STATIC AND DYNAMIC PROPERTIES
OF SYSTEMS WITH
MULTIPOLE INTERACTIONS
AND
INTERNAL DYNAMIC STRUCTURE

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Myron Jay Mandell, Ph.D.
Cornell University 1973

ABSTRACT

The area of this thesis is theoretical solid state and chemical physics. Recently experimental studies have been made in certain ferroelectrics, in polymers, and in molecular crystals, of properties (susceptibility, optical, thermal) which are determined by the dynamics of interacting multipole systems. Unlike the simpler ferromagnetic systems, these highly anharmonic interacting systems are composed of units which in the quantum case have finite or anharmonic sets of energy levels, or in the classical case possess internal kinetic energy and possibly viscosity. The interaction between the units may be highly anisotropic

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electric multipole interactions.

A simple and illustrative example of such a system is a pair of free rotor dipoles.* The excitations, susceptibilities, and correlation functions of this system are discussed.

The applicability of this work to real systems is considered. Distinctions between quantum and classical effects and among various types of interactions are discussed. Applications are considered to van der Waals binding energy and excitonic properties of rare gas solids, to orientational order in such molecular crystals as H_2 , D_2 , N_2 , CO, hydrogen halides, and alkali cyanides, to excitations in certain rare-earth paramagnets, to collective effects in interacting impurity systems, to hydrogen-bonded ferroelectrics, and to polymeric systems.

Some general considerations on the many particle problem are given. A general formalism, primarily applicable to quantum systems, is presented, leading to an approximate (RPA) solution for the normal modes, susceptibility, and binding energy. It is shown that the approximate normal modes satisfy a Dyson-like equation, from which higher approximations may be generated.

Three calculations are presented for model quantum systems. A one-dimensional array of free-rotor dipoles is treated using temperature-dependent Green's functions. A one-dimensional array of singlet-triplet particles, and

a primitive model for hydrogen-bonded ferroelectrics, are treated using the previously described general formalism.

It is shown that the static orientational properties of a one-dimensional classical multipolar array can be found exactly. Results are presented for pure dipole, pure quadrupole, and mixed systems. A program is suggested for treating the dynamic properties. The author has previously published a paper[†] on a simpler model, the dynamics of which is governed by viscous effects, and shown that a high temperature expansion can be developed for the dynamic properties, both in the viscous limit and for finite viscosity.

The second and fourth frequency moments for coherent angular momentum excitations (paralibrons) in hcp ortho-hydrogen are calculated. The results are compared with Raman data and with a previous calculation of the specific heat.

* M. J. Mandell, "A Note on the Two-Dipole Problem." Sol. St. Comm. 9, 1323 (1971).

† M. J. Mandell, "Dynamic Susceptibility of a Model Polymer in Several Limits -- Theory and Calculations." J. Chem. Phys. 57, 4858 (1972).

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I. Introduction

Dense (solid or liquid) matter is composed of atoms, molecules, or ions whose properties may differ greatly or only slightly from the properties they would have had in a dilute system. However slight these differences may be, they hold the key to the properties of the dense phase. For example, the low-lying excited states of rare-gas atoms are not much different in the solid than in the isolated atom, but these differences are intimately connected with the van der Waals binding energy of the crystal (Lucas, 1967). In this thesis we attempt to study how atomic and molecular properties, particularly excitations, manifest themselves in static and dynamic properties of solids.

We will concentrate our attention on solids composed of diatomic molecules, though the ideas developed here are applicable to many other systems whose units have internal dynamic structure. Diatomic molecules may be permanent quadrupoles, such as H_2 or N_2 , or may have dipole as well as higher multipole moments, as do HCl, HBr, CO, etc.

The dielectric properties of dipolar molecules in the gas phase were well understood by 1931, when Van Vleck published his Theory of Electric and Magnetic Susceptibilities (Van Vleck, 1931). The static susceptibility is

given by

$$\frac{\chi}{N} = \frac{2p^2/3\Delta}{\sum_{j=0}^{\infty} (2j+1) \exp\{-j(j+1)\Delta/2k_B T\}} \quad (1.1)$$

where $\Delta = h^2/I$ is the splitting between the rotational ground state and the first excited (triplet) state. In the classical (high temperature) limit the denominator becomes $2k_B T/\Delta$, giving $\chi = Np^2/3k_B T$, while at the low temperature limit the denominator becomes unity. In addition, the transitions among the various rotational states may be observed, for example by optical absorption.

The problem of what happens to such rotating molecules was the subject of a 1936 review by Smyth (Smyth, 1936), at which time the only available theory was that of Pauling (Pauling, 1930). Smyth lists over 70 molecules or ions as candidates for maintaining rotational properties in the solid in some range of temperature. It was known at that time that H_2 behaved nearly as a free rotor down to the lowest temperatures, while N_2 , HCl , and other molecules exhibit rotation just below melting, but the rotation becomes "frozen out" as the temperature is lowered.

Pauling's idea (elaborated upon in Fowler, 1936, and in Kirkwood, 1940) was that at low temperatures each molecule would librate in a potential $V = V_0(1 - \cos \theta)$ for dipoles, or $V = V_0(1 - \cos 2\theta)$ for quadrupoles. Rotation would

begin when particles gained sufficient thermal energy to surmount the potential barrier.

From a modern perspective the shortcomings of Pauling's theory are obvious, and these were pointed out by Frenkel in 1946. Frenkel presented a mean field theory of the onset of long range order in HCl, but he was aware of the errors inherent in such a treatment, particularly as regards dynamical properties, stating

"The rotational motion of molecules above the Curie point is not at all free, but consists in rotational oscillations about irregularly distributed equilibrium orientations of a limited duration."

