Monte Carlo Studies of the Orientational Order-Disorder Phase Transition in Solid Ammonium Chloride

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Abstract

Monte Carlo methods are used to study the phase transition in $NH_4Cl_{(s)}$ from the orientationally ordered δ phase to the orientationally disordered γ phase. An effective pair potential is used to model the interaction between ions. Thermodynamic properties are computed in the canonical and isothermal-isobaric ensembles. Each ammonium ion is treated as a rigidly rotating body and the lattice is fixed in the low-temperature CsCl geometry. A simple extension of the Metropolis Monte Carlo method is used to overcome quasiergodicity in the rotational sampling. In the constant-NVT calculations the lattice is held rigid; in the constant-NpT calculations the lattice parameter is allowed to fluctuate. In both ensembles the order parameter rapidly falls to zero in the range (200 - 250)K, suggesting that the model disorders at a temperature in fair agreement with the experimental disordering temperature (243K). Peaks in the heat capacity and thermal expansivity curves are also found in the same temperature range.

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I. INTRODUCTION AND EXPERIMENTAL SUMMARY

The general study of phase transitions has been of continuing interest to condensed matter chemistry and physics for many years. Particular efforts have been made to characterize and understand second-order (or continuous) phase transitions and associated critical phenomena [1]. Good examples of such continuous phase transitions are found in certain atomic and molecular solids when they undergo order to disorder transitions [2]. These order-disorder transitions are probed experimentally by observing anomalies in thermodynamic properties like heat capacities and various susceptibilities. Some examples of systems that are known to exhibit disordering phenomena are $NH_4Cl_{(s)}$, β-brass, and $KCN_{(s)}$.

In this study we focus on the order-disorder phase transition in $NH_4Cl_{(s)}$, an interesting case that has received considerable previous theoretical and experimental attention [2]. A helpful review of the experimental data up to 1978 is given by Parsonage and Staveley [2]. As discussed in Reference 2 ammonium chloride has three phases. The two phases generally referred to as δ and γ share the CsCl lattice type shown in Figure 1, whereas the α phase has a NaCl lattice type. First measured and reported by Simon in 1922 [3] and subsequently by other workers [4–7], the $\delta \rightarrow \gamma$ transition has been used as a textbook example of an order-disorder phase transition [8]. From experiment it is known that in the low-temperature δ phase, most of the NH_4^+ molecules are in the same orientation, (the ammonium ions orient with their hydrogen atoms pointing towards the "same" crystallographic axes), and the δ phase is said to be "orientationally ordered." In the γ phase, the orientations with respect to the chloride ions have no long range order [2]. This model of the $\delta \rightarrow \gamma$ phase transition has been supported by various spectroscopic measurements, including neutron scattering experiments and NMR studies [9–14].

The origin of the orientational order in NH_4Cl can be understood in terms of the intermolecular forces of the crystal. There are attractive interactions between the hydrogen atoms in an ammonium ion and the adjacent cage of chloride ions (see Figure 1). Any isolated ammonium ion in a chloride cage tends to align with either of two equivalent sets

of four chloride ions. In Figure 1 the hydrogen atoms point toward the set of chloride ions that has been shaded. In addition to the interactions of ammonium ions with the near-neighbor chloride cage, the ammonium ions interact with each other electrostatically, with the lowest-order, non-zero contribution to the interaction arising from the octapole-octapole interactions characteristic of tetrahedral charge distributions. The octapole-octapole interaction has an asymptotic decay of R^{-7} (R is the distance between the nitrogen centers on any two ammonium ions). There is an absolute potential energy minimum if two interacting ammonium ions are aligned, and there is a higher energy local minimum if two ammonium ions have opposite alignments. We can think of the two potential minima for the ammonium ion in a chloride cage as two available states. These two available states can be mapped onto a two-state Ising model by identifying one orientation with an up spin and the other possible orientation with a down spin [15]. The order-disorder transition has often been interpreted [16] in terms of such a two state Ising model with a positive ferromagnetic coupling constant between near neighbor spins. We shall investigate the energetics of this Ising picture within a simple pair site potential model in Section II of this paper.

Although the interpretation of the transition in terms of the two-state Ising model has been insightful, it is not a perfect description of the transition. At atmospheric pressure, a measurement of the heat capacity C_p as a function of temperature shows a distinctly λ-like shape with a peak at 243K [7]. While this λ character has been used to support the interpretation of this transition in terms of the Ising model, it is known that there is a discontinuous change in the specific volume at this temperature [17–19], as well as a latent heat of transition [5,6]. This transition at atmospheric pressure is, at least, weakly first order, not withstanding the qualitative similarity the system has to an Ising lattice. The first-order character of the transition has led to descriptions of the system in terms of a compressible Ising model [16,20–23].

It has also been established that there is hysteresis associated with the $\delta \to \gamma$ phase transition in measurements of the specific volume [17,18], the spin-lattice relaxation time [11,12], and neutron scattering measurements of the [111] Bragg intensity [12]. Pressure-dependent

3

studies of this system [5,11,19] show that the nature of the transition is a function of pressure. At high pressures (greater than 1400 atmospheres), the transition changes from first order to continuous. This transformation in behavior is characteristic of a tricritical point [1]. The location of the tricritical point on the phase diagram is known to shift to lower pressures when the ammonium ions are deuterated [18,19], implying the importance of quantum effects. To date no complete explanation of the microscopic origin of the tricritical point in ammonium chloride and its deuterated counterparts is available.

The purpose of the work presented here is to provide information leading to a microscopic description of the order-disorder phenomena in ammonium chloride that is more complete than the traditional Ising picture. Our motivation for the study comes from recent investigations [24] into the analogues of phase transition phenomena in small clusters. Many small clusters have thermodynamic properties as a function of temperature that have been interpreted as analogues of bulk phase transition behavior. As examples of first-order transition behavior, small clusters of rare gas atoms exhibit heat capacity anomalies [25], and rapid increases in diffusivities [24] that are characteristic of bulk melting. Recently, the study of phase transition analogues in small clusters has been extended to cases that are similar to second-order transitions. Lopez and Freeman [26] observed heat capacity anomalies in model Pd-Ni alloy clusters, that are reminiscent of the order-disorder transitions known to occur in some bulk alloy materials like β-brass [27]. Studies of analogues to second-order phase transitions in other kinds of materials continue to be of interest. Given this background, it is our intention ultimately to investigate the possibility of orientational disordering transitions in ammonium chloride clusters. To do justice to such a study a detailed simulation of the analogous bulk transition using the same model potential is important. Providing bulk information for future work on the cluster systems is an important motivation of the work we report.

A review of some previous computational studies of transitions in molecular and ionic crystals has been given by Klein [28]. There have also been studies related to the present work by Smith [29] and by Hüller and Kane [30] who focused on the orientational motion of

4

the ammonium ions and by O'Shea [31] who studied related octapolar solids. More pertinent to the present discussion is the work of Klein, McDonald and Ozaki [32] who studied NH_4Br, $KClO_4$ and Li_2SO_4 using molecular dynamics methods. Klein *et al.* [32] introduced a suitable order parameter to monitor the disordering transition in ammonium bromide. We shall make use of the same order parameter in the work we report.

