COMPUTER STUDY OF A CLASSICAL QUADRUPOLE SOLID

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August 1973

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Computer Study of a Classical Quadrupole Solid*

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Abstract

The Monte Carlo method is applied to a system of thirty-two classical free rotors on a face-centered cubic lattice with toroidal boundary conditions. The particles interact via nearest-neighbor electric-quadrupole interactions, characterized by an energy $\Gamma = 6Q^2/25R^5$. A first order phase transition is found at about $k_B T = 10\Gamma$. Results are given for energy, specific heat, correlations of the form $\langle Y_2^m(\vec{k})^* Y_2^n(\vec{k}) \rangle$, and various other quantities. Suggestions are made for further experimental and theoretical studies.

I. Introduction

Many molecular solids, including N_2 , CO, hydrogen halides and alkali cyanides, exhibit transitions from free to hindered rotation governed at least in part by electrostatic multipole interactions between the molecules¹. Such systems have been studied using mean field theory by Krieger and James², and in one dimension by the author³ and by Raich and Etters⁴. This paper relates primarily to solid N_2 ⁵⁻¹⁰, which has substantial electric quadrupole interactions, has a phase transition at 35.6°K, and, as we shall see, should exhibit only small quantum effects above about 30°K. Solid CO, which has negligibly small dipolar interactions, exhibits behavior similar to that of N_2 .⁵

The hydrogens, H_2 and D_2 , in which the rotational properties of the molecules must be treated in the quantum limit, have been extensively studied both experimentally and theoretically¹¹⁻¹⁹. The rotational excitations at low temperature (librons) in the hydrogens are extremely anharmonic due to the large zero-point rotation¹¹. Theoretical studies of the Raman spectrum of N_2 have found that the anharmonicity due to zero-point rotation is fairly moderate, with a root-mean-square (rms) displacement of about 18° ^{5,7,8}. In the hydrogens the high temperature phase has been studied to some extent by Raman¹² and neutron scattering¹³, as well as by magnetic relaxation¹⁴⁻¹⁵, but the author is unaware of any such work on N_2 .

Some other systems having electric quadrupole interactions are worthy of mention. In the hydrogen halides²⁰⁻²¹, quadrupole interactions dominate dipolar effects in HI and HBr, and are

competitive in HCl. There is some reason to believe that quadrupole interactions play a dominant role in the upper phase transitions of the alkali cyanides RbCN, KCN, NaCN.²¹⁻²² Finally, the electric quadrupole interaction is thought to be important among the cerium ions in cerium ethylsulfate $(\text{Ce}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O})$.²³

Real solids have the disadvantage that effects such as anisotropy of dispersive and repulsive forces,^{5,10} magnetic effects, phonon interactions,⁹ and structural changes¹⁸ (H_2 , D_2 and N_2 are hcp in their high temperature phases, and fcc at low temperatures) modify the behavior due to quadrupolar forces. In computer experiments no such difficulties exist. The object of this work is to determine the finite temperature properties of a pure quadrupole solid on a rigid fcc lattice, such as might be studied by thermal methods or by Raman or neutron scattering. Such a system was studied most recently at finite temperatures by Raich and Etters,⁶ who treated the low temperature phase by mean field theory, and the high temperature phase as free rotor like. They predicted a phase transition at $T = 13.77\Gamma$, where $\Gamma = 6Q^2/25R^5$ is the quadrupole interaction constant. (Throughout this work we set $k_B = 1$.) In this work we find a lower transition temperature (near $T = 10\Gamma$) in good agreement with the correct value for N_2 . Such agreement may, of course, be regarded as largely fortuitous.

In Section II we pose more precisely the problem to be studied in this work. Also in this section are brief descriptions of the Monte Carlo (MC) technique used and some other

computational details, and a discussion of why we expect useful results from a system as small as thirty-two particles.

The results are given in Section III. We present and discuss the energy and specific heat, and the correlation functions between $l = 2$ spherical harmonics relevant to Raman^{12,17} or neutron scattering. (See Appendix.) The dynamic properties are discussed in terms of second moments, and some preliminary molecular dynamics (MD) results for the spectral functions are presented. Also discussed are the angular deviations and order parameters in the ordered phase, and the orientational distribution function in the disordered phase.

In the final section we summarize the results and give some prospects for future work.