It should be noted that Frenkel was led by a multiplication error to strongly overstate his case.*

The introduction of nuclear magnetic resonance as a tool for the investigation of dynamic properties of solids soon provided confirmation of these ideas. The measurements of Alpert (Alpert, 1948) indicated that rotation becomes hindered about 40° above the phase transition in HCl, and gave similar results for other hydrogen halides. We

* Frenkel calculates the interaction parameter as

$$\begin{aligned} p^2/a^3 &= (10^{-18})^2 / (3 \times 10^{-8})^3 \\ &\approx 3 \times 10^{-12} \text{ ergs} = 2 \times 10^4 \text{ }^\circ\text{K}, \end{aligned}$$

suggesting that HCl has nearly harmonic librations at all ordinary temperatures.

shall postpone discussion of more recent work on diatomic molecular crystals to later chapters.

The considerations applicable to the rotation of diatomic molecules are not limited to this application, but may be extended to any system of interacting particles which individually have some set of (quantum mechanical) energy levels, or a (classical) kinetic energy. From the point of view of the theorist, the most important single-particle spectrum is the harmonic oscillator. The problem of interacting harmonic oscillators can be solved exactly (Tyablikov, 1967), unless the interaction is so strong that the system becomes unstable. We shall see that a system of particles whose higher levels are less dense than those of the harmonic oscillator is approximately equivalent to a harmonic system whose effective interaction strength increases as the temperature is lowered, possibly leading to a phase transition.

The experimental systems which first engaged my attention were impurity tunnelling systems in alkali halides, e.g., KCl:Li. Dilute systems of these impurities were studied at Cornell experimentally by Pohl, Sack, Sievers, Silsbee and co-workers (a review article is Narayanamurti and Pohl, 1970), and theoretically by Krumhansl and Gomez (Gomez et al., 1967). The individual particles have (in common with the harmonic oscillator or free rotor) a singlet ground state and triplet excited state, plus higher

states. Dense systems were studied at Cornell by Fiory (Fiory, 1971). The behavior of these systems is suggestive of a "smeared out" phase transition to a ferroelectric-like phase when the concentration of impurities is sufficiently high. However, the combined effects of spatial disorder and anharmonicity have prevented a truly satisfactory theoretical treatment.

Another experimental problem to which I have given some attention is that of magnetism in rare earth materials (Cooper and Vogt, 1971), in which the single-particle levels are due to crystal field splittings. Also worthy of mention is the Ising model in a transverse field (Elliot et al., 1970; Pfeuty, 1970), a singlet-singlet system whose behavior is thought to be closely related to the question of soft modes in KDP-type ferroelectrics.

The second chapter illustrates the sorts of effects that may be expected in interacting systems by considering two interacting quantum dipoles (Mandell, 1971). Chapter III discusses the applicability of the considerations of this thesis to various real systems. The fourth chapter deals with general considerations for the many-particle problem. The remainder of the thesis is a series of calculations for various models. Chapter V deals with free rotors, with the singlet-triplet model, and with a primitive model for hydrogen-bonded ferroelectrics. Chapter VI

is concerned with one-dimensional classical systems having dipolar, quadrupolar, or mixed interactions. Some previously published work on an interacting classical system with viscosity is presented in Appendix C. The final chapter deals with diffuse angular momentum excitations in hcp orthohydrogen.

II. The Two Dipole Problem

An instructive example of a system having single-particle energy levels and orientation-dependent interactions is a pair of free-rotor dipoles. This calculation was originally undertaken in the hope of explaining susceptibility maxima observed in dipolar impurity systems (Kanzig et al, 1964; Flory, 1971) in terms of pair effects. While these results do not provide a satisfactory explanation of such phenomena, they are nonetheless useful since they foreshadow the results of calculations for many-particle systems and are presented here primarily for that purpose.

The hamiltonian for a pair of dipoles may be written as

$$H = \sum_i L_i^2 - \frac{\Gamma^2}{2} \sum_{i \neq j} V(\Omega_i, \Omega_j) \quad (2.1)$$

where L_i^2 is the square of the orbital angular momentum operator for particle i and has eigenvalues $L(L+1)$, Γ is a parameter whose value is of order $(Ip^2/\hbar^2 r^3)^{1/2}$, I is the moment of inertia, p the dipole moment, r the interparticle distance, and

$$V(\Omega_i, \Omega_j) = 2 \cos \theta_i \cos \theta_j - \sin \theta_i \sin \theta_j \cos(\phi_i - \phi_j). \quad (2.2)$$

The potential can be written in operator notation by the substitutions

$$\cos \theta = a^\dagger + a \quad (2.3)$$

$$\sin \theta e^{\pm i\phi} = \pm a (L \pm m)^{-1} L^\pm \mp L^\pm (L \mp m)^{-1} a^\dagger \quad (2.4)$$

$$a^\dagger Y_{L-1,m} = \left| \frac{L^2 - m^2}{4L^2 - 1} \right|^{\frac{1}{2}} Y_{Lm} \quad (2.5)$$

$$L^\pm Y_{Lm} = \{(L \mp m)(L \pm m + 1)\}^{\frac{1}{2}} Y_{L,m\pm 1} \quad (2.6)$$

As pointed out in Jungst and v. Meyenn (1971) there are three good quantum numbers for the eigenstates of this Hamiltonian:

- (1) the eigenfunctions will be symmetric (s) or antisymmetric (a) under interchange of the two particles forming the pair. For a translationally invariant system, each state has a wavevector $\underline{k}$.
- (2) the quantity $\sum_i L_i$ will be either even (g) or odd (u).
- (3) the orbital angular momentum about the interparticle axis, $\sum_i m_i$, is a good quantum number.

If we take advantage of these symmetries, and if, for the purpose of calculating the properties of the low energy states, we neglect those states having very high values of $\sum_i L_i^2$, the problem is reduced to finding the eigen-

values and eigenvectors of relatively small matrices.