The contents and organization of the remainder of this paper are as follows. In the next section the model potential is discussed along with the basic structural features of the ammonium chloride lattice implied by the model. In Section III we discuss the computational details including how we resolve quasiergodicity problems in the simulations. We present the computed thermodynamic properties in Section IV including a discussion of the chosen order parameter. Of the properties given in Section IV, we show that the model predicts no peak in the isothermal compressibility at the disordering transition for the simulation sample sizes used in the current work. In Section V we identify the lack of peak in the compressibility with finite size effects by presenting results of thermodynamic properties predicted in a compressible Ising calculation as a function of sample size. We summarize our findings and discuss their significance in Section VI.

II. THEORETICAL MODEL

A. Model Potential

In the present study we use classical Monte Carlo methods to compute thermodynamic properties for $NH_4Cl_{(s)}$ as it undergoes an order to disorder transition. The application of classical mechanics to pair models of ionic solids has been explored by Klein and coworkers [28,32], who have used molecular dynamics methods to study dynamical processes in several ionic crystals. Their work gives us good reason to expect that useful information about the order to disorder transition in ammonium chloride can be obtained using a simple pair model potential dominated by Coulombic contributions. We independently evaluate the success of this approach by using the model potential to predict such bulk properties as

the lattice constant and the barrier to rotation of a single ammonium ion between the two local potential minima. We shall confirm that the model potential yields values for these observables that are in reasonable agreement with experiment, and we can expect that the potential is sufficiently accurate for our purposes. The approach we use to validate the effective pair potential has been advocated elsewhere [33].

The specification of the potential surface is somewhat simplified by the dynamical model we assume. In all calculations reported here, we treat the NH_4^+ molecular ions as rigidly rotating bodies, with the center of mass of each NH_4^+ fixed at the center of each cubic cell. This dynamical model makes it unnecessary to specify an internal vibrational potential for the NH_4^+ molecule. We need only set NH_4^+ - NH_4^+, NH_4^+ - Cl^-, and Cl^- - Cl^- interactions to specify a useful effective interaction potential. Each of these interactions is further decomposed into a total of six pair atom-atom interaction terms. Letting $\mathbf{r}$ designate the coordinates of all interacting particles in the system under consideration, we assume that the total interaction potential $U(\mathbf{r})$ is given by

$$U(\mathbf{r}) = \sum_i \sum_{j>i} u_2(r_{ij}) \tag{1}$$

where r_{ij} is the distance between particle i and particle j, and u_2 is a pair potential of the form

$$u_2(r_{ij}) = A_{ij} \exp(-\alpha_{ij} r_{ij}) + \frac{D_{ij}}{r_{ij}^{12}} + \frac{q_i q_j}{r_{ij}} - \frac{C_{ij}}{r_{ij}^6}. \tag{2}$$

Most of the parameters used to define the potential are presented in Table 1. In addition as used elsewhere [32,34] we set $q_H = .35$ and $q_N = -.40$. We also set $q_{Cl} = -1.00$ [35]. The charges used on the nitrogen and hydrogen atoms of the ammonium ion were confirmed by independent *ab initio* calculations [36]. In Table 1 we have assumed transferability of most of the atom-atom interaction parameters from other, similar systems studied previously by Klein *et al.* [32] and Pettit and Rossky [37]. For the parameters not available from previous work, we use standard combination rules, i.e. relations of the form

$$A_{ij} = \sqrt{A_{ii} A_{jj}}, \tag{3}$$

$$C_{ij} = \sqrt{C_{ii}C_{jj}}, \tag{4}$$

and

$$\alpha_{ij} = \frac{\alpha_{ii} + \alpha_{jj}}{2}. \tag{5}$$

The specific sources for the parameters used in Eq.(2) are given as footnotes in Table 1.

As in any calculation, to generate the results that follow both in this and subsequent sections, a finite representation of the lattice was used. To reduce the importance of edge effects, we also used standard minimum image periodic boundary conditions [33]. In the main (or central) sample cell we included either 8 ion pairs (48 atoms) corresponding to a 2x2x2 lattice, or 27 ion pairs (162 atoms) corresponding to a 3x3x3 lattice. To evaluate efficiently the sums over the periodic images we also used standard Ewald methods with vacuum boundary conditions [33]. We found the Ewald calculations to be converged by setting the decay parameter of the error functions to 5.55 in units of the inverse length of a side of the central sample cell [38] and including 125 reciprocal lattice vectors in the reciprocal lattice sum.

B. Properties of the lattice within the model potential

A primary indication of the validity of the parameters listed in Table 1 is given by comparing the lattice constant and cohesive energy at 0K predicted by the model potential with experiment. Using the parameters in Table 1, we have minimized the energy of ammonium chloride using the cesium chloride phase. We have assumed all ammonium ions in the lattice are oriented in the same direction with respect to the crystallographic axes in the manner shown in Figure 1. The number of ion pairs in the central simulation cell was taken to be 27, and the Ewald sums have been evaluated as discussed above. The resulting lattice constant a_0 (the distance between the nitrogen atom on an ammonium ion and an adjacent chloride ion) is calculated to be 3.789 Å with a cohesive energy of -759.7 kJ mol^{-1}. The agreement with the experimental lattice constant (3.868 Å) [39] and the experimental cohesive energy

at 298K (-697 kj mol^{-1}) [40] is within acceptable limits. The differences between the calculated and experimental values are a result of finite size and thermal effects as well as the details of the model potential.

Another indication of the accuracy of the model potential is given in Figure 2 where the potential energy U of the lattice with 27 ion pairs in the central lattice is plotted as a function of the rotation angle ϕ of the central ammonium ion [see Figure 1]. At an angle of $\phi = 0$ (where we set the zero of energy in this figure) all the ammonium ions in the lattice are oriented with respect to a set of crytallographically equivalent chloride ions. The central ammonium ion is then rotated as in Figure 1 until an angle of $\phi = \pi/2$ where the central ammonium ion is oriented with respect to the alternate set of chloride ions in the lattice. At this angle the ammonium ion finds a local potential minimum higher in energy than the absolute minimum at $\phi = 0$. The ~18 kJ mol^{-1} barrier to rotation evident in Figure 2 is in good agreement with experimental estimates based on NMR and other data [2]. This agreement is another indication that the potential model can be expected to be at least sufficiently accurate to account qualitatively for the order to disorder phenomenology of the system.

In addition to calculating the barrier to rotation for the ammonium ions, we investigated the effective range of the ammonium-ammonium interactions in the lattice. As an initial geometry we considered a lattice with all ammonium ions oriented in the same direction with respect to a set of crytallographically equivalent set of chloride ions except for the central ammonium ion in the simulation cell. This central ammonium ion was oriented to the other set of chloride ions (i.e. at an angle of $\phi = \pi/2$ in Figure 2). We then compared the energy of the lattice with a single ammonium ion out of orientation, with the energy obtained by rotating another ammonium ion in the lattice at a distance R from the central ammonium ion so that the central ion and the additional ion were oriented in the same direction. It is important to recognize that the energy calculations were performed without any nearest neighbor assumptions about the range of the interactions. The change in potential energy ΔU obtained from this process is given in Figure 3 as a function of R. At distances beyond

the first ammonium ion cage, ΔU becomes constant, and as is evident from Figure 3, the interaction between ammonium ions can be well represented by a nearest neighbor model.

