

Molecular Dynamics of the Phase Transition in Compressible Ammonium Chloride

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Abstract

The effects of pressure on the dynamical behaviour of an NH_4^+ ion near the λ transition under the influence of its nearest neighbours in ammonium chloride have been studied by using the computer simulation technique. The Lennard Jones (6-12) potential is used as the representative interaction between NH_4^+ and Cl^- . The present calculations reveal a decrease in entropy of the system with increasing pressure. The libration frequency of the NH_4^+ ion is estimated to be approximately 170, 182 and 210 cm^{-1} at pressures of 1 atm, 3 and 10 kbar respectively, in agreement with the Raman spectrum study of NH_4Cl at high pressure (Ebisuzaki and Nicol 1969).

1. Introduction

Recently there has been increasing attention paid to the detailed behaviour near the order-disorder transition, generally known as the ' λ transition', in compressible solids. The λ -type transition is now well established around 242 K in ammonium chloride at 1 atm (1.01×10^5 Pa). Early high pressure work by Bridgman (1931) indicated that the transition temperature increased substantially with pressure. Ammonium chloride crystals have been found to be relatively soft resulting in appreciable volume contraction with pressure. Garland and Renard (1966) measured the elastic constants of a single crystal of ammonium chloride as a function of temperature (150-320 K) and pressure (0-12 kbar, 1 bar = 10^5 Pa) in the region of the λ transition. It was noticed that the transition temperature was fairly strongly dependent on pressure, increasing from approximately 242 K at 1 atm to 308 K at 10 kbar. Trappeniers and van der Molen (1966) also investigated the effect of pressure on the transition of ammonium chloride up to 2700 atm by means of differential thermal analysis. They noticed a reduction in the transition entropy with increasing pressure. Amitin *et al.* (1973) carried out measurements of the specific heat of NH_4Cl in the 200-320 K range under normal and elevated (up to 3.6 kbar) pressures. Their investigations showed that at a pressure of about 3 kbar the specific heat increased only by a factor of 2, whereas under normal pressure it rose by a factor of 30-40 near the phase transition temperature. More recently, Garland and Baloga (1977) reported constant heat capacity measurements of NH_4Cl in the vicinity of the order-disorder transition at 1 atm, as well as at high pressure (1.5 and 3.134 kbar), with a high resolution a.c. calorimetry technique and observed the corresponding transition temperatures to be 256 and 269 K respectively.

The nature of the phase transition in compressible solids is not yet fully understood. Moreover, the NH_4Cl system is of special interest because a small discontinuous phase change is observed at low pressure, whereas it becomes continuous at high pressure. The order of the phase transition around 242 K at 1 atm is still a matter of controversy. It seems that very little attempt has been made to understand these transitions theoretically; only statistical theories of the phase transition in a compressible Ising system have been put forward.

In recent years computer simulation studies of the motion of atoms and molecules have become a powerful technique in understanding the various physical properties of condensed matter, especially at low temperature. In an earlier communication (Pandey and Trikha 1984), computer simulation studies were carried out to investigate the nature of the phase transition around 242 K in ammonium chloride at 1 atm pressure. This λ transition was explained in terms of the change in the dynamical behaviour of NH_4^+ under the influence of its nearest chlorine neighbours. The present study is an extension to the case of a compressible ammonium chloride crystal and assumes a uniform volume contraction up to 10 kbar. The libration frequency of NH_4^+ is found to increase slightly with pressure, in agreement with the Raman spectrum study of ammonium chloride at high pressure by Ebisuzaki and Nicol (1969). The present calculations also indicate a decrease in the entropy of the compressible system in terms of the fluctuation of the potential and rotational kinetic energy of the NH_4^+ ion.