The low-lying energy levels for the two-dipole system are shown (relative to the ground state) in figure 2.1. (These results are adapted from table 3a of the preprint version of Jungst and v. Meyenn (1971), which agree with our own results.) It is worthwhile to point out the nature of the two lowest states. The main components of these states have $m_1 = m_2 = 0$, and, in the basis $|L_1 L_2\rangle$ have the form $\{a|00\rangle + b|11\rangle\}$ and $\{|01\rangle + |10\rangle\}$, where the coefficients b increase with increasing Γ . The latter state has a decrease in energy to first order in the potential, and becomes nearly degenerate with the ground state as Γ becomes large. In an analogous way, a translationally invariant, infinite array of dipoles at zero temperature will, in the absence of interaction, have excited states consisting of one dipole in the state $L = 1, m = 0, \pm 1$. For small Γ these states are more properly written

$$|\underline{k}, \gamma\rangle = N^{-1/2} \sum_i e^{i\underline{k} \cdot \underline{r}_i} c_{\gamma, i}^\dagger(\underline{k}) |\Omega\rangle$$

where $|\Omega\rangle$ is the non-interacting ground state and $c_{\gamma, i}^\dagger(\underline{k})$ is a linear combination of $a_i^\dagger$, $L_i^+ a_i^\dagger$, and $L_i^- a_i^\dagger$. These states form bands centered about $E = 2$ and having bandwidth of order Γ^2 . In a many-particle system the energy of the lowest excited state will reach zero (or asymptotically approach zero in the one-dimensional case) for some value

Figure 2.1. Low-lying energy levels (measured relative to the ground state) for two free-rotor dipoles. The degeneracies of the states are not indicated.

of Γ , signalling the onset of long-range order. The other low-lying modes then form libron bands, the libronic energy being approximately Γ .

It is useful to assign names to the bands of excitations for small Γ . Let us call the band near $E = 2$ "rotational excitons," near $E = 4$ "nearly harmonic bi-excitons," near $E = 6$ "anharmonic bi-excitons," and near $E = 8$ "tri-excitons." The energies of single excitons and tri-excitons vary linearly with Γ^2 , while those of bi-excitons vary quadratically. (It is worth noting that the ground state energy varies quadratically with Γ^2 . This is the origin of the r^{-6} van der Waals potential.) In a many-particle system the multi-excitons of any order are dominated by the nearly harmonic variety, but two isolated excitons have a substantially different energy from two nearby excitons. This results in exciton-exciton scattering. Some attempts at dealing with this problem are given in later chapters.

For the case of two dipoles we have calculated, as a function of inverse temperature, the quantities

$$(\cos \theta_1 + \cos \theta_2)^2 = \frac{1}{Z} \sum_i e^{-E_i/kT} \langle i | O_{\theta}^2 | i \rangle \quad (2.7)$$

and

$$\chi_{\theta,1} = \frac{1}{Z} \sum_{i \neq j} e^{-E_i/kT} \frac{\langle i | O_{\theta,1} | j \rangle \langle j | O_{\theta,1} | i \rangle}{(E_j - E_i)} \quad (2.8)$$

Figure 2.2. The parallel correlation, $\{(\cos \theta_1 + \cos \theta_2)^2 - 2/3\}$, as a function of inverse temperature.

Figure 2.3. The parallel susceptibility (solid line; left scale) and perpendicular susceptibility (dashed line; right scale) as defined in equation 2.8 as a function of inverse temperature.

where

$$Q_{11} = \sum_i \cos \theta_i$$

$$Q_1 = \sum_i \sin \theta_i \cos \phi_i$$

$$Z = \sum_i \exp (-E_i/kT).$$

The calculations were done using the exact eigenstates and eigenvectors for all states of energy less than 7 in the restricted Hilbert space of $\sum_i L_i^2 \leq 12$, except that for the states $\{s, g, m = 0\}$ we considered $\sum_i L_i^2 \leq 14$. For the range of temperature and Γ considered the results seemed insensitive to these cutoffs; higher values of Γ and/or higher temperatures would require higher energy levels to be considered as well. In the scheme used the largest matrix to be diagonalized was 10×10 , and most were 4×4 or 5×5 .

The quantities 2.7 and 2.8 are plotted in figures 2.2 and 2.3. The behavior of the static susceptibilities is disappointingly dull. The parallel susceptibility rises with Γ , and the transverse susceptibility is correspondingly depressed. Neither shows a peak as a function of temperature. There is a slight peak in the correlation function, which would correspond to a peak in the high frequency susceptibility. This peak is due to the first excited state's being more correlated than the

ground state, at the expense of some kinetic energy.

In an attempt to salvage a susceptibility peak we have calculated the parallel polarization as a function of field at zero temperature (figure 2.4). For small values of Γ the curve remains linear up to relatively high fields. For large Γ the curve bends over fairly soon. If we assume that a pair is in a local field (at $T=0$) given by $(2IpE_{loc}/N^2) = \Gamma^2$, we find the differential susceptibility lowered by a factor of 0.7 for $\Gamma = 0.8$, and by a factor of 0.09 for $\Gamma = 1.6$. Such local fields are not at all unreasonable in the light of measurements of remanent polarization by Fiory (1971) of several micro-coulombs/m². These values correspond to $(2IpE/N^2) \sim 10^{-2}$. This average field will certainly be much enhanced in the immediate neighborhood of a strongly interacting pair.

We next ask if, at the experimental concentrations, it is reasonable to expect large numbers of strongly interacting pairs. For the case of OH^- in alkali halides, neglecting any lattice effects, only near-neighbor pairs would show significant effects. If we assume that individual impurities are randomly distributed, there are probably too few near-neighbor pairs to be significant. There are, however, two factors favoring the formation of such pairs. The first is that the lattice polarization enhances the interaction of more distant pairs. The second is that at high concentrations the assumption of random

Figure 2.4. The polarization, $(\cos \theta_1 + \cos \theta_2)$ at $T=0^\circ\text{K}$ as a function of field in units of $\hbar^2/p$.

distribution of impurities is probably unrealistic. The van der Waals forces between OH^- ions (proportional to p^2I) are comparable to those between HF molecules, and HF liquifies at room temperature. Furthermore, the properties of crystals with the highest concentrations of Li^+ have been observed to change with time when stored at room temperature (A. T. Fiory and R. O. Pohl, private communication). This suggests that clustering effects may be highly significant.