C. Implications

The simple pair model expressed in Eq.(2) gives rise to a stable CsCl lattice with the ammonium ions oriented in the same direction in its lowest energy 0K structure. The orientational ordering is a consequence of the attractive octapole-octapole interaction between the ammonium ions. For ammonium chloride the octapole-octapole coupling is sufficiently weak that interactions beyond the near neighbors can be neglected.

These preliminary indications lend support to representing the system by a simple Ising model with a positive ferromagnetic coupling constant. However, as indicated in the Introduction the simple Ising picture is not of sufficient complexity to explain the phenomenology of the order to disorder transition. The transition from first order to second order behavior, characteristic of a tricritical point, provides justification for investigating the transition with more detail than the Ising picture. In the next section we develop the necessary Monte Carlo tools to investigate the system within the model potential of Eq.(2). By performing simulations in the isothermal-isobaric ensemble, coupling between lattice motions and rotational motions of the ammonium ions will be included.

III. SIMULATION METHOD

The details of the Metropolis Monte Carlo method [41] both in the canonical and in the isothermal-isobaric ensemble been discussed in many references [33,42,43]. In this section we explain some of the details specific to the simulations performed in the current work, and the approach we used to insure that the simulations were done in an ergodic fashion.

Since the Ewald sums constituted the dominant fraction of the computational effort in this work, we examined the consequences of decreasing the number of reciprocal lattice vectors. Although the absolute value of the cohesive energy was sensitive to including fewer

reciprocal lattice vectors, we found the lattice constant and the barrier to rotation of the ammonium ions (See Section II B) to change by $\sim$0.3 percent when only 8 reciprocal lattice vectors (rather than the converged 125) were included. Our interest is in the order to disorder transition, and the transition can be expected to be sensitive to the barriers and not to the absolute value of the cohesive energy of the crystal. We tested this assumption by comparing fluctuation quantities (e.g. heat capacities, compressibilities, etc.) sensitive to the location of the transition in the canonical ensemble with 8 and 125 reciprocal lattice vectors included. We observed no significant changes in the computed properties. Most of the Monte Carlo results were determined with the smaller set of reciprocal lattice vectors.

The calculations in the canonical ensemble were performed using central cell sizes of both 8 ion pairs and 27 ion pairs. For each central cell size, the lattice parameters were adjusted to give the minimum energy for the orientation having all the ammonium ions in the same direction. About each ammonium ion in the lattice we constructed a set of orthogonal Cartesian axes. Each Monte Carlo point in the canonical simulations consisted of a rotation of a randomly chosen ammonium ion about one Cartesian axis randomly chosen [44]. The maximum allowed rotation angle was adjusted so that about fifty percent of the moves were accepted. As is typical in Monte Carlo simulations, this maximum allowed rotation angle was a function of temperature and was found by performing short run experiments at each temperature. In addition to these normal Metropolis moves, we found it necessary to include moves with larger maximum displacements ten percent of the time. The purpose of the moves with magnified displacements (magwalking) was to insure that the ammonium ions were given the opportunity to overcome the potential barrier separating the two minima in the potential surface (See Figure 2). Consequently, the maximum displacement in the magwalking moves was taken to be $\pi/2$.

Evidence that the magwalking scheme discussed in the previous paragraph provides an ergodic distribution is given in Figure 4 where the average potential energy of the 8 ion pair lattice is plotted as a function of temperature. The data used in generating both curves of Figure 4 was initiated with configurations having the ammonium ions in random

10

orientations. Quasiergodicity difficulties [25,45] can be anticipated at low temperatures where all the ammonium ions are expected to have the same orientation with respect to the chloride ions. The data in the upper curve of Figure 4 was generated using Metropolis Monte Carlo methods with a fixed step size for all moves. The unstable behavior at low temperatures is evident. The instability is a result of rapid quenching of the initial random orientations of the ammonium ions into local, high-energy minima. This disordered trapping causes the quasiergodicity in the sampling of the rotations. In the lower curve of Figure 4, the magwalking scheme described in the previous paragraph was used. The sensible behavior at low temperatures is clear, and the simple magwalking scheme can be expected to solve the quasiergodicity problems in this system.

In the isothermal-isobaric simulations the Monte Carlo sampling is with respect to the distribution

$$\rho(\mathbf{r}) = \Delta^{-1} \exp(-\beta U(\mathbf{r}) - \beta p V) \tag{6}$$

where U is the system potential energy, $\beta = 1/k_B T$ where T is the temperature and k_B is the Boltzmann constant, p is the pressure, V is the volume and Δ^{-1} is a normalization. To perform the isothermal-isobaric simulations in addition to the rotational moves used in the canonical study, the lattice parameter (and consequently the system volume) was varied. From numerical experiments we found that including volume fluctuations about forty percent of the time gave good convergence of the computed properties. The volume fluctuations were included with Metropolis Monte Carlo moves again with a maximum displacement chosen so that about fifty percent of the attempted fluctuations were accepted. Unlike the rotational moves, we found no evidence of quasiergodicity in the volume fluctuations. When a mixture of maximum step sizes were used in the volume moves, we found no statistically significant changes in the computed thermodynamic properties.

The volume fluctuations included in this work correspond to a single vibrational breathing mode for the lattice. Of course, the real lattice dynamics in NH_4Cl is more complex than this simple picture. However, at least we have been able to include important contributions

to the coupling between the rotational and vibrational modes of the lattice.

In the calculations that follow, we have calculated several fluctuation quantities in addition to the energy E and enthalpy $H = E + pV$ of the crystal. These fluctuation quantities include the constant volume and constant pressure heat capacities

$$C_V/k_B = \frac{3N}{2} + \beta^2[<U^2> - <U>^2] \tag{7}$$

and

$$C_p/k_B = \beta^2[<H^2> - <H>^2] \tag{8}$$

the isobaric coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{N,p} \tag{9}$$

$$= (k_B T^2 V)^{-1}[<VH> - <V><H>] \tag{10}$$

and the isothermal compressibility

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T} \tag{11}$$

$$= (k_B T V)^{-1}[<V^2> - <V>^2] \tag{12}$$

In Eq.(7) the notation $<>$ represents averages in the canonical ensemble, and in Eqs.(8),(10) and (12) the notation $<>$ represents averages in the isothermal-isobaric ensemble. In the results we report in the next section, C_V, C_p, α and κ were calculated directly from these fluctuation expressions.

In the calculations that follow, error bars were estimated at the double standard deviation level by "binning" the data and estimating the variance of the bin averages about the total walker average. In the limit of large numbers, this method is known to be appropriate for the correlated data generated by a Metropolis walk. However, for finite Monte Carlo samples the suitability of the binning parameters should be checked for a given model system to ensure

the reliability of the error estimates. We performed these checks by comparing the computed error estimates to those obtained through covariance calculations of the error [46,47]. We observed the two methods to give similar results, indicating that suitable binning parameters were chosen for this study.