2. Crystal Structure of Compressible Ammonium Chloride

As in our earlier work, we only consider a single unit cell of NH_4Cl and the nearest neighbour interaction of the static chlorine atoms, in order to avoid excessive computational work. We believe that, even if the next nearest neighbour interaction is included, it would not significantly affect the result because of the shape of the Lennard Jones (6-12) potential. X-ray studies of NH_4Cl have shown its structure to be of CsCl type with a unit cell length of 0.386 nm at 1 atm pressure. The nitrogen atom is taken to be 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 atom. Lewis *et al.* (1966) investigated the effect of a pressure of several hundred kbar on the compressibility of NH_4Cl without noticing any change in the CsCl type of structure. Making use of the P - V data, we have estimated the size of the unit cell to be 0.384 and 0.380 nm corresponding to 3 and 10 kbar respectively. We further assume that the N-H bond length (0.103 nm) remains unaffected by the application of ≈ 10 kbar pressure, with the moment of inertia of NH_4^+ being $7.094 \times 10^{-47} \text{ kg m}^2$.

3. Interaction Potential and Mathematical Formulation

In order to compute the potential energy of the dynamical system we prefer to use the well-known Lennard Jones (6-12) potential

$$\phi(r) = 4\epsilon\{(\sigma/r)^{12} - (\sigma/r)^6\} \quad (1)$$

as the representative interaction between NH_4^+ and Cl^- under pressures up to 10 kbar; σ represents the distance of closest approach ($\approx 0.35 \text{ nm}$).

The equations to be solved are

$$\dot{\mathbf{l}}_\alpha(t) = \mathbf{W}(t) \times \mathbf{l}_\alpha(t), \quad (2)$$

$$\dot{\boldsymbol{\Omega}}(t) = \boldsymbol{\tau}(t), \quad (3)$$

$$\mathbf{W}(t) = \mathbf{I}^{-1} \cdot \boldsymbol{\Omega}(t). \quad (4)$$

Here \mathbf{l}_α ($\alpha = 1, 2, 3$) are the unit vectors along the principal axes of the molecule at any instant of time; $\boldsymbol{\Omega}$ and \mathbf{W} represent the angular momentum and angular velocity respectively; $\boldsymbol{\tau}$ is the torque exerted on the NH_4^+ ion by its nearest eight chlorine neighbours and \mathbf{I} denotes the inertia tensor.

The rotational motion of NH_4^+ is governed by the algorithm equations:

$$\mathbf{l}_\alpha(t + \Delta t) = \mathbf{l}_\alpha(t) + \dot{\mathbf{l}}_\alpha(t)\Delta t + \frac{1}{6}\{4\ddot{\mathbf{l}}_\alpha(t) - \ddot{\mathbf{l}}_\alpha(t - \Delta t)\}\Delta t^2, \quad (5)$$

$$\boldsymbol{\Omega}(t + \Delta t) = \boldsymbol{\Omega}(t) + \frac{1}{6}\{2\boldsymbol{\tau}(t + \Delta t) + 5\boldsymbol{\tau}(t) - \boldsymbol{\tau}(t - \Delta t)\}\Delta t, \quad (6)$$

where $\dot{\mathbf{l}}_\alpha(t)$ and $\ddot{\mathbf{l}}_\alpha(t)$ are the first and second time derivatives of the direction cosines.

The mathematical details of the calculation are given by Pandey and Trikha (1984). The algorithm used in the present study 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.

4. Discussion and Results

In the present analysis, the NH_4Cl system (consisting of a unit cell) is studied by imparting angular momentum in the range 1.0–8.0 (in reduced units) to the NH_4^+ ion about the z-axis. The effect of pressure 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) has been studied up to 10^4 time steps. The time increment $\Delta t = 0.01$ is expressed in reduced units and is of the order of 10^{-13} s. From a detailed analysis of the direction cosine data of the moving frame of reference attached to the NH_4^+ ion, we find that the NH_4^+ ion performs a three-dimensional torsional oscillation corresponding to phase III, with the angular momentum in the range 1–3 at normal as well as at elevated pressure.