III. Applications

This chapter is concerned with the classification and discussion of real systems to which the formalisms of this thesis may be applied. These discussions are in the light of previous results and of the model calculations of following chapters.

The model can be discussed in terms of a fairly general hamiltonian

$$H = \sum_i H^{SP}(i) + \frac{1}{2} \sum_{i \neq j} \{H^{orientational}(i,j) + H^{CT}(i,j)\} + H^{phonon} + H^{interaction}. \quad (3.1)$$

Here $H^{SP}(i)$ is a "single-particle" hamiltonian concerned with "internal" degrees of freedom of the units or particles of which the system is composed; $H^{orientational}$ concerns the interaction of anisotropic single-particle excitations on nearby particles; H^{CT} , the "charge transfer" hamiltonian, concerns mutual electronic and vibrational excitations not included in $H^{orientational}$, such as hydrogen bonding effects; the center of mass motions of the particles are contained in H^{phonon} , and the remainder of the hamiltonian is regarded as interactions among the previously described pieces.

The single-particle hamiltonian will be supposed to have considerable effects on the dynamics of the system. The system will be considered quantum-mechanical if the static properties also depend strongly on the single-particle hamiltonian. To see this, consider a free rotator which obeys the uncertainty relation

$$\Delta L \Delta \theta \geq \hbar. \quad (3.2)$$

To point in a given direction, then, requires some angular momentum, and thence rotational kinetic energy. If this energy is small (compared with thermal or interaction energies) the particle is said to have a permanent moment and may be treated classically; otherwise it must be treated quantum mechanically. The single-particle hamiltonian may find its origin in dilute systems, as is the case for condensed gases, or may result from effects peculiar to the solid, as in tunnelling or crystal field systems. We show some single-particle spectra in figure 3.1, and a chart classifying some of the systems to be considered in table 3.1.

Figure 3.1. Various types of single-particle spectra.

Table 3:1

	Electric Dipole	Electric Quadrupole	Magnetic Exchange	Others
Quantum	Rare gas solids KCl:Li other van der Waals crystals	$o\text{-H}_2$ $p\text{-D}_2$	NO? O_2 Pr_3Tl and other rare earths	Hydrogen- bonded ferroelectrics (KDP)
Classical	KCl:CN Hydrogen Halides Alkali Cyanides 	N_2 CO	Magnets with large spin quantum numbers	Polymers

A. Rare Gas Solids

The approach of this thesis may be regarded as an alternative to band structure calculations (Hermansson and Phillips, 1966; Reilly, 1967) for treating excitons in rare gas solids. Since the exciton energies are large compared with $k_B T$, the harmonic approximation used by Lucas (1967) works rather well. Rare gas atoms are not harmonic, however, but have many states only slightly higher in energy than the first excited triplet.

To get an idea of the order of magnitude of such anharmonic effects we have calculated the corrections to the van der Waals energy one would have if the atoms possessed the singlet-triplet structure. These are shown in figure 3.2.

Many-body van der Waals forces also bear on the lattice dynamics of rare gases, and work along these lines has been done by Lucas (1968) and by Huller (1971). One might proceed further and try to calculate exciton-phonon interactions, but such calculations become fairly complex.

Figure 3.2. Van der Waals binding energy for rare gases. Here α is the atomic polarizability and $\hbar\omega_0$ is the bare exciton energy (taken to be the first ionization potential). The solid line is the binding energy in harmonic approximation, in agreement with the results of Lucas (1967). The dashed line is a "corrected" value assuming the singlet-triplet structure. The percentage correction varies as $(4\pi N\alpha)^2$, and is about 8% for Xenon.

B. Diatomic Molecular Crystals

Diatomic molecules exhibit a richer variety of phenomena than rare gases because energies of rotation and of interaction are in the thermal range. Table 3.2 shows relevant parameters for several molecules. A previous set of model calculations may be found in Raich and Etters (1971).

Before dealing with particular cases one must ask whether it makes any sense at all to treat diatomic molecules in crystals as nearly free rotors with electrostatic interactions. It might be thought that "steric hindrances" provide the most important effects. That this is not the case may be seen by comparing the molecular and crystalline dimensions. Internuclear distances in diatomic molecules fall in the range $0.8\text{--}1.2 \times 10^{-8}$ cm., while intermolecular distances in crystals are about 4×10^{-8} cm. This suggests that the outer electrons form a reasonably spherical distribution. Furthermore, experiments on the rotational magnetic moment of H_2 (Ramsey, 1956) suggest that the outer electrons do not rotate with the molecule, but simply deform their distribution in accordance with the instantaneous molecular orientation. An experimental test for nearly free rotation is to look for the charac-

Table 3.2
Molecular Constants

Molecule	Dipole Moment (a) $p(\text{esu-cm}) \times 10^{18}$	Quadrupole Moment (a) $Q(\text{esu-cm}^2) \times 10^{26}$	Rotation Constant (b) $\hbar^2 / 2I \text{ (}^\circ\text{K)}$	$V = p^2 / a^3 \text{ (c)}$ ($^\circ\text{K}$)	$\Gamma = 6Q^2 / 25a^5 \text{ (c)}$ ($^\circ\text{K}$)
H ₂	0	+ .662	87.5	0	.84 ^(d)
D ₂	0	+ .649	44?	0	1.04 ^(d)
N ₂	0	-1.52	2.9	0	3.9
O ₂	0	- .39	2.1	0	.26
CO	.112	-2.5	2.8	1.42	10.1
NO	.158	-1.8	2.5?	2.8	5.5
HF	1.736	+2.6	30	340	13
HCl	1.07	+3.8	15	130	25
HBr	.788	+4	12	70	27
HI	.382	+6	9.4	17	61
CN ⁻	.5 ^(e)	4.6 ^(f)	2.7	—	—

Notes to Table 3.2

- (a) Strogyn and Strogyn, 1966.
- (b) Leighton, 1959
- (c) At 4×10^{-6} cm nearest neighbor distance, except H_2 and D_2 .
- (d) Best experimental values. H. Meyer, private communication.
- (e) CN^- impurity in KCl. (Fiory, 1971)
- (f) Estimated from transition temperature of KCN relative to N_2 .

teristic rotational bends in infrared absorption.