IV. RESULTS

In this section we provide results of the Monte Carlo studies of the properties of the NH_4Cl lattice as a function of temperature. As expected we shall find features in the thermodynamic properties as a function of temperature that can be associated with a transition from rotational order to disorder. To monitor the degree of orientational order in the lattice, we use an order parameter introduced by Klein *et al* [32]. To define the order parameter we place the origin of a set of Cartesian axes on the nitrogen atom of each ammonium ion, and we orient the Cartesian axes so that the z-axis is orthogonal to a square face of chloride ions in the chloride cage. The x and y axes are then oriented along the edges of the lattice as shown by the coordinates displayed in Figure 1. For each ammonium ion we define

$$M_j = \frac{3\sqrt{2}}{4} \sum_{i=1}^{4} x_j^i y_j^i z_j^i \tag{13}$$

where x_j^i is the x-component of the coordinate of a unit vector pointing from the origin toward the i'th hydrogen atom on ammonium ion j and the summation runs over the 4 hydrogen atoms on the ammonium ion. M_j is defined so that $M_j = 1$ when ammonium ion j is oriented exactly to one set of chloride ions, and $M_j = -1$ when it is oriented exactly to the alternate set of chloride ions (see Figure 1). Of course M_j is a continuous function of the coordinates, so that it takes on values of $\pm$ 1 only when the hydrogen atoms point exactly to a set of chloride ions. This definition of M_j enables a mapping of the orientations of the ammonium ions onto a spin variable. When M_j is positive we can think of ammonium ion j as having a positive or "up" spin and when M_j is negative, we can think of ammonium ion j as having a "down" or negative spin. To clarify the mapping, in Figure 5 we display a particular configuration of the ammonium chloride lattice taken from a canonical simulation

13

with 8 ion pairs in the central cell at 300K. We have placed arrows on each nitrogen atom in the lattice to carry information about the algebraic sign of M_j. Positive M_j is represented by an up arrow and can be interpreted as an up spin. Similarly, negative M_j is represented by a down arrow and can be interpreted as a down spin. To simplify the discussion often we shall describe the orientations of the ammonium ions in terms of these spin variables. In analogy with the Ising model, we can also define the *magnetization per site M* of the lattice by

$$M = \frac{1}{N} \sum_{j=1}^{N} M_j \tag{14}$$

where the summation on j is over the N ammonium ions in the lattice. Associated with the magnetization is a susceptibility per site χ defined by

$$\chi = N(< M^2 > - < M >^2) \tag{15}$$

where the notation $<>$ in Eq.(15) represents an ensemble average. We use M as the order parameter for the orientational order to disorder transition in the system.

A. Canonical simulations

In the canonical simulations for each temperature we included 50000 passes without the accumulation of data followed by 200000 passes with data accumulation. Each pass consisted of cycling through the ammonium ions in the central simulation cell and attempting to rotate each ion once.

We begin by examining the changes in computed thermodynamic properties that accompany alterations in the size of the central sample cell. In Figure 6 we present the constant volume heat capacity C_V per ion pair in units of the Boltzmann constant as a function of temperature. The upper curve gives results when the central cell consists of 8 ion pairs and the lower curve gives results for a 27 ion pair central cell. By increasing the size of the central cell the width of the heat capacity maximum narrows as expected.

By examining configuration files it is possible to verify that the maxima in the heat capacity seen in Figure 6 are a result of the rotational disordering of the ammonium chloride lattice. We can confirm this interpretation by monitoring the magnetization as a function of temperature. In Figure 7 the curve connected by diamonds are computed values of $< M^2 >$ as a function of temperature for the 27 ion pair lattice. We have chosen to present $< M^2 >$ rather than $< M >$ because in any finite lattice $< M >= 0$ at any finite temperature. In a completely oriented configuration as the temperature approaches zero, M^2 is always 1 whereas M can be either 1 or -1. Then at low temperatures $< M^2 >$ must approach unity, and at high temperatures $< M^2 >$ must approach zero. This behavior is evident in Figure 7. At the transition temperature of $\sim$210K $< M^2 >$ changes rapidly. This transition temperature matches the peak of the maximum in C_V as a function of temperature. Also presented in Figure 7 is the result of mapping the magnetization onto a spin model. The data for this spin model are plotted in Figure 7 as points represented by triangles. In the spin model we set

$$M_s = \frac{1}{N} \sum_{j=1}^{N} \text{sign}(M_j) \tag{16}$$

where $\text{sign}(M_j)$ is the algebraic sign of M_j and M_s represents the magnetization of the system described by the spin variables.

The difference between the two curves given in Figure 7 clarifies the extent to which the decrease in the magnetization can be attributed to librational modes. Since M is a continuous function of the coordinates of each ammonium ion, the magnetization will decrease as a function of temperature even if all the ions remain ordered. In contrast, M_s will change only if an ammonium ion in a particular configuration changes its "spin;" i.e. overcomes the barrier between the two minima in the rotational potential surface. By comparing the decay of the order parameter to the decay of the Ising-like spin parameter in Figure 7, we observe that the initial decay of the order parameter is a result of the onset of librational motions. At the transition temperature, the order parameter rapidly decays to zero because of the loss of long range order of the NH_4^+ orientations.

Although in a finite system $< M_s >=0$, in an actual Monte Carlo simulation $< M_s >$ may differ from zero, because both inverted configurations may be reachable only in Metropolis walks that are sufficiently long. The length of the walk required to actually calculate a zero value for $< M_s >$ will grow both with decreasing temperature and increasing system size. The effect of the finite walks can be made apparent by examining the susceptibility χ as a function of temperature. Such a graph is given in Figure 8 for the lattice consisting of 27 ion pairs in the central cell. The maximum of χ occurs at the same temperature as the temperature at which $< M^2 >$ changes rapidly. The fluctuations in χ at this temperature are also large. Of course in the limit of an infinite system $< M >\neq 0$, and the susceptibility we calculate should approach the infinite system result with increasing system size.

B. Isothermal-isobaric simulations

Canonical simulations do not have sufficient flexibility to incorporate coupling of the rotational modes of the ammonium ions with the vibrational modes of the lattice. To obtain preliminary understanding of the effects of such couplings, we have performed Monte Carlo simulations of the thermodynamic properties of the system in the isothermal-isobaric ensemble. By fixing the pressure of the system, the isothermal-isobaric simulations more closely match the experimental situation than the canonical studies. In exchange for this closer connection with experimental data, calculations in the isothermal-isobaric ensemble are computationally more demanding than calculations in the canonical ensemble. The range of system sizes that can be studied while achieving acceptable levels of convergence is restricted.