In Fig. 1 the variation of the average total energy $\langle E \rangle$ (sum of the potential and rotational kinetic energy) is shown as a function of the average rotational kinetic energy $\langle E_{\text{RK}} \rangle$ of the NH_4Cl system for different pressures. In each case, the two solid lines of different slope correspond to phases II and III, which are well separated by a transition gap. The computed values of the rotational kinetic energy, corresponding to different angular momenta, appear to be pressure-independent, whereas the magnitude of the potential energy of the NH_4^+ ion increases with the increase in pressure. Further, we notice that the gradient for phase II is steeper at 1 atm pressure than at higher pressures, as shown by the differences between the solid and dashed lines. In the case of 10 kbar (Fig. 1c), our calculations show that phases II and III almost lie on a common line, indicating that the discontinuous phase change at low pressure (≈ 1 atm) is converted into a continuous phase change.

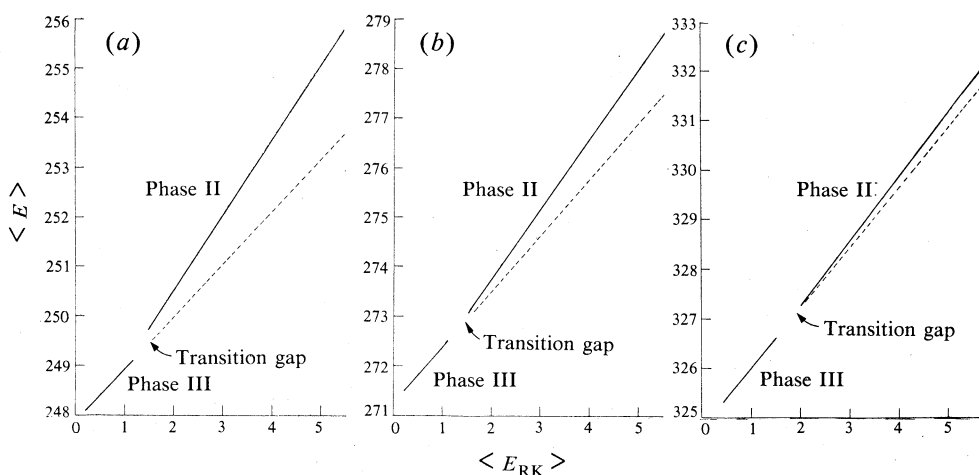


Fig. 1. Average total energy against average rotational kinetic energy (in reduced units) for the NH_4^+ ion, with the Lennard Jones potential, at pressures of (a) 1 atm, (b) 3 kbar and (c) 10 kbar for $\Delta t = 0.01$.

For phase II, a detailed analysis of the data further revealed that the NH_4^+ ion is found to be comparatively freer but still unable to perform free rotation as discussed in our previous paper (Pandey and Trikha 1984). This is associated with the vibrational motion and the plane of vibration of NH_4^+ can become inverted; the dominance of the potential energy could explain this type of motion. However, free rotation has been observed in a molecular dynamics calculation of solid methane by Singh and Trikha (1984), where the potential energy of the central methane molecule (under the influence of 12 neighbours) was found to be comparable in magnitude with the rotational kinetic energy. It seems that free rotation of the NH_4^+ ion could occur at still higher temperatures of about 456 K near the phase II \leftrightarrow phase I transition, where the CsCl type structure changes into the NaCl type.

Fig. 2a shows the potential energy (solid curves) and rotational kinetic energy (dashed curves) of the NH_4Cl system as a function of time step for angular momenta 1 and 3 at a pressure of 3 kbar. The potential energy is found to dominate. In Fig. 2b we have plotted the energy for angular momenta 1 and 3 at 10 kbar. The corresponding energy pattern curves at 1 atm pressure have already been reported by Pandey and Trikha (1984). A comparison of Figs 2a and 2b shows that the variation of energies with respect to time step is similar, indicating the ordered motion of NH_4^+ (except that the fluctuation of the energy seems to increase with an increase in pressure), which corresponds to phase III of the NH_4Cl system.

Figs 3a–c show the potential energy (solid curves) and rotational kinetic energy (dashed curves), for angular momentum 8.0 with $\Delta t = 0.01$, as a function of time step up to 1450. These plots depict our calculations for the energy variation experienced by the NH_4^+ ion at pressures of 1 atm, 3 and 10 kbar. In all three cases we notice rapid fluctuations in the potential and rotational kinetic energy, corresponding to phase II. Here again we find the dominance of potential energy compared with rotational kinetic energy. The percentage fluctuations in energy decrease

slightly with an increase of pressure, indicating the decrease in entropy of the compressible system, in agreement with the experimental work of Trappeniers and van der Molen (1966).