Molecules which cannot be treated as nearly free rotors include those whose electronic ground state is not a singlet, such as O_2 (Wachtel and Wheeler, 1971) and NO. In these cases a small electronic overlap is sufficient to create intermolecular magnetic exchange interactions. We shall not deal with such crystals in this thesis.

Homonuclear molecules, which lack dipole moments, exhibit simpler behavior than molecules having both types of moments. The two most important examples are N_2 , which is usually treated classically, and H_2 , a quantum case with which we deal in chapter VII. In a classical system the interaction energy between two molecules is a sum of terms of the form

$$\Gamma \text{Tr} \langle Y_2^m(\Omega_1) Y_2^{-m}(\Omega_2) e^{-\beta H} \rangle / \text{Tr} \langle e^{-\beta H} \rangle \quad (3.3)$$

which is proportional to

$$(4\pi)^{-2} \frac{\Gamma^2}{k_B T} + O(T^{-2}) + \dots \quad (3.4)$$

In the quantum ($o\text{-}H_2$) case, however, this sum, if evaluated by expanding the exponential, would diverge because $k_B T$ is less than the energy of transition between states of different rotational angular momentum. This means that all initial, final, and intermediate states used in calculating 3.3 must belong to the $J=1$ multiplet, so that 3.4 becomes

$$(10\pi)^{-2} r^2/T + O(T^{-2})$$

Thus quantum considerations reduce the effective interaction by 4/25.

Most of the work on quadrupolar crystals, both theoretical and experimental, has been in the ordered state. The low temperature quadrupolar arrangement is discussed by Felsteiner et al. (1971). The interest in these crystals centers on the torsional excitations, or librations, which they exhibit (Raich and Etters, 1972; Goodings and Henkelman, 1971; Berlinsky and Coll, 1972). In N_2 as well as H_2 these excitations are highly anharmonic in the sense that anharmonic calculations give markedly better fits to the observed libron frequencies than harmonic calculations. The zero-point motion in N_2 is estimated at 18° at $T=0$ (Goodings and Henkelman, 1971).

The transition to the ordered phase in N_2 occurs at $35.6^\circ K$ (Goodings and Henkelman, 1971). The high temperature phase seems not to have been well studied, but the classical analogues to the methods used on the high temperature phase of orthohydrogen (chapter VII) should give useful information. It is useful to note that one-dimensional N_2 would have a specific heat maximum at $T=4\Gamma$ or $T \approx 16^\circ K$.

Carbon monoxide (Goodings and Henkelman, 1971; Felsteiner and Litvin, 1971; Melhuish and Scott, 1964; Curl et al., 1968) exhibits quadrupolar ordering similar to N_2 . An additional feature of CO is that it has a small dipole moment which, according to simple arguments, should cause dipolar ordering at a few degrees absolute. That such ordering is not seen is usually attributed (Curl et al., 1968) to a very slow approach to equilibrium. The considerations of chapter VI, however, suggest that the dipole-quadrupole interaction may be responsible for the lack of ordering.

The hydrogen halides (Krieger and James, 1954; Niimura et al., 1972; Arnold and Heastie, 1967; Hoshino et al., 1967; Genin et al., 1968; Ito et al., 1969; Hanamura, 1970a, b) have both dipole and quadrupole moments and all but HF exhibit solid-solid phase transitions. Recent experimental data have shown that these substances exhibit complex phenomena far beyond the scope of such mean field theories as that of Krieger and James (1954).

The moments of inertia are such that all these substances may be treated classically, except that quantum corrections of a few percent may be expected in HCl. The molecules are thought to form long zigzag chains in the high temperature (cubic) phase. Recent results in HCl (Niimura et al., 1972) indicate the setting in of the zig-

zag phase at about 120°K, with no crystallographic change at the 98°K ferroelectric phase transition. It is usually considered that the quadrupole interaction predominates in all hydrogen halides but HF and HCl. The results of chapter VI suggest that the quadrupole interaction dominates in HCl also, the ratio V/Γ being about 5, causing the formation of the zigzag chains. Eventually, the long-range dipolar interaction leads to the ferroelectric transition.

It seems to me that further Raman and infrared studies of excitations $\leq 50 \text{ cm}^{-1}$ would yield useful information about the high temperature phases. Also, one should mention the study of charge transfer effects by Hanamura (1970a).

There is a moderate amount of experimental work on alkali cyanides (Structure Reports, 1955; Price et al., 1972; Coogan and Gutowsky, 1964), particularly on KCN, but rather little theory. These highly poisonous compounds (RbCN, KCN, NaCN) have the NaCl structure at high temperatures, and undergo a transition to an orthorhombic structure. There is also a lower temperature ferroelectric transition. (CsCN exhibits similar behavior, but has the CsCl structure.)

So far as I am aware, it has not been previously suggested that the cubic-orthorhombic transition is caused primarily by electric quadrupole interactions among the

Table 3.3
Properties of Alkali Cyanides

	NaCN	KCN	RbCN
Cubic Phase Lattice Constant, a (10^{-8} cm)	5.88	6.49	6.77
Transition Temperatures ($^{\circ}\text{K}$) (T_P ; T_C)	172;288	83;167	?;120
Quadrupole Interaction Γ ($^{\circ}\text{K}$)	31.5	18.3	13.1
$T_C \times a^5 \times 10^{34}$	2.02	1.92	1.71

cyanide radicals. This hypothesis gives a reasonable value for the $CN^\bullet$ quadrupole moment (see Table 3.2) and is very consistent for the three compounds (last line of Table 3.3) if increased screening by the larger, more polarizable cations is taken into account. Further work on these compounds should prove interesting.

A further class of simple molecules whose rotational properties are poorly understood is the methanes (Colwell, 1969).

