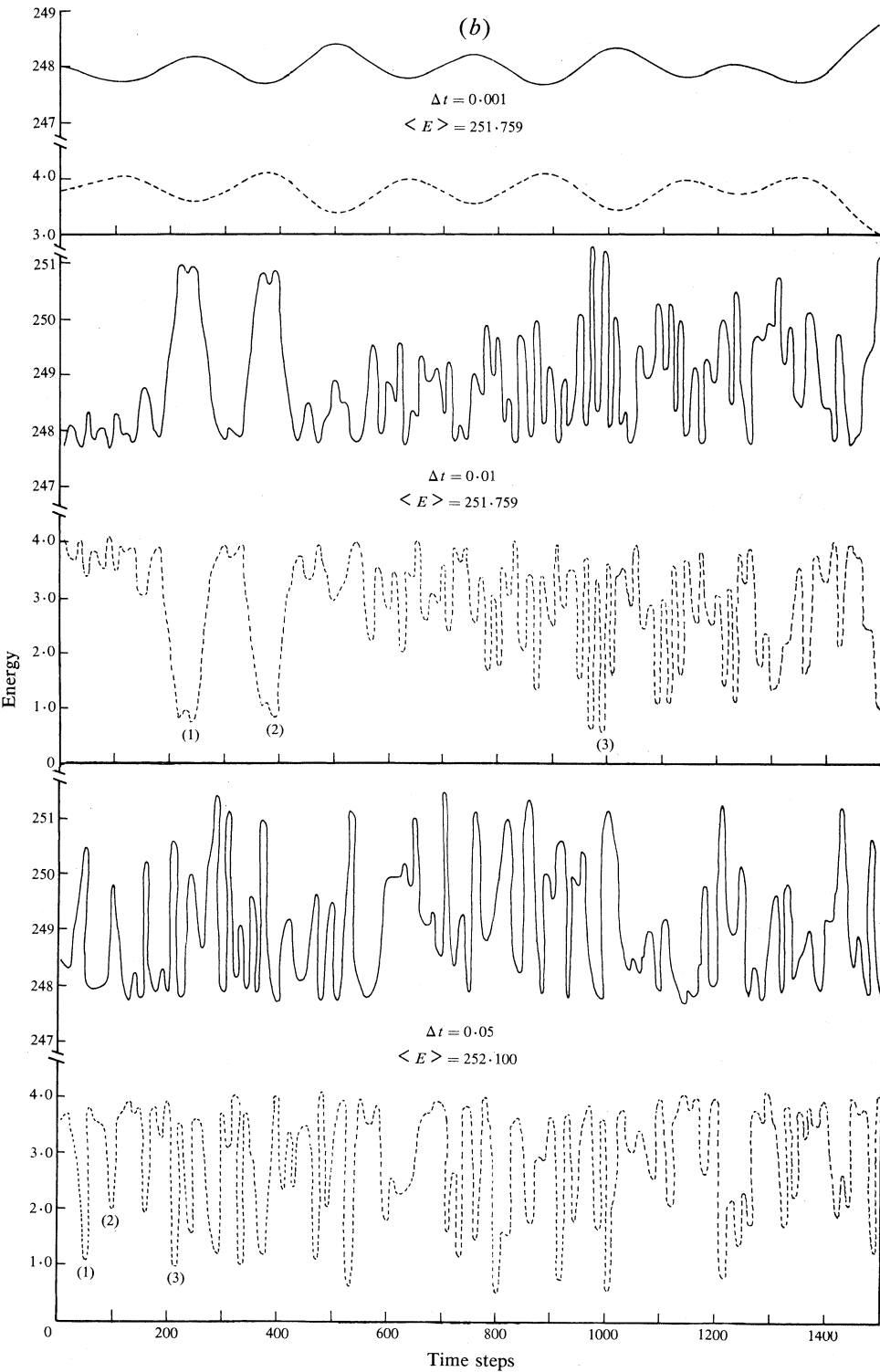
Fig. 3b. *[see opposite page]*

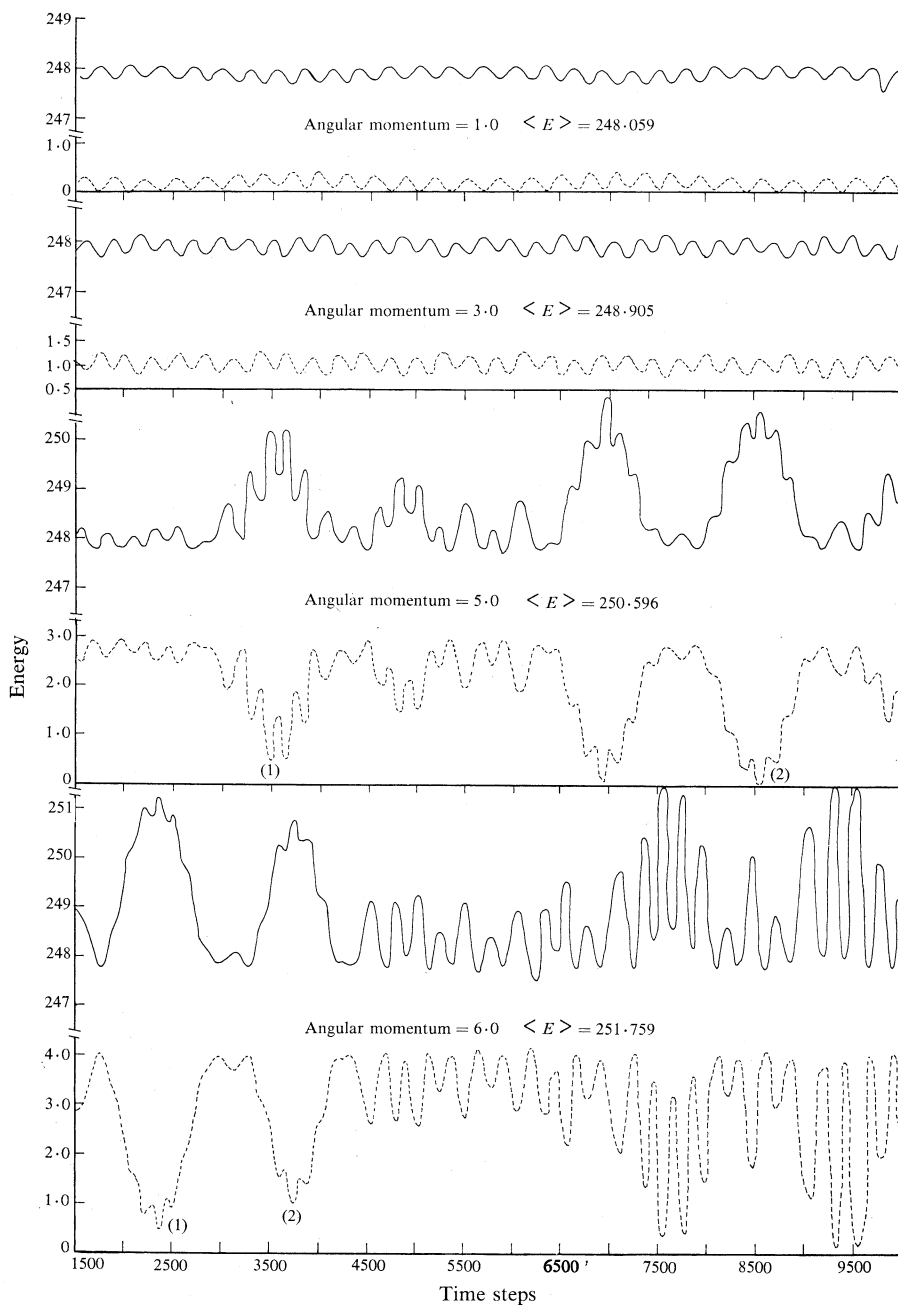**Fig. 4.** Potential energy (solid curves) and rotational kinetic energy (dashed curves) for the NH$_4^+$ ion with time increment $\Delta t = 0\cdot001$ corresponding to angular momenta $1\cdot0$, $3\cdot0$, $5\cdot0$ and $6\cdot0$ as a function of the time step 1500 to 10 000.

(3)   The computed libration frequency of NH$_4^+$ turns out to be of the order of $\sim170\,\text{cm}^{-1}$, which is much less than the quoted value of $383\,\text{cm}^{-1}$ by Hüller and Kane (1974). The libration frequency corresponds to the transition temperature of

242 K. However, our calculated value seems to be in better agreement with the measurements on the low frequency Raman spectra in the NH_4Cl crystal around the transition temperature by Couzi *et al.* (1973), who were able to separate the libration frequency of NH_4^+ from the Cl^- ion.

(4) Since we have assumed the structure of ammonium chloride to be of the CsCl type throughout our work, the discontinuity in the $\langle E \rangle$ versus $\langle E_{RK} \rangle$ curves therefore corresponds only to phases II and III of NH_4Cl.

Acknowledgments

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