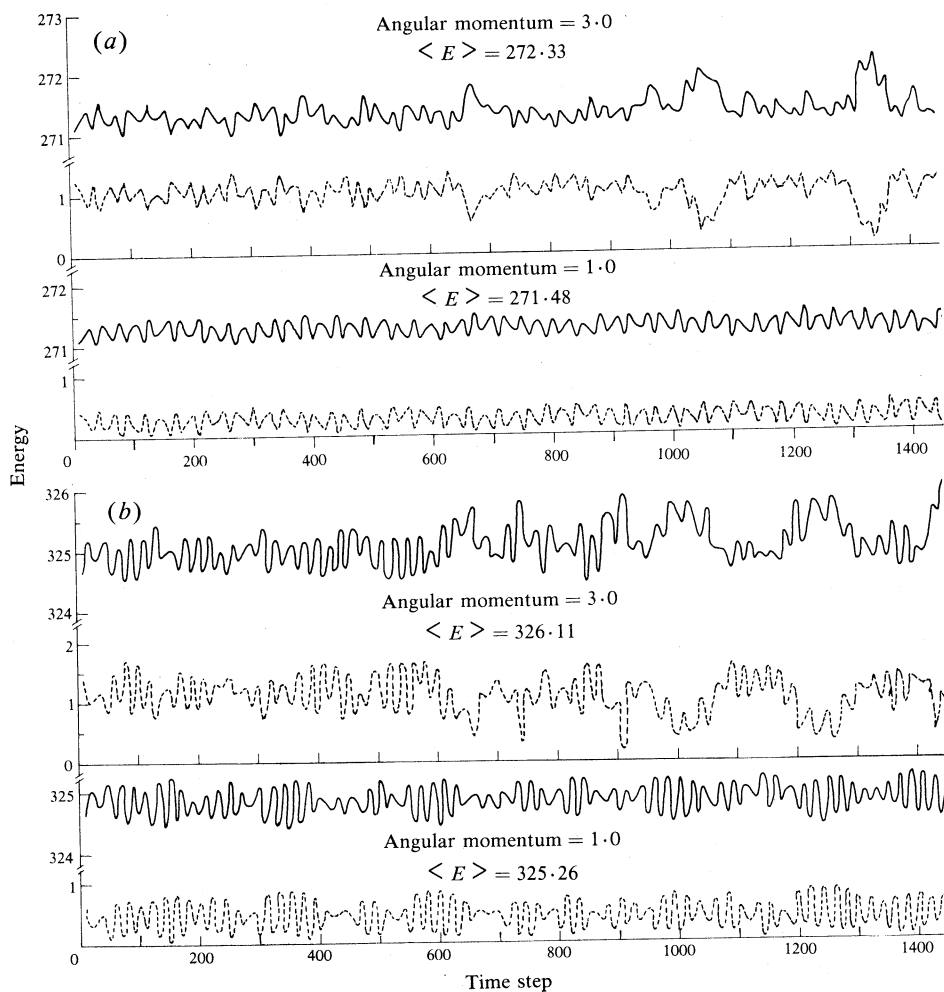


Fig. 2. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the NH_4^+ ion as a function of time step for angular momenta 1.0 and 3.0 (in reduced units) at pressures of (a) 3 kbar and (b) 10 kbar for $\Delta t = 0.01$. The average energy in each case is indicated.

5. Conclusions

The following conclusions can be drawn from the present study:

- (i) Similar to our earlier work, the rotating model of the NH_4^+ ion in the compressible ammonium chloride system supports the Pauling (1930) hypothesis. Contrary to our earlier work, the NH_4^+ ion is found to be partially free in phase II, as depicted by the present detailed analysis of the direction cosine data. However, the free rotation of the NH_4^+ ion, as envisaged by Pauling, would correspond to phase I near 456 K.