C. Magnetic Systems

Magnetic rare-earth atoms or ions often have single-particle dynamic structure due to the presence of crystal fields. Singlet ground state magnetism was studied by Bozorth and Van Vleck (1960) and by Bleany (1963), and more recently by Cooper (1972), by Pink (1968), by Hsieh and Blume (1972), and experimentally by Birgenau et al. (1971, 1972). In particular, Pr_3Tl is very interesting in that it has a ferromagnetic phase transition at a temperature (12°K) much less than the crystal field splitting (70°K). The low temperature phase is fairly well understood on the basis of mean-field-like theories (Cooper, 1972), but the expected mode softening is not seen in the high temperature region. This lack of mode softening is probably due to the presence of higher crystal field states. Some work in this direction has been done by Peschel et al. (1972). There is some indication of mode softening, however, in dhcp Pr (Rainford and Glyden-Houmann, 1971).

There is much still to be learned by doing self-consistent theories, and particularly theories which take scattering into account, for more realistic models of rare-earth magnets.

D. Other Systems

Impurities in solids often exhibit interesting single-particle properties. We have previously mentioned the work on dipolar impurities in alkali halides (Fiory, 1970; Narayanamurti and Pohl, 1970). Magnetic impurities also exhibit fascinating properties, but here the particles interact through the electron gas, leading to more complex behavior (Klein, 1969).

An interesting theoretical system is the Ising model with transverse field, treated by Pfeuty (1970), by Elliot et al. (1970), and by Wang and Cooper (1968,1969). This model is given by the hamiltonian

$$H = \Delta \sum_i S_z(i) + \frac{1}{2} \sum_{i \neq j} J_{ij} S_x(i) S_x(j) \quad (3.5)$$

where $\underline{S}$ is a spin one-half operator. This model can be solved exactly in one dimension (Pfeuty, 1970). It is the simplest system illustrating the ability of a single-particle property (viz., Δ) to prevent long-range order even at $T=0^\circ\text{K}$.

Hydrogen-bonded ferroelectrics such as KDP are usually thought of as systems of hydrogen bonds having the hamiltonian 3.5, and interacting strongly with optic phonons. We present a model calculation for such a system in chapter V.

In large molecules, and in polymers in particular, it is often useful to consider various portions of the molecule as interacting units. For example, poly-4-chloro-styrene has the structure

with the side-chain having a dipole moment of 1.1×10^{-18} esu-cm. This suggests that the dielectrically active side-chain rotates almost freely in the plane normal to the polymer chain. We have applied our ideas to such polymers in a previously published paper (Mandell, 1972), included as Appendix C.

IV. General Considerations on the Many Particle Problem

In this chapter we consider, in terms as general as possible, the properties of a dipolar system having a hamiltonian

$$H = \sum_i (h_i - \underline{P}_i \cdot \underline{E}) + \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} \underline{P}_{i\alpha} J_{\alpha\beta}(\underline{r}_i - \underline{r}_j) \underline{P}_{j\beta} \quad (4.1)$$

where h_i is a single-particle hamiltonian, $\underline{P}_i$ a dipole moment operator, $\underline{E}$ an applied field, and $\underline{J}$ a coupling which may be a dipole-dipole coupling

$$|\underline{R}|^3 J_{\alpha\beta} = \delta_{\alpha\beta} - 3R_\alpha R_\beta / R^2. \quad (4.2)$$

The ideas developed in this chapter are applicable as well to other coupling mechanisms such as magnetic exchange coupling in the rare earths.

A. Susceptibility and Phase Transformations Using Mean Field Theory

In mean field theory the hamiltonian 4.1 is replaced by an effective single-particle hamiltonian

$$H = \sum_i (h_i + \sum_{\alpha} P_{i\alpha} \times \{ \sum_{\substack{j \neq i \\ \beta}} J_{\alpha\beta}(\underline{r}_i - \underline{r}_j) \langle P_{j\beta} \rangle - E_{\alpha} \}). \quad (4.3)$$

We suppose $\langle P_{i\alpha} \rangle = \chi_{\alpha\beta}^{SP} E_{\beta}^{eff}$ where

$$E_{\alpha}^{eff} = E_{\alpha} - \sum_{\beta} J_{\alpha\beta}(0) \langle P_{j\beta} \rangle \quad (4.4)$$

$$J_{\alpha\beta}(0) = \sum_{j \neq i} J_{\alpha\beta}(\underline{r}_i - \underline{r}_j) \quad (4.5)$$

and $\chi_{\alpha\beta}^{SP}$ is the single particle susceptibility found, for example, by the methods described by Van Vleck (1931). We may consider $J_{\alpha\beta}(0)$ diagonal. Then self-consistency demands

$$\chi = \frac{\langle P_{i\alpha} \rangle}{E_{\alpha}} = \chi^{SP} \times \{1 - J_{\alpha\alpha}(0) \chi\} \quad (4.6)$$

or

$$\chi = \frac{\chi^{SP}}{1 + J_{\alpha\alpha}(0) \chi^{SP}}.$$

If, then, $J_{\alpha\beta}(0)$ has a negative eigenvalue, the susceptibility will become singular if $\chi^{SP} = -\{J_{\alpha\alpha}(0)\}^{-1}$. This is

sometimes called a "polarization catastrophe." For the dipole-dipole interaction it is always the case that $J_{\alpha\beta}(0)$ has a negative eigenvalue; in three dimensions for cubic structures this eigenvalue is $-4\pi N/3$, N being the particle number per unit volume.

If χ^{SP} is temperature dependent, then there is the possibility of seeing a polarization catastrophe as the temperature is varied, i.e., a ferroelectric phase transition. For example, if h_1 is a harmonic oscillator hamiltonian χ^{SP} will be independent of temperature and there will be no phase transition. For free rotors there will be a transition provided $p^2 J(0)/\Delta > 3/2$. If the interaction (for free rotors) is large enough that the system may be treated classically, mean field theory predicts a transition at $T_c = p^2 J(0)/3$.