II. Computations

A. Statement of Problem

The computational problem is to sample the 64-dimensional space of the angular orientations of thirty-two particles, whose centers of mass are fixed on a face-centered cubic lattice with periodic (more precisely, toroidal) boundary conditions, according to the Monte Carlo method. One may thus calculate averages of physical interest. The potential, electric quadrupole interactions between nearest neighbors, is given by

$$V = \frac{\Gamma}{2} \frac{20\pi}{9} (70\pi)^{\frac{1}{2}} \sum_{i, \vec{\delta}} \sum_{m, n=-2}^2 C(224; mn) \times Y_4^{m+n}(\vec{n}_{\vec{\delta}})^* Y_2^m(\vec{n}_i) Y_2^n(\vec{n}_{i+\vec{\delta}}) \quad (2.1)$$

where Γ is the quadrupole coupling constant, $C(224; mn)$ is a Clebsch-Gordan coefficient, and Y_ℓ^m a spherical harmonic. Needed for the computation is the change in energy upon reorientation of particle i , which can be reduced to

$$\begin{aligned} \frac{\Delta E}{\Gamma} = & \operatorname{Re} \left\{ (Y_2^0(\vec{n}_i')) - Y_2^0(\vec{n}_i) \right\} G(i, 0) \\ & + 2 \left[(Y_2^1(\vec{n}_i')) - Y_2^1(\vec{n}_i) \right] G(i, 1) \\ & + (Y_2^2(\vec{n}_i') - Y_2^2(\vec{n}_i)) G(i, 2) \} \end{aligned} \quad (2.2)$$

$$G(i, m) = \sum_{n=-2}^2 C(224; mn) \sum_{\vec{\delta}} A(m+n, \vec{n}_{\vec{\delta}}) Y_2^n(\vec{n}_{i+\vec{\delta}})$$

$$A(m, \vec{n}_{\vec{\delta}}) = \frac{20\pi}{9} (70\pi)^{\frac{1}{2}} Y_4^m(\vec{n}_{\vec{\delta}})^*$$

Throughout this work the polar axis is taken along the threefold axis, i.e., along the (111) direction, because this direction

corresponds closely to the c-axis of the hexagonal close-packed lattice.

B. The Monte Carlo Method²⁴

The Monte Carlo method samples configuration space via a Markov process. Each step is determined by an algorithm having the property that a sample distributed with density proportional to $e^{-E/T}$ is transformed to a similarly distributed sample. Such an algorithm is

- 1.) For a given particle, choose a proposed new angular orientation randomly on the sphere;
- 2.) If $\Delta E \leq 0$, accept this as a new configuration;
- 3.) If $\Delta E > 0$, accept with probability $e^{-\Delta E/T}$. Otherwise, count the old configuration again.

(This is a special case of what is often called the "asymmetrical procedure.") Samples of configuration space were generated by applying this algorithm to each particle successively and recording the successful moves. For low temperatures the algorithm was modified to restrict the maximum distance of each move to about 30° .

C. Further Computational Details

The program preparation and a substantial amount of production were done on the Cornell University IBM 360/65. The speed on this machine was about 20 configurations per second. (A configuration is here taken to mean a successful reorientation of one particle.) In addition, many long production runs were done on the CDC 6600 at New York University - Courant Institute of Mathematical Sciences.

The numbers quoted in this paper are typically the result

of three or four runs, each consisting of about fifty configurations per particle. The cited errors are given by

$$\Delta a = \left[\sum_{i=1}^n (a_i - \bar{a})^2 / n(n-1) \right]^{1/2}, \quad (2.3)$$

where a_i is the average of an observable for the i^{th} run. Each run began with a near-equilibrium configuration, e.g., the end result of a previous run. For each run, the energy, specific heat, and most of the correlation functions were calculated as the configurations were generated. Sufficient information was put on punched cards or otherwise stored that other properties could be examined later.

D. Discussion of Sample Size

A sample of thirty-two particles ($2 \times 2 \times 2$ unit cells $\times$ 4 particles per unit cell) is much smaller than sample sizes commonly encountered in MC calculations on fluids (often $6 \times 6 \times 6 \times 4 = 864$ particles). Some discussion of this point is required. We argue that this sample is large enough to give values for properties away from the transition point, T_0 , (say $|T - T_0|/T_0 \geq 0.2$), as well as a reasonable estimate of T_0 .

First, note that fluctuations in particle density, including long wavelength fluctuations, play a crucial role in properties of fluids. The environment of each particle fluctuates as to number and proximity of its near neighbors. These fluctuations would be severely restricted by the requirement of thirty-two particles in a given volume. In the quadrupole system, however, each particle has twelve neighbors in fixed positions, and the centers of mass form a periodic lattice.

Thus, at least the specific reason for requiring large numbers of particles in the fluid system is absent here.