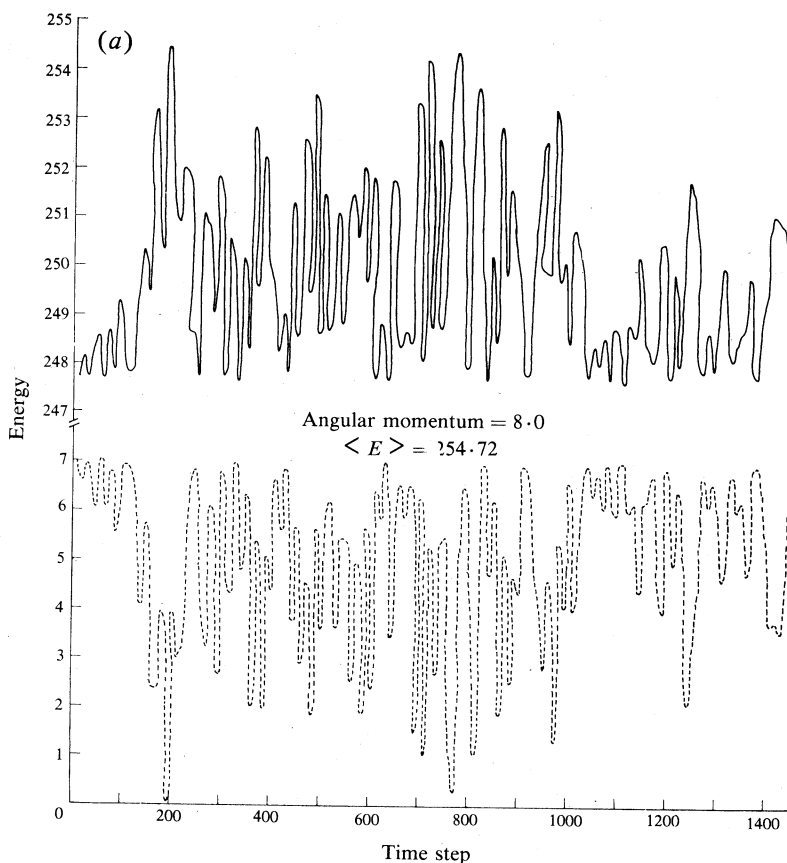
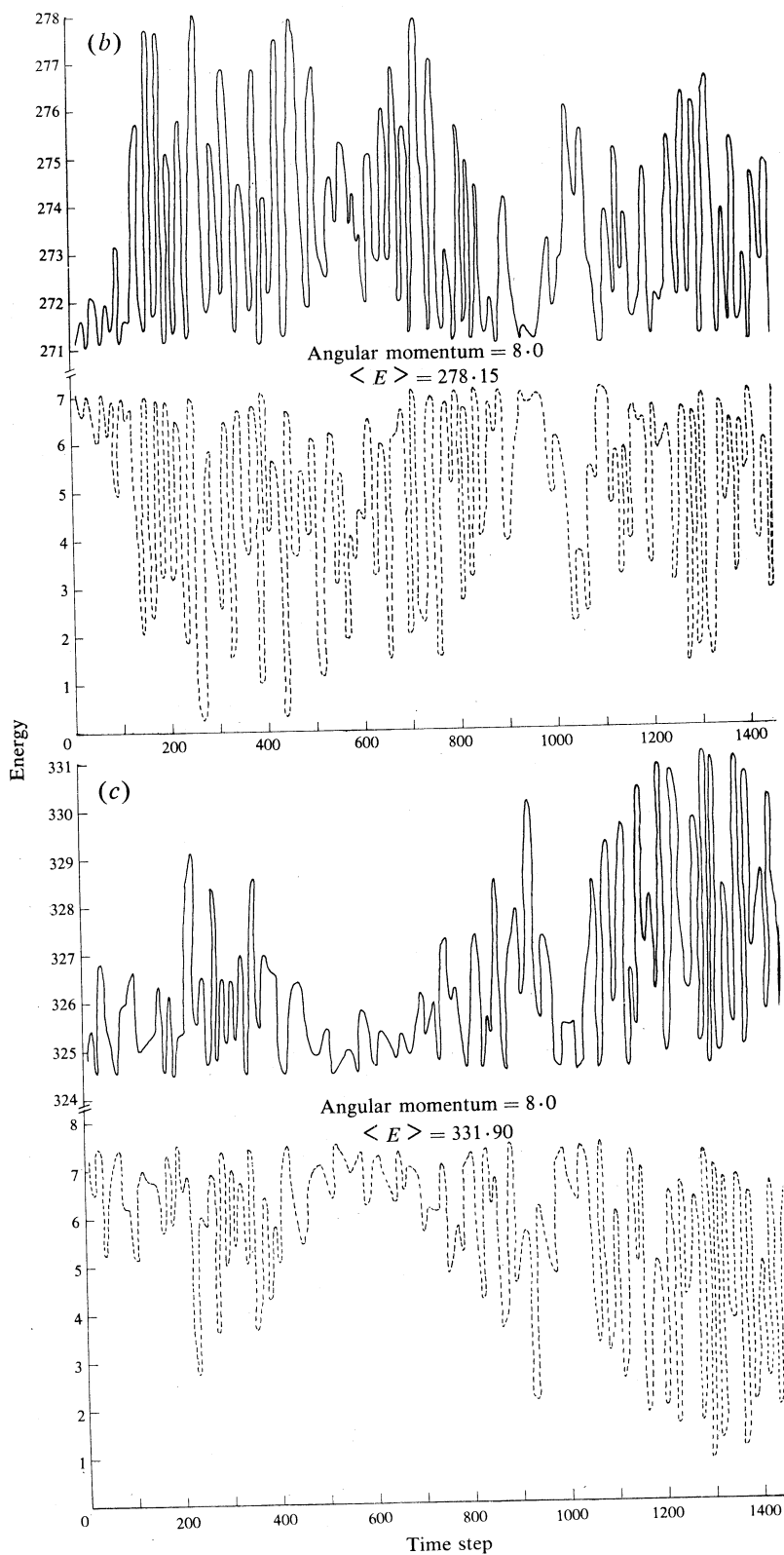