We wish to draw from this discussion two main conclusions: (1) Anharmonic effects in the single-particle hamiltonian may lead to temperature-dependent properties and thence to phase transitions. (2) Quantum effects may prevent a phase transition if the interaction is sufficiently weak.

B. Elementary Excitations

In this subchapter we develop a formalism for computing the energies of elementary excitations for systems having the hamiltonian 4.1. The technique we use here would be exact (a Bogolyubov transformation) (Tyablikov, 1967; Lucas, 1967) if the elementary excitations could be treated as bosons. The approximation we make here may be regarded as a random phase approximation; in the last subsection of this chapter we outline a method for obtaining corrections to this approximation.

We begin by defining bare exciton operators $c_{\alpha\beta}^{\dagger}(\underline{r}_i)$ having the properties

$$c_{\alpha\beta}^{\dagger}(\underline{r}_i)|\gamma_i\rangle = \delta_{\gamma\beta}|\alpha_i\rangle \quad (4.7)$$

$$h_i|\beta_i\rangle = \epsilon_{\beta}|\beta_i\rangle \quad (4.8)$$

$$c_{\beta\alpha}(\underline{r}_i) = c_{\alpha\beta}^{\dagger}(\underline{r}_i)$$

$$[c_{\alpha\beta}^{\dagger}(\underline{r}_i), c_{\gamma\delta}^{\dagger}(\underline{r}_j)] = \delta_{ij}\{c_{\alpha\delta}^{\dagger}(\underline{r}_i)\delta_{\beta\gamma} - c_{\gamma\beta}^{\dagger}(\underline{r}_i)\delta_{\alpha\delta}\} \quad (4.10)$$

$$[h_i, c_{\alpha\beta}^{\dagger}(\underline{r}_i)] = (\epsilon_{\alpha} - \epsilon_{\beta}) c_{\alpha\beta}^{\dagger}(\underline{r}_i). \quad (4.11)$$

(The usual boson operator is

$$a^{\dagger} = \sum_{n=1}^{\infty} \sqrt{n} c_{n,n-1}^{\dagger}.) \quad (4.12)$$

We assume that the polarization operator P_i may be written as a linear combination of bare exciton operators

$$P_{i\alpha} = \sum_{\substack{\beta\gamma \\ (\epsilon_\beta > \epsilon_\gamma)}} A_{\alpha\beta\gamma} \{c_{\beta\gamma}^\dagger(\underline{r}_i) + c_{\beta\gamma}(\underline{r}_i)\}. \quad (4.13)$$

The first step in finding approximate normal mode operators is to transform to reciprocal space according to

$$c_{\alpha\beta}^\dagger(\underline{k}) = N^{-1/2} \sum_i e^{i\underline{k} \cdot \underline{r}_i} c_{\alpha\beta}^\dagger(\underline{r}_i) \quad (\epsilon_\alpha > \epsilon_\beta) \quad (4.14)$$

$$c_{\alpha\beta}(-\underline{k}) = N^{-1/2} \sum_i e^{i\underline{k} \cdot \underline{r}_i} c_{\alpha\beta}(\underline{r}_i) \quad (\epsilon_\alpha > \epsilon_\beta) \quad (4.15)$$

$$\begin{aligned} P_\alpha(\underline{k}) &= N^{-1/2} \sum_i e^{i\underline{k} \cdot \underline{r}_i} P_\alpha(\underline{r}_i) \\ &= \sum_{\beta\gamma} A_{\alpha\beta\gamma} \{c_{\beta\gamma}^\dagger(\underline{k}) + c_{\beta\gamma}(-\underline{k})\} \end{aligned} \quad (4.16)$$

$$\begin{aligned} [c_{\alpha\beta}^\dagger(\underline{k}), c_{\gamma\delta}(\underline{q})] &= \delta_{\beta\gamma} c_{\alpha\delta}^\dagger(\underline{k}-\underline{q}) \\ &\quad - \delta_{\alpha\gamma} c_{\delta\beta}^\dagger(\underline{k}-\underline{q}) \end{aligned} \quad (4.17)$$

$$H = H_0 + H_1 \quad (4.18)$$

$$H_0 = \sum_i \epsilon_i = \sum_\alpha \epsilon_\alpha c_{\alpha 0}^\dagger(\underline{0}) c_{\alpha 0}(\underline{0}) \quad (4.19)$$

$$H_1 = \frac{1}{2} \sum_{\underline{k}\alpha\beta} P_\alpha(\underline{k}) J_{\alpha\beta}(\underline{k}) P_\beta(\underline{k}) \quad (4.20)$$

$$J_{\alpha\beta}(\underline{k}) = \sum_j e^{i\underline{k} \cdot (\underline{r}_i - \underline{r}_j)} J_{\alpha\beta}(\underline{r}_i - \underline{r}_j) \quad (4.21)$$

We wish to find operators

$$d_{\alpha}^{\dagger}(\underline{k}) = \sum_{\substack{\beta\gamma \\ \epsilon_{\beta} > \epsilon_{\gamma}}} D_{\alpha\beta\gamma}(\underline{k}) c_{\beta\gamma}^{\dagger}(\underline{k}) + D'_{\alpha\beta\gamma}(\underline{k}) c_{\beta\gamma}(-\underline{k}) \quad (4.22)$$

satisfying (approximately)

$$[H, d_{\alpha}^{\dagger}(\underline{k})] = E_{\alpha}^0(\underline{k}) d_{\alpha}^{\dagger}(\underline{k}). \quad (4.23)$$

The commutator takes the form

$$\begin{aligned} [H, d_{\alpha}^{\dagger}(\underline{k})] &= \sum_{\beta\gamma} (\epsilon_{\beta} - \epsilon_{\gamma}) \{ D_{\alpha\beta\gamma} c_{\beta\gamma}^{\dagger}(\underline{k}) - D'_{\alpha\beta\gamma} c_{\beta\gamma}(-\underline{k}) \} \\ &+ \frac{1}{2} \sum_{\underline{q}\beta\gamma} \{ [P_{\beta}(-\underline{q}), d_{\alpha}^{\dagger}(\underline{k})] J_{\beta\gamma}(\underline{q}) P_{\gamma}(\underline{q}) \\ &+ P_{\beta}(\underline{q}) J_{\beta\gamma}(\underline{q}) [P_{\gamma}(-\underline{q}), d_{\alpha}^{\dagger}(\underline{k})] \}. \end{aligned} \quad (4.24)$$