A further justification comes from comparison with perturbation theory. We refer in particular to the calculation of the specific heat of H_2 by Berlinsky and Harris.¹⁶ (The contributions of various diagrams differ between the quantum and classical cases by numerical factors resulting from the evaluation of

$$\langle \prod_{i=1}^n Y_2^{m_i}(\Omega) \rangle_{T=\infty} = \frac{\text{Tr} \langle J, \mu | \prod_{i=1}^{m-1} (Y_2^{m_i} Q) Y_2^m | J, \mu \rangle}{\text{Tr} \langle J, \mu | J, \mu \rangle} \quad (2.4)$$

where $Q = \sum_{J, \mu} |J, \mu\rangle \langle J, \mu|$.

In the quantum (orthohydrogen or paradeuterium) case all J 's are restricted to 1, while they take on all values classically. For $n=2$, the quantum value is 2/5 the classical value. For our purposes, these differences need not be of concern.) Study of reference 16 suggests that large contributions come from diagrams of a form we shall call "compact", by which we mean one of the diagrammed particles is necessarily a first neighbor of all the others. (See figure 1.) Non-compact diagrams, in particular the four- and five-membered open rings, make only small contributions to the specific heat. The unimportance of non-compact diagrams is probably due to the extreme anisotropy of the interaction. Similar conclusions were reached by the author in calculating moments of the spectral functions for H_2 . Comparing the perturbation series for a thirty-two particle periodically continued system with that for an infinite system, one finds that all compact diagrams are counted correctly;

the first miscounted diagram being the four-membered open ring, which we have argued is not of great importance.

III. Results

A. Energy and Specific Heat

To set the scale of energies, first consider a pair of cylindrically symmetric quadrupoles with coupling constant Γ . At high temperatures the quadrupoles interact energy of 7Γ . The low energy configuration, with one quadrupole along the interparticle axis and the other perpendicular, has an energy of -12.5Γ . On a linear or square lattice it is possible to order the particles such that each interparticle bond has this minimum energy.

For our case of an fcc lattice, the low energy configuration, as discussed by Felsteiner²⁵ and others, is a simple cubic lattice with the four quadrupoles per unit cell pointing along the (111) directions. This arrangement has an energy of about -40Γ per particle, or -6.7Γ per bond, i.e., less than the rms energy at high temperatures.

For the thirty-two particle system, the total energy and the orientational specific heat per particle are shown in Figure 2 and Table I. Several points should be made:

(1) The energy and specific heat fall well below their perturbation theory values, even at $T=40\Gamma$.

(2) A phase transition, which appears to be first order with a latent heat of $2-4\Gamma$ per particle, takes place at a temperature, T_0 , of about 10Γ . It is difficult to determine the transition point precisely in a finite system, as only a finite energy fluctuation is required for complete "melting". (Probability of refreezing is negligible due to phase space considerations.) This result is substantially lower (and closer to

experiment) than the 13.77Γ calculated by Raich and Etters. The reason is that they treated the high-temperature phase as completely free-rotor-like. (The inclusion of second neighbors should lower the energy of both phases and have only a minor effect on T_0 .)

(3) The specific heat has been calculated in two ways: the crosses represent the specific heat calculated as a differential quantity

$$C(T_2) = N^{-1} (E(T_3) - E(T_1)) / (T_3 - T_1) \quad (3.1)$$

$T_3 > T_2 > T_1$

while the points represent the specific heat calculated as a fluctuation quantity

$$C = (\overline{E^2} - \bar{E}^2) / NT^2. \quad (3.2)$$

The former method proved less satisfactory because the temperature T_2 is uncertain, and because, for reasonably closely spaced points in temperature, the value of the specific heat is overly sensitive to small errors in the energy. (Note, for example, the two crosses surrounding $T=18\Gamma$. These could be put into agreement with the dashed curve by correcting the energy at $T=18\Gamma$ by the quoted error.) In applying the differential method, it must be noted that the energy for each run is chosen such as to minimize the specific heat, and a correction term must be added. Thus, the specific heat per particle averaged over n equal length runs is

$$C = n^{-1} \sum_{i=1} [C_i + (E_i - \bar{E})^2 / NT^2] \quad (3.3)$$

(4) Below $T = 6\Gamma$ the specific heat per particle is very nearly equal to k_B , indicating that each particle is effectively a two-dimensional harmonic oscillator. Above this temperature anharmonicity sets in rather rapidly. We shall return to this point in Sections B and C.