The simulations in the isothermal-isobaric ensemble were performed on a 27 ion pair representation of the ammonium chloride lattice in the central cell. At each temperature 300000 Monte Carlo passes were performed without data accumulation followed by about one million passes with data accumulation. Each pass consisted of sequential attempted rotations of each ammonium ion in the same manner as in the canonical simulations. Additionally,

volume fluctuations were attempted in forty percent of the passes. Ten percent of the rotational moves used a maximum rotation angle of $\pi/2$ using the magwalking scheme found to be successful in the canonical simulations. The remaining ninety per cent of rotational moves used a maximum rotational displacement determined so that about fifty percent of the attempted moves were accepted.

In Figure 9 we present $< M^2 >$ as a function of temperature calculated both using the definition of the order parameter given in Eq.(13) (the points represented by diamonds) and the projection of the order parameter onto spin variables (the points represented by triangles). The projected spin order parameter is the same as that used in the canonical simulations and discussed previously. The region of rapid change in the order parameter is at a temperature of about 250K. The onset of the transition is more clearly seen in Figure 10 where we plot the susceptibility as a function of temperature. The maximum occurs at a temperature of about 250K, a temperature where the fluctuations in χ are large.

We measure the average volume of the crystal in terms of the lattice parameter a_0. The average volume is of interest because we would expect to observe a rapid volume change near any first order transition. In Figure 11 the lattice parameter in Å is plotted as a function of temperature. Although no rapid change in the lattice parameter is seen, there is a clear change of slope at the transition temperature.

In Figure 12 we give the constant pressure heat capacity C_p per ion pair, the isothermal compressibility κ and the isobaric coefficient of thermal expansion α as a function of temperature. The onset of the maxima in C_p and α match the onset of the order to disorder transition as identified by the order parameter. From basic considerations [48] a maximum is expected in κ at the transition temperature as well. As is evident from Figure 12, κ is found to be a monatomic increasing function of the temperature with no apparent peak. To test the sensitivity of the behavior of κ to the number of reciprocal lattice vectors included in the Ewald sums, we increased the set from 8 to 125 reciprocal lattice vectors. No significant change in the compressibility as a function of temperature was observed. We believe that the lack of peak is a consequence of the finite size of the central simulation cell, and we give

17

evidence for this in the next section.

V. A COMPRESSIBLE ISING MODEL

In the previous section we showed that in the isothermal-isobaric ensemble at the disordering transition, peaks were observed in the constant pressure heat capacity and in the isobaric coefficient of thermal expansion. The location of the peak maxima were in good agreement with the temperature at which there were rapid changes in the order parameter. The identification of the peak maxima with the disordering phenomena seems well justified.

In contrast to the properties discussed in the previous paragraph, no maximum was observed in the isothermal compressibility. Since the compressibility should have a specific heat-like divergence at the transition temperature in the infinite system [48], the lack of observation is a concern. In this section we show that similar behavior is found in finite representations of a compressible two-dimensional Ising model on a square lattice, and the lack of peak in the isothermal compressibility we observed for NH_4Cl may be attributable to finite size effects.

The compressible model we use is based on the two-dimensional Hamiltonian

$$H = -\frac{a}{R^7} \sum_{<ij>} S_i S_j + 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \tag{17}$$

where S_i is the spin on site i and can take on values of + or - 1, the notation $<ij>$ on the sum represents summation over nearest neighbors only, a, ϵ and σ are parameters and R is the lattice constant. The first term in the Hamiltonian is the standard spin-spin interaction in the Ising model with a lattice-parameter dependent coupling constant. We choose the R-dependence of the coupling constant to decay with distance like the octapole-octapole interaction in ammonium chloride (R^{-7}). The second term in the Hamiltonian is in the form of a usual Lennard-Jones potential and provides a balance for the volume fluctuations so that the lattice will relax to a physical nearest neighbor distance. In the Ising simulations that follow we have attempted to choose parameters for Eq. (17) that mimic the ammonium

18

chloride results of the previous section. For the bulk Lennard-Jones σ parameter, we take a value that can make the equilibrium lattice distance near that of the real crystal. We then take $\sigma = R_e/2^{1/6}$ where $R_e = 7.31$ Bohr. We take ϵ to match the ammonium chloride lattice energy of 8380K. Since the barrier to changing the orientation of a single ammonium ion in a completely ordered ammonium chloride lattice is about 1000K, we take $a = 2000R_e^7/N_{\text{spin}}$, where N_{spin} is the number of spins in the primary cell.

We determined the properties of the two-dimensional compressible Ising lattice defined by Eq.(17) using Monte Carlo simulations in the isothermal-isobaric ensemble. The simulations consisted of two-million moves without data accumulation followed by 10 million Monte Carlo moves with the accumulation of data at each temperature. Changes in the R-parameter were made forty per cent of the time and the two-dimensional pressure was arbitrarily set to 1 atomic unit of pressure. Simulations were performed on 4x4, 8x8, 16x16 and 32x32 lattices with periodic boundary conditions included.

Shown in Figure 13 is the constant pressure heat capacity of the compressible Ising model for 4x4, 8x8, 16x16 and 32x32 lattices from top to bottom in the figure. The peak at 240K in the heat capacity occurs at the same temperature as rapid changes in the magnetization of the model. As the number of spins in the simulation is increased the width of the peak narrows as expected. Given in Figure 14 is the isothermal compressibility as a function of temperature. Again from top to bottom is κ for a 4x4, 8x8, 16x16 and 32x32 lattice. For the 4x4 lattice, no peak appears in the compressibility. As the sample size is increased, a peak develops in the compressibility at the transition temperature. Evidently, the existence of a peak in the compressibility is more sensitive to finite size effects than the heat capacity. Although not shown here, the isobaric coefficient of thermal expansion shows a peak at the transition temperature for all lattice sizes. These Ising results lend support to our assumption that the lack of peak in κ in the isothermal-isobaric simulations of ammonium chloride is a result of finite size effects.

VI. SUMMARY AND DISCUSSION

In this work we have applied Monte Carlo methods in the canonical and isothermal-isobaric ensembles to calculate the thermodynamic properties of $NH_4Cl_{(s)}$ modeled by simple point charge pair interaction potentials. In both ensembles the model potential predicts an order to disorder transition associated with the rotational orientations of the ammonium ions in the lattice. In the isothermal-isobaric ensemble at 1 atmosphere pressure, the transition temperature is about 250K, as determined from the rapid growth of the susceptibility. Although we have made no effort to determine the transition temperature with any precision, the agreement between the approximately determined temperature and the experimental result (243K) is satisfying.

The central sample cell used in the simulations contained a maximum of 27 ion pairs. Extensions to larger central cell sizes were inhibited by the large portion of the computer time needed to evaluate the Ewald corrections. Apparently this size limitation produced unreliable values for the isothermal compressibility, a quantity that compressible Ising calculations imply is sensitive to the size of the central cell.

There are several outstanding questions about the behavior of ammonium chloride that require further attention. We found no evidence in our simulations for a rapid change in the molar volume at the transition temperature. Since the transition is known to be first order at atmospheric pressure [19], it is worth examining some of the physical effects not included in the simulations. A true discontinuity in the lattice constant would require an infinite central simulation cell. The unseen rapid change in volume may be another example of a finite size effect. However, in the simulations presented here we have included only those low frequency vibrational modes where the overall crystal symmetry is unaltered. Calculations that include more general variations in the locations of the ionic mass centers would clearly be of interest. Inclusion of the internal vibrations on the ammonium ions can be expected to be of less importance owing to the high frequencies of those motions.