Fig. 3. Potential energy (solid curves) and rotational kinetic energy (dashed curves) of the NH_4^+ ion as a function of time step for angular momentum 8.0 (in reduced units) at pressures of (a) 1 atm, (b) 3 kbar and (c) 10 kbar for $\Delta t = 0.01$. The average energy in each case is indicated.

- (ii) Since the magnitude of the potential energy of the system increases with an increase in pressure, whereas the rotational kinetic energy of NH_4^+ remains unchanged, we believe that the system tends towards orderliness. In other words, the entropy of the system decreases with pressure, in agreement with Trappniers and van der Molen (1966).
- (iii) The computed libration frequency of NH_4^+ was estimated to be approximately 170, 182 and 210 cm^{-1} at pressures of 1 atm, 3 and 10 kbar respectively. This is in agreement with the so-called reststrahlen frequency (representing the vibration of the NH_4^+ sublattice against the Cl^- sublattice) as a function of pressure in a study of the Raman spectrum of ammonium chloride by Ebisuzaki and Nicol (1969).
- (iv) Since we have assumed the structure of compressible ammonium chloride to be of CsCl type in our entire calculation, the discontinuity in the $\langle E \rangle$ versus $\langle E_{\text{RK}} \rangle$ lines (Fig. 1) therefore corresponds only to phases II and III of NH_4Cl . Further, we notice that the slope of the line corresponding to



Figs 3b and 3c.
[see opposite page].

phase II decreases with an increase in pressure. For a pressure of 10 kbar, the two separate lines of phases II and III appear to be almost continuous, one of the reasons for a diminished λ -type peak in the specific heat data at high pressure, as observed by the experimentalists.

- (v) Consideration of pressures greater than 10 kbar leads to truncational errors in the computation and, therefore, we have confined ourselves to the compressible ammonium chloride system up to only 10 kbar.

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