B. Correlation Functions and Order Parameter

(1) Preliminaries

We shall discuss in this section properties of the spherical harmonics

$$Y_2^m(\vec{k}) = \sum_{i=1}^{32} e^{i\vec{k} \cdot \vec{r}_i} Y_2^m(\vec{n}_i), \quad (3.4)$$

in particular their correlation functions $\langle Y_2^m(\vec{k})^* Y_2^n(\vec{k}) \rangle$.

The discussion focusses on three points of the Brillouin zone of the fcc lattice: the zone center ((000) or Γ -point) and the zone boundaries in the (111) and (100) directions (L-point and X-point respectively). In the low temperature (simple cubic) phase, the Brillouin zone shrinks and the X-point becomes a vector of the reciprocal lattice, while the L-point remains on the zone edge.

For evaluating the spherical harmonics, the polar direction is taken along the threefold axis (111), and the x-direction along (110). The normalization is such that $\langle Y_2^m(\vec{k})^* Y_2^n(\vec{k}) \rangle$ is proportional to N , except at the X-point below T_0 where it is proportional to N^2 . These correlation functions are intimately connected with the differential cross-sections for light^{12,17} and neutron scattering. (See Appendix.) Our results for some of these correlation functions are shown in figures 3 and 4 and in Table I.

(ii) High Temperatures

At very high temperatures only the diagonal ($m=n$) correlation functions are nonzero, and are given by

$$\langle |Y_2^m(k)|^2 \rangle_{T=\infty} = \frac{N}{4\pi} = 2.55. \quad (3.5)$$

At lower temperatures correlations between nearest neighbor particles become important. These are, to first order in Γ/T ,

$$\begin{aligned} \langle Y_2^m(i)^* Y_2^n(j) \rangle &\approx \frac{(-1)^n}{T} \frac{\text{Tr } Y_2^m(i)^* Y_2^{-n}(j) H}{\text{Tr } e^{-H/T}} \\ &\approx (-1)^n \frac{\Gamma}{T} \left(\frac{20\pi}{9}\right) (70\pi)^{\frac{1}{2}} (4\pi)^{-2} C(224; m, -n) Y_4^{m-n}(\vec{\rho}_{ij})^*. \end{aligned} \quad (3.6)$$

When the fourier transforms are worked out, it is seen that at the Γ and L points the correlations have terms first order in Γ/T only for $m-n = 0, \pm 3$; at the X-point they have such terms for all m, n . As in the energy and specific heat, the results show rapid departure from low-order perturbation theory.

(iii) Low Temperatures

At low temperatures ($T \lesssim 6\Gamma$) the solid is nearly harmonic. Accordingly, at the Γ and L points all correlation functions vanish linearly with temperature. At the X-point, the $\langle Y_2^m(X) \rangle$ are order parameters, so that the correlations $\langle Y_2^m(X)^* Y_2^n(X) \rangle$ approach constants, while the fluctuations $\langle (Y_2^m(X) - \langle Y_2^m(X) \rangle)^* (Y_2^n(X) - \langle Y_2^n(X) \rangle) \rangle$ vanish linearly with temperature. As is to be expected, the order parameters $\langle Y_2^m(X) \rangle$ decrease only slightly in this regime as the temperature is raised toward T_0 .

(iv) Transition Region

In the transition region, $8\Gamma < T < 12\Gamma$, the diagonal correlation functions are characterized by sharp increases at the

X-point and sharp decreases at the L-point. Striking changes are also seen in off-diagonal correlations.

Rather spectacular behavior is seen at the Γ -point in $\langle |Y_2^0(\Gamma)|^2 \rangle$. At temperatures of 8Γ and 10Γ this correlation function assumes surprisingly large values, suggesting that anharmonic softening in a modes associated with this function leads to the instability of the ordered phase.

C. Dynamic Properties

The time dependent correlation functions

$$A_{mn}(\vec{k}, t) = \langle Y_2^m(\vec{k}, t)^* Y_2^n(\vec{k}, 0) \rangle \quad (3.7a)$$

and their fourier transforms

$$A_{mn}(\vec{k}, \omega) = \int_0^\infty dt \cos \omega t A_{mn}(\vec{k}, t) \quad (3.7b)$$

are not directly obtainable from MC studies, but may be found using molecular dynamics. Some preliminary MD studies were done, and it was concluded that great expense would be required to achieve satisfactory results. Nonetheless, our preliminary results showed some rather striking phenomena, which the MC studies seem to support. Some of these results are shown in figure 5.