Another approximation in the results has been the application of classical mechanics.

Classical calculations can be interpreted as the infinite mass limit of a corresponding quantum calculation. If quantum effects were not important, our simulations would be equally applicable to the phase diagram of $ND_4Cl_{(s)}$. Experimentally, a significant shift of the tricritical point to lower pressures is known to occur when the ammonium ions are deuterated [18,19]. It is possible that the classical system at atmospheric pressure has a continuous disordering transition, and the location (or existence) of a tricritical point is a consequence of quantum effects. A quantum path integral study of ammonium chloride within the same model potential would clearly be of interest.

ACKNOWLEDGEMENTS

TABLES

TABLE I. The parameters used in the model potential[d]

Pair	A_{ij}	α_{ij}	C_6	D_{12}
H-H[a]	1.0162	1.9950	2.9973	0
N-N[b]	104.74	1.5611	25.393	0
Cl-Cl[b]	125.55	1.7489	113.68	0
H-N[a]	10.318	1.7780	8.7229	0
H-Cl[c]	0	0	10.033	43884.0
N-Cl[a]	114.22	1.6550	53.736	0

[a] Combining rules

[b] Reference [32]

[c] Reference [37]

[d] Units of energy in Hartree and units of length in Bohr

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[15] When the hydrogen atoms point directly to the chloride ions in any cubic cage, there are 24 possible orientations. The 24 orientations consist of two sets each set of which has 12 equivalent configurations. In the Ising picture the order to disorder transition

corresponds to the spontaneous breaking of the symmetry that takes one set of 12 configurations to the other set of 12 configurations.

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FIGURE CAPTIONS

1. The two "spin" orientations of an ammonium ion in a cage of 8 chloride ions. Each orientation represents a potential minimum with the hydrogen atoms on the ammonium ion pointing to the shaded chloride ions. The two orientations are related to one another by rotating the ammonium ion by an angle of $\pi/2$ about the z-axis. The arrows between the hydrogen atoms and the chloride ions are included for clarity. [49]

2. The potential energy U in kJ mol^{-1} of an oriented ammonium chloride lattice with 27 ion pairs in the central cell and Ewald corrections included. The energy is given as a function of the rotation angle ϕ for a central ammonium ion as it is rotated out of orientation with the remaining ammonium ions in the lattice (see Figure 1).

3. The difference in energy ΔU in kJ mol^{-1} between an ammonium chloride lattice with with all ammonium ions oriented in the same direction except the central ion and an ammonium chloride lattice with all ammonium ions oriented in the same direction except for the central ion and another ion a distance R in Å from the central ion. The rapid approach to an asymptote is a consequence of the octapole-octapole interaction and lends support to the representation of the lattice by a nearest neighbor Ising model.

4. The average potential energy in kJ mol^{-1} of NH$_4$Cl using 8 ion pairs in the central simulation cell as a function of temperature. Both curves were generated from an initial configuration with the ammonium ions in a random rotational configuration. In the upper curve ordinary Metropolis moves were used whereas in the lower curve a magnified step size was included ten percent of the time. The quasiergodicity problems evident in the upper curve at the lower temperatures are removed by the "magwalking" strategy. The error bars are smaller than the plotted points.

5. An 8 ion pair representation of the ammonium chloride lattice. The representation is a particular configuration taken from a canonical simulation at 300K. The arrows

attached to each ammonium ion represent the algebraic sign of M_j. The up arrows are on ammonium ions with positive M_j and the down arrows are on ammonium ions with negative M_j. The arrows represent a mapping of the ammonium ion orientation onto a spin variable. [49]
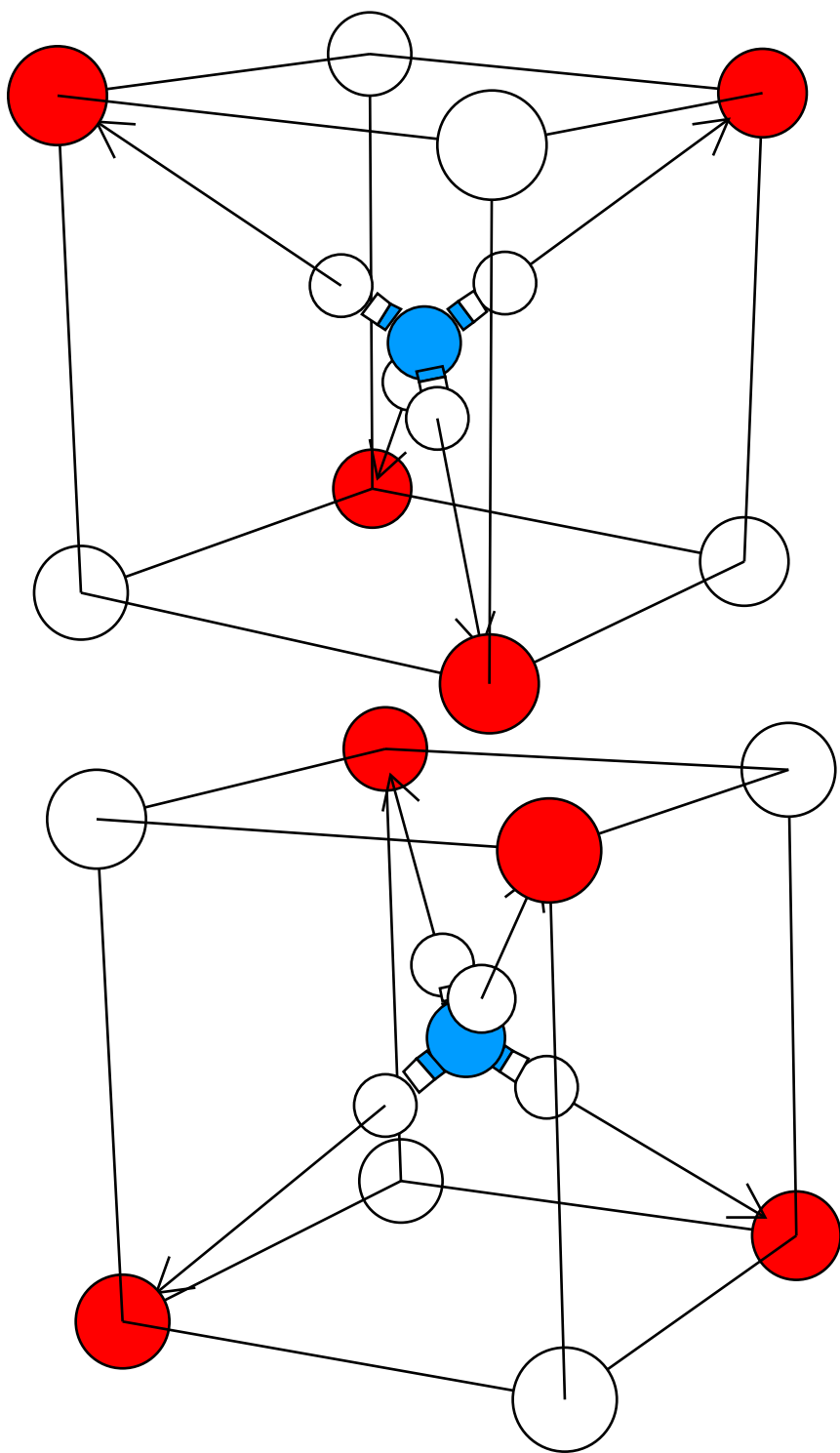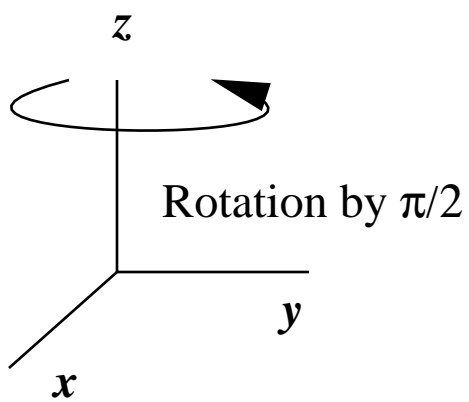
6. The constant volume heat capacity per ion pair in units of k_B of ammonium chloride as a function of temperature. The data in the upper curve were obtained from canonical simulations with 8 ion pairs in the central cell, and the data in the lower curve were obtained from canonical simulations with 27 ion pairs in the central cell. By increasing the size of the central simulation cell the heat capacity narrows with a peak maximum at 210K. The error bars are at the double standard deviation level.