From MC studies one can obtain the $2j$ th moments

$$M_{mn}^{(2j)}(\vec{k}) = \int_0^\infty d\omega \omega^{2j} A_{mn}(\vec{k}, \omega) / \int_0^\infty d\omega A_{mn}(\vec{k}, \omega). \quad (3.8)$$

In particular, the second moment is given by

$$M_{mn}^{(2)}(\vec{k}) = \frac{\langle Q_m(\vec{k})^* Q_n(\vec{k}) \rangle}{\langle Y_2^m(\vec{k})^* Y_2^n(\vec{k}) \rangle} \quad (3.9)$$

where $Q_m(\vec{k})$ is the Poisson Bracket $[H, Y_2^m(\vec{k})]$. We have

$$Q_m(\vec{k}) = -I^{-1} \sum_j e^{i\vec{k} \cdot \vec{r}_j} \left\{ p_{\theta_j} \frac{\partial}{\partial \theta_j} Y_2^m(j) + im \frac{p_{\theta_j}}{\sin^2 \theta_j} Y_2^m(j) \right\}. \quad (3.10)$$

Since

$$p_{\theta_i} p_{\theta_j} = \frac{p_{\phi_i} p_{\phi_j}}{\sin^2 \theta_j} = IT \delta_{ij} \text{ and } p_{\phi_i} p_{\theta_j} = 0 \quad (3.11)$$

we find

$$\begin{aligned} \langle Q_m(k)^* Q_n(k) \rangle &= N \left(\frac{\Gamma}{I} \right) \left(\frac{T}{I} \right) \langle \left(\frac{\partial}{\partial \theta} Y_2^m(j) \right)^* \frac{\partial}{\partial \theta} Y_2^n(j) \\ &+ \frac{mn}{\sin^2 \theta_j} \left(Y_2^m(j) \right)^* Y_2^n(j) \rangle. \end{aligned} \quad (3.12)$$

Note that (3.12) is essentially a single particle property; the $\vec{k}$ -dependence of (3.9) resides solely in the denominator. The high temperature limit of (3.9) is $6NT/I$. The numerators $\langle Q_m(\vec{k})^* Q_n(k) \rangle$ are given in Table I. The calculations indicate that well above T_0 these numerators have significant values only in the diagonal case. Slightly above T_0 the diagonal numerators are joined by $m-n = \pm 3$; other off-diagonal numerators seem to remain near zero.

While the fine structure in the MD results (figure 5) is not to be taken seriously, the second moments agree well in nearly all cases with the MC results. Particularly striking is $A_{00}(L, \omega)$, which shows a high-frequency peak developing well above the transition. This should be observable in inelastic neutron scattering. The MC results (figure 6) show the rms frequency for this spectral function remaining constant at a high value for $T \lesssim 20$. Also noticeable is the increase in low

frequencies (onset of diffusive character) of several modes.

The MC results for the second moments also support the contention that the melting instability is associated with $A_{00}(\Gamma, \omega)$. This is the lowest frequency mode in the ordered phase, and goes very soft near the transition. The order parameter fluctuations, whose second moments are about double those at the Γ -point, exhibit rather little softening as the transition is approached from below, although they become quite soft above (figure 6). The high frequency Raman active mode of references 7 and 8 corresponds primarily to fluctuations in the $m = 1$ order parameter, $\langle Y_2^1(X) \rangle$. This mode exhibits moderate anharmonicity, having an rms frequency given (roughly) by $(I\omega^2/\Gamma)^{1/2} \cong 20 \sim .75(T/\Gamma)$.

D. Other Results

An important parameter in quadrupole solids is the mean square angular displacement $\langle \theta^2 \rangle$ of a molecule from its equilibrium position. Our results are shown in Table II. In a quantum solid $\langle \theta^2 \rangle$ approaches a constant at low temperature, while in a classical harmonic solid $\langle \theta^2/T \rangle$ is constant. Other works^{5,7} indicate that the rms deviation for N_2 at low temperature is about 18° . This suggests that low-temperature N_2 is equivalent to a classical solid at $T \sim 7\Gamma$. In addition, our estimate of the rms deviation at the transition agrees with that of reference 5. The rapid increase of $\langle \theta^2 \rangle/T$ above $T=6\Gamma$ indicates the onset of anharmonicity.

A related matter is the rate at which molecules flip end-for-end. This bears on the observability of a possible ferroelectric transition at low temperature in CO^{26} . We found

that flipping occurred at a non-negligible rate at $T=10\Gamma$, but none was observed for $T\leq 8\Gamma$. This tends to support the conclusions of Curl, Hopkins and Pitzer regarding the slow approach to equilibrium in low temperature CO.

We also looked for anisotropy in the single-particle orientational distribution above T_0 . Below the transition this anisotropy is manifested in $\langle Y_4^0(\vec{n}) \rangle$ and $\text{Im} \langle Y_4^3(\vec{n}) \rangle$. These quantities are nearly an order of magnitude less at $T = 12\Gamma$ than at $T = 8\Gamma$, and drop to noise level about $T = 15\Gamma$. The m -dependence of the second moment numerators (see Table I) vanishes with similar rapidity. Thus the single-particle orientational distribution function rapidly becomes isotropic above T_0 .

IV. Conclusions

We have studied using the Monte Carlo technique the properties of thirty-two classical free-rotor quadrupoles on a rigid fcc lattice with toroidal boundary conditions. Among our findings are:

- (1) The system has a phase transition at a temperature of about 10Γ . The transition appears to be first order, with a latent heat of about $2-4\Gamma$ per particle.
- (2) The properties of the system differ from first order perturbation theory even at temperatures as high as $T = 40\Gamma$. This is particularly apparent at the L-point (along the threefold axis) where a relatively high energy excitation seems to appear, and is not greatly altered by the phase transition. This mode should be observable by neutron scattering.
- (3) As the transition is approached from above, fluctuations at the X-point, along with $m=1$ fluctuations at the L and Γ points, become diffusive (low energy) in character.
- (4) There is little or no softening in the second moments of the order parameter fluctuations as the transition is approached from below. Rather, the instability of the low temperature phase is associated with anharmonic behavior of $\langle Y_2^0(\Gamma, t) Y_2^0(\Gamma, 0) \rangle$.
- (5) Comparison with other results^{5,7,8} suggests that low temperature N_2 is comparable to a classical solid at about $T = 7\Gamma$. At this temperature the solid is moderately anharmonic, and becomes rapidly more anharmonic as the temperature is raised. N_2 may be regarded as nearly classical above about 30°K .

Among the effects neglected in this work are: (1) finite size effects; (2) lattice structure effects (these solids are hcp in their high temperature phases); (3) further-than-nearest-neighbor interactions; (4) lattice vibrations;^{4,9} (5) non-quadrupolar interactions.^{5,10,17} Of these, the first three are subject to Monte Carlo study, while the others pose more difficult theoretical problems. Previous work has shown that second neighbors perturb various properties by ~10%, while the effect of third neighbors and beyond is very small. Thus, second neighbors should be included in any further study. Two further studies would seem fruitful: (1) Study of 108 particles on an fcc lattice at temperatures roughly 6Γ - 10Γ , including an improved determination of the "melting point"; (2) Study of 64 particles on an hcp lattice at roughly $T=10\Gamma$ - 24Γ . (This system also overcounts diagram (f) of figure 1, though not so badly as the study of this paper.) The author hopes to pursue these studies in the near future.

It is hoped that this work will stimulate neutron and Raman scattering studies of N_2 near and above the phase transition. Of particular interest are the high temperature excitations along the threefold axis, and the anharmonic mode at the Γ -point below T_0 .

Acknowledgements

The author expresses his gratitude to J. A. Krumhansl, G. V. Chester, and M. J. Kurkijärvi for many useful discussions during the course of this work. He would also like to thank M. Kalos and K. S. Liu for their hospitality at New York University, and Miss Jean Fuchs for typing the manuscript.

Appendix

In this appendix we derive the cross-section for neutron scattering from diatomic molecules on a rigid lattice. Neglecting dependence of the scattering amplitude on nuclear spin, the cross-section for scattering with momentum transfer $\vec{k}$ is proportional to

$$S(\vec{k}) = \left\langle \sum_{ij} \sum_{\alpha\beta} \exp i\vec{k} \cdot (\vec{r}_{i\alpha} - \vec{r}_{j\beta}) \right\rangle \quad (\text{A.1})$$

where the Latin indices denote lattice sites and the Greek indices denote nuclei within a molecule. We have

$$S(\vec{k}) = \left\langle \sum_{ij} \sum_{\sigma\sigma'} \exp i\vec{k} \cdot [(\vec{R}_i + \sigma\hat{u}_i) - (\vec{R}_j + \sigma'\hat{u}_j)] \right\rangle \quad (\text{A.2})$$

where R_i indicates the lattice site, $\sigma, \sigma' = \pm\delta$, δ is one-half the internuclear distance, and $\hat{u}$ is a unit vector along the internuclear axis. Summing over σ, σ' , we find, after some algebra,

$$S(k) = 4 \sum_{ij} e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} [\langle \cos k\delta z_i \rangle \langle \cos k\delta z_j \rangle + (\langle \cos(k\delta z_i) \cos(k\delta z_j) \rangle - \langle \cos k\delta z_i \rangle \langle \cos k\delta z_j \rangle)] \quad (\text{A.3})$$

where $k = |\vec{k}|$, $z = \vec{k} \cdot \hat{u} / k$.