7. The square of the magnetization as a function of temperature for a 27 ion pair representation of the ammonium chloride lattice in the canonical ensemble. The points represented by diamonds were computed directly using Eq.(13). The points represented by triangles were obtained by mapping each ammonium ion orientation onto a spin variable as discussed in the text. The magnetization changes rapidly at the same temperature that the heat capacity shows a maximum in Figure 6. The error bars in this figure are smaller than the representations of the plotted points.

8. The susceptibility as a function of temperature for a 27 ion pair representation of the ammonium chloride lattice in the canonical ensemble. The error bars are at the double standard deviation level. The maximum in the peak of the susceptibility matches the maximum in the heat capacity and the region of rapid change in the magnetization.

9. The square of the magnetization as a function of temperature for a 27 ion pair representation of the ammonium chloride lattice in the isothermal-isobaric ensemble at a pressure of 1 atmosphere. The points represented by diamonds were computed directly using Eq.(13). The points represented by triangles were obtained by mapping each ammonium ion orientation onto a spin variable as discussed in the text. The
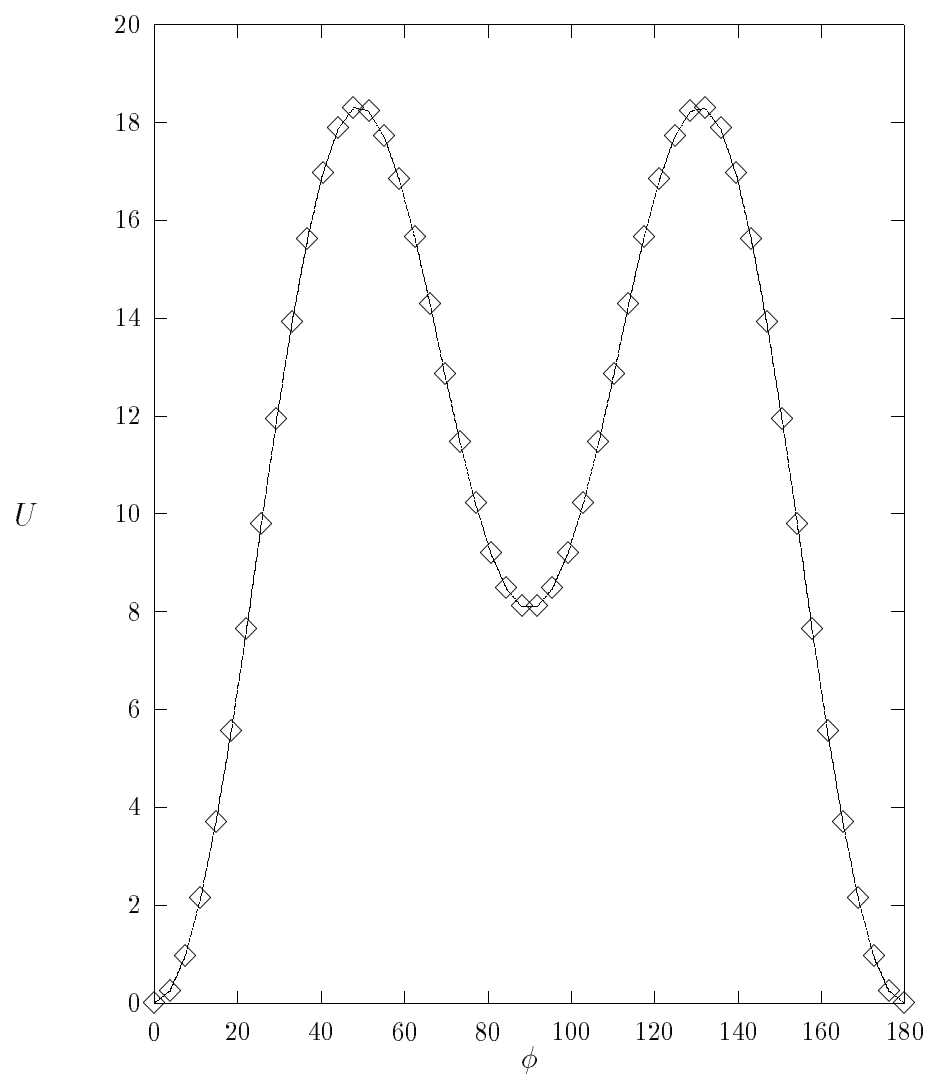
28