In the absence of long-range order, the first term in square brackets contributes only for $\vec{k}$ on the reciprocal lattice. If, in addition, the single particle orientational distribution function is isotropic, this term is $\sin^2 k\delta / (k\delta)^2$. Our main interest lies in the second term. By expanding the cosines,

and assuming cubic structure and no long-range order, this term is shown to be

$$\frac{(k\delta)^4}{36} \langle (3z_i^2 - 1) (3z_j^2 - 1) \rangle + O(k\delta)^6. \quad (\text{A.4})$$

This takes the desired form of correlation functions among $l = 2$ spherical harmonics.

Figure Captions

- Figure 1. Compact diagrams (a-e) make important contributions to the properties of a quadrupole solid. Noncompact diagrams (f-h) are relatively unimportant. Diagram f is the first overcounted diagram in the thirty-two particle system.
- Figure 2. Total energy (upper curve) and specific heat per particle (lower curve). For the specific heat, the full points are calculated from energy fluctuations, and the crosses from energy differences. The full lines are lowest order high temperature perturbation theory.
- Figure 3. Diagonal correlation functions $\langle |Y_2^m(k)|^2 \rangle$. In those cases where it does not excessively add to the confusion, curves have been extrapolated to their high temperature expansion values at $T = 100\Gamma$, and linear perturbative results have been indicated by solid lines. The corresponding numbers (except for $T = 13\Gamma, 14\Gamma$) may be found in Table I.
- Figure 4. Two off-diagonal correlation functions, $\text{Re}\langle Y_2^{-1}(X)^* Y_2^1(X) \rangle$ (solid points, left scale) and $\text{Im}\langle Y_2^{-2}(L)^* Y_2^1(L) \rangle$ (open points, right scale) which show abrupt changes near the transition point.
- Figure 5. Molecular dynamics results for some of the spectral functions $A_{mm}(k, \omega)$. The MC and MD results for the second moments $M_{mm}^{(2)}(k)$ are indicated. The vertical lines indicate $\omega = (6T/I)^{1/2}$.

Figure 6. Rms frequencies for the spectral functions $A_{00}(k, \omega)$. The upper curve for the X-point is the rms frequency for the fluctuations only below the phase transition. The solid line indicates the high-temperature limit, $\omega = (6T/I)^{1/2}$. Raman frequencies according to Jacobi and Schnepf are indicated at left. (These values need not be in exact correspondence with ours.) These and other rms frequencies may be calculated from the data in Table I.

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- * This work has been supported by the U. S. Atomic Energy Commission under contract #AT(11-1(3161), Technical Report #C00-3161-16.
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Table I

Temperature T/r	40	30	24	18	15	12	10	8	6	4	2
Total Energy E/r	-214 $\pm$ 7	-281 $\pm$ 6	-343 $\pm$ 4	-418 $\pm$ 6	-496 $\pm$ 4	-649 $\pm$ 23	-873 $\pm$ 26	-982 $\pm$ 4	-1077 $\pm$ 4	-1148 $\pm$ 5	-1207 $\pm$ 2
Specific Heat Per Particle	.148 $\pm$.008	.261 $\pm$.013	.38 $\pm$.03	.55 $\pm$.02	.80 $\pm$.08	2.04 $\pm$.47	3.14 $\pm$.55	2.19 $\pm$.33	1.02 $\pm$.14	1.13 $\pm$.19	1.09 $\pm$.14
Diagonal Correlation Functions $\langle Y_2^m(R) ^2 \rangle$											
$R = (000)$ or r											
m=2	2.55 $\pm$.09	2.43 $\pm$.18	2.55 $\pm$.11	2.81 $\pm$.14	2.29 $\pm$.07	3.1 $\pm$ 0.5	2.12 $\pm$.35	2.02 $\pm$.28	1.24 $\pm$.08	.63 $\pm$.15	.29 $\pm$.02
m=1	2.91 $\pm$.21	2.71 $\pm$.16	2.67 $\pm$.12	2.94 $\pm$.09	3.06 $\pm$.37	4.2 $\pm$ 0.6	2.04 $\pm$.23	2.21 $\pm$.41	1.27 $\pm$.12	.59 $\pm$.08	.28 $\pm$.04
m=0	1.84 $\pm$.09	1.84 $\pm$.17	1.76 $\pm$.09	1.89 $\pm$.04	1.51 $\pm$.06	1.41 $\pm$.14	3.6 $\pm$.9	2.67 $\pm$.75	.70 $\pm$.10	.54 $\pm$.14	.23 $\pm$.08
$R = (111)$ or L											
m=2	2.05 $\pm$.07	2.15 $\pm$.06	2.14 $\pm$.18	2.14 $\pm$.11	1.95 $\pm$.15	1.85 $\pm$.31	1.01 $\pm$.14	.54 $\pm$.03	.47 $\pm$.03	.30 $\pm$.03	.15 $\pm$.02
m=1	3.24 $\pm$.31	3.27 $\pm$.22	4.16 $\pm$.31	3.94 $\pm$.32	5.14 $\pm$.13	4.7 $\pm$.9	1.41 $\pm$.44	.60 $\pm$.03	.46 $\pm$.04	.27 $\pm$.01	.14 $\pm$.03
m=0	1.91 $\pm$.19	1.53 $\pm$.06	1.46 $\pm$.08	1.15 $\pm$.04	.99 $\pm$.07	.80 $\pm$.09	.56 $\pm$.05	.39 $\pm$.04	.28 $\pm$.04	.17 $\pm$.03	.06 $\pm$.01
$R = (100)$ or X											
m=2	2.63 $\pm$.24	2.97 $\pm$.30	3.75 $\pm$.31	3.92 $\pm$.34	4.74 $\pm$.58	8.7 $\pm$ 2.7	18.2 $\pm$ 2.3	18.5 $\pm$ 1.2	24.6 $\pm$ 0.7	25.6 $\pm$ 1.1	28.1 $\pm$.8
m=1	3.06 $\pm$.17	3.35 $\pm$.29	3.71 $\pm$.20	4.13 $\pm$.89	4.58 $\pm$.53	10.7 $\pm$ 3.5	10.3 $\pm$ 1.0	14.4 $\pm$ 1.0	13.6 $\pm$ 0.7	15.8 $\pm$ 0.5	15.4 $\pm$.2
m=0	2.59 $\pm$.12	3.07 $\pm$.37	3.31 $\pm$.22	4.23 $\pm$.23	4.97 $\pm$.94	11.0 $\pm$ 3.7	32.3 $\pm$ 2.1	33.7 $\pm$ 1.7	38.5 $\pm$ 1.5	40.6 $\pm$ 0.7	41.3 $\pm$.8
Second Moment Numerators $\langle Q_m(R)^* Q_n(R) \rangle$ (eq. 3.12)											
m=n=2	611	454	372	275	228	182	138 $\pm$ 1	109.1	84.5	56.4	28.2
m=n=1	607	474	362	277	231	188	183 $\pm$ 4	148.2	112.1	75.8	38.6
m=n=0	621	442	366	272	227	178	121 $\pm$ 8	96.4	65.2	41.2	19.1
$\text{Im} \langle Q_{-2}(\vec{k})^* Q_1(\vec{k}) \rangle$	-	-	-	-	-	1.4	34 $\pm$ 5	38.0	35.0	26.9	14.8

Table II

T/Γ	$ \langle Y_2^2(X) \rangle $	$ \langle Y_2^1(X) \rangle $	$ \langle Y_2^0(X) \rangle $	$\langle \theta^2 \rangle$ (Radians ²)	$\Gamma \langle \theta^2 \rangle / T$ (Radians ²)	$\langle \theta^2 \rangle^{\frac{1}{2}}$ (Degrees)
10	4.0 $\pm$.4	3.0 $\pm$.2	5.5 $\pm$.3	.24 $\pm$.07	.024 $\pm$.007	28 $^{\circ}$ $\pm$ 4 $^{\circ}$
8	4.1	3.8	5.6	.125 $\pm$.01	.0156 $\pm$.001	20 $^{\circ}$ $\pm$ 1 $^{\circ}$
6	4.90	3.70	6.10	.067	.0112	15 $^{\circ}$
4	5.15	3.88	6.31	.0384	.0096	11 $^{\circ}$
2	5.43	3.86	6.50	.020	.01	8 $^{\circ}$

Figure 1

Figure 2

Figure 3

Figure 4

$\Gamma = 15\Gamma$ $\Gamma = 18\Gamma$ $\Gamma = 40\Gamma$ $\Gamma, m=2$ $L, m=0$ $L, m=1$ $X, m=1$ MC 100
MD 82230
24450
4961
55MC 98
MD 112238
23067
7870
68MC 240
MD 215325
254187
201200
210

Figure 6