magnetization changes rapidly at the same temperature that the heat capacity and isobaric coefficient of thermal expansion have maxima. The error bars in this figure are smaller than the representations of the plotted points.
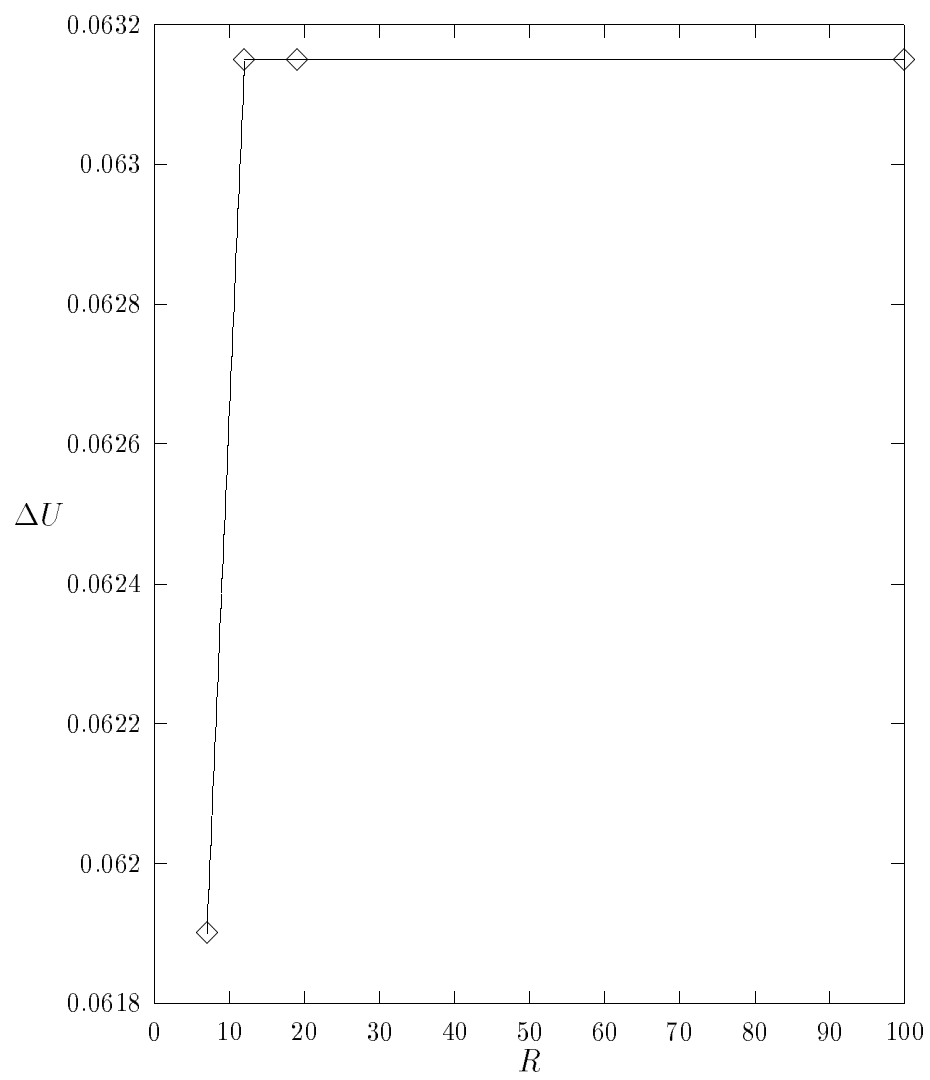
10. The susceptibility as a function of temperature for a 27 ion pair representation of the ammonium chloride lattice in the isothermal-isobaric ensemble. The error bars are at the double standard deviation level. The maximum in the peak of the susceptibility identifies the onset of the order to disorder transition.

11. The lattice parameter a_0 in Å as a function of temperature for the 27 ion pair representation of the ammonium chloride crystal at 1 atmosphere pressure calculated in the isothermal-isobaric ensemble. Although no discontinuous change in the lattice parameter is seen, a slope change is apparent at the transition temperature. The inflection matches the location of the peak in the isobaric coefficient of thermal expansion. The error bars are at the double standard deviation level.

12. The constant pressure heat capacity C_p per ion pair in units of k_B, the isobaric coefficient of thermal expansion α in K^{-1} and the isothermal compressibility κ in atmospheres^{-1} as a function of temperature for the 27 ion pair representation of the ammonium chloride crystal at 1 atmosphere pressure in the isothermal-isobaric ensemble. The maxima in C_p and α match the temperature at which there are rapid changes in the order parameter. The lack of a maximum in κ is likely a result of finite size effects (see text). The error bars are at the double standard deviation level.

13. The constant pressure heat capacity for the compressible Ising model. The four panels from top to bottom are results for 4x4, 8x8 16x16 and 32x32 lattices with periodic boundary conditions. The error bars are at the double standard deviation level.

14. The isothermal compressibility in inverse atomic units of pressure for the compressible Ising model. The four panels from top to bottom are results for 4x4, 8x8 16x16 and
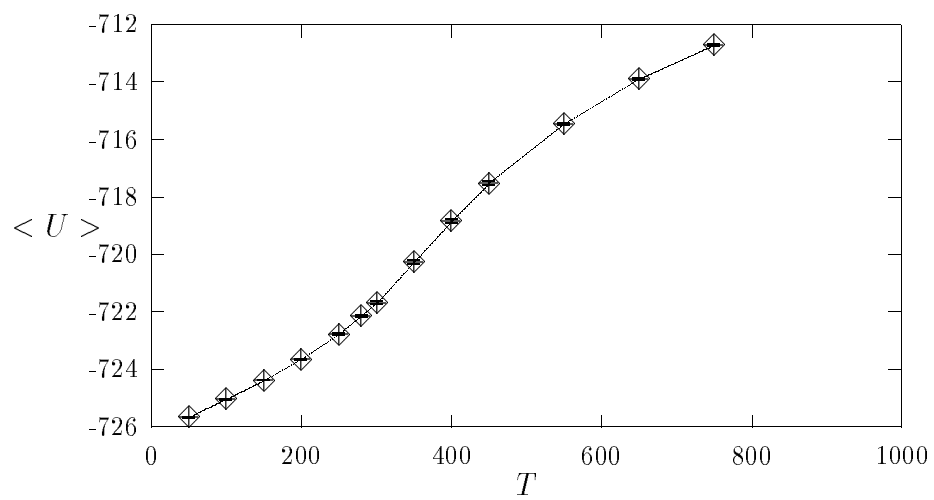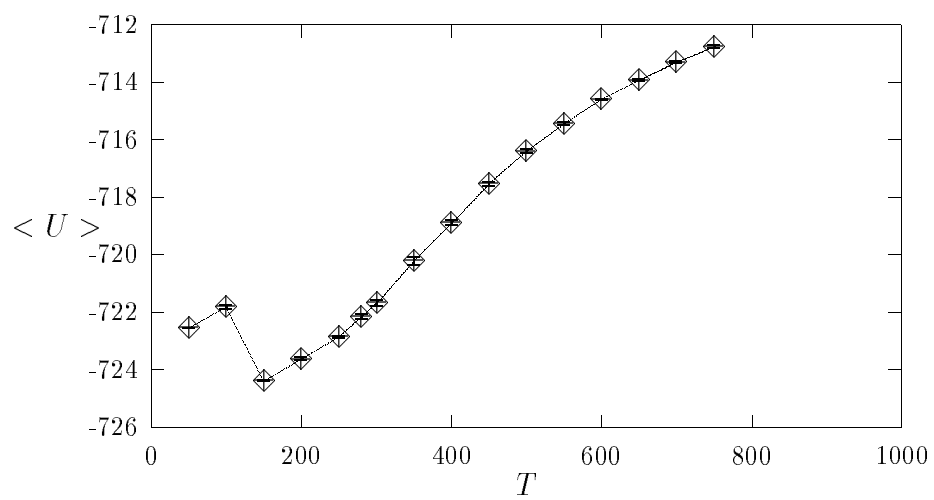
32x32 lattices with periodic boundary conditions. The error bars are at the double standard deviation level.

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