Terms appearing in the commutators of the right hand side of 4.24 for which $\underline{q}=\underline{k}$ may be regarded as static properties of the medium proportional to $N^{-1} \sum_i \langle c_{\alpha\beta}^{\dagger}(\underline{r}_i) \rangle$. This leads to

$$\begin{aligned} [H, d_{\alpha}^{\dagger}(\underline{k})] &= \sum_{\beta\gamma} F_{\alpha\beta\gamma}(D, D', A, J) c_{\beta\gamma}^{\dagger}(\underline{k}) \\ &+ F'_{\alpha\beta\gamma}(D, D', A, J) c_{\beta\gamma}(-\underline{k}) \\ &+ R_{\alpha}^{\dagger}(\underline{k}) \end{aligned} \quad (4.25)$$

where the anharmonic term $R_{\alpha}^{\dagger}(\underline{k})$ consists of products of two bare exciton operators. We suppose that the static properties may be determined either perturbatively or self-

consistently, and that the anharmonic terms may, to a first approximation, be ignored. The remainder of 4.25 is then a linear eigenvalue problem whose solution gives temperature dependent, undamped excitations. $R_{\alpha}(\underline{q})$ represents, to lowest order, scattering among these excitations, as will be seen in a later chapter. If the energy of an excitation "softens" to zero at some temperature, the presence of a phase transition is suggested.

C. Green's Functions; Anharmonic Effects

In this subchapter we define Green's functions (correlation functions) which will prove useful in treating the binding energy, susceptibility, and anharmonic effects.

Define Green's functions by

$$G_{\alpha\beta}^R(\underline{k}, \underline{k}', t) = -i \langle d_{\alpha}(\underline{k}, t) d_{\beta}^{\dagger}(\underline{k}', 0) \rangle \theta(t) \quad (4.26a)$$

$$G_{\alpha\beta}^A(\underline{k}, \underline{k}', t) = -i \langle d_{\alpha}^{\dagger}(\underline{k}, t) d_{\beta}(\underline{k}', 0) \rangle \theta(t) \quad (4.26b)$$

where $O(t) = e^{iHt} O e^{-iHt}$ and the operators $d_{\alpha}(\underline{k})$ are the approximate normal mode operators of the previous subchapter. For our purposes we may restrict consideration to diagonal Green's functions $G_{\alpha}^{R,A}(\underline{k}, t)$.

We may express the Green's functions for $t=0^+$ in terms of the static properties of the system and the normal mode energies. First note

$$G_{\alpha}^R(\underline{k}, 0^+) - G_{\alpha}^A(\underline{k}, 0^+) = -i \langle [d_{\alpha}(\underline{k}), d_{\alpha}^{\dagger}(\underline{k})] \rangle \quad (4.27)$$

which may equally well be written as a linear combination of commutators of bare exciton operators with equal wave-vector. Define

$$\langle [d_{\alpha}(\underline{k}), d_{\alpha}^{\dagger}(\underline{k})] \rangle = \langle c_{\alpha} \rangle. \quad (4.28)$$

Next, note that

$$G_{\alpha}^R(\underline{k}, 0^+) = \exp\{\beta E_{\alpha}(\underline{k})\} G_{\alpha}^A(\underline{k}, 0^+) \quad (4.29)$$

which may be seen by expanding the definitions 3.26 in terms of stationary states. This gives

$$G_{\alpha}^R(\underline{k}, 0^+) = \frac{-i\langle G_{\alpha} \rangle}{1 - e^{-\beta E_{\alpha}(\underline{k})}} \quad (4.30)$$

A Dyson-like equation may be derived for these Green's functions from which one can calculate the damping of the excitations and further corrections to their energies. The derivation is analogous to that given for the singlet-triplet case in the next chapter, equations 5.34-5.40.

D. Susceptibility and Binding Energy

To calculate the susceptibility and binding energy we take advantage of the fact that the polarization operator $\underline{P}(\underline{k})$ is a linear combination of the approximate normal mode operators $d_{\alpha}(\underline{k})$ and the hamiltonian (using 4.18-4.20) is a quadratic form in these operators

To find the susceptibility it is sufficient to find

$$\begin{aligned} \langle P_{\alpha}(\underline{k}) P_{\beta}(-\underline{k}) \rangle_{\omega} &= (2\pi)^{-1} \\ &\times \int_{-\infty}^{\infty} \langle P_{\alpha}(\underline{k}, t) P_{\beta}(-\underline{k}, 0) \rangle e^{-i\omega t} dt. \end{aligned} \quad (4.31)$$

We then have (Landau and Lifschitz, 1969)

$$\begin{aligned} \chi_{\beta\alpha}^{*}(\underline{k}, \omega) - \chi_{\alpha\beta}(\underline{k}, \omega) &= -\frac{4\pi i}{\hbar} \\ &\times \langle P_{\alpha}(\underline{k}) P_{\beta}(-\underline{k}) \rangle \tanh \frac{\hbar\omega}{2T} \end{aligned} \quad (4.32)$$

which becomes, in the case of diagonal susceptibility,

$$\chi_{\alpha\alpha}''(\underline{k}, \omega) = \frac{2\pi}{\hbar} \langle P_{\alpha}(\underline{k}) P_{\alpha}(-\underline{k}) \rangle_{\omega} \tanh \frac{\hbar\omega}{2T}. \quad (4.33)$$

The real part of the susceptibility, χ' , is then given by the Kramers-Kronig formula

$$\chi_{\alpha\alpha}'(\omega) = \frac{2}{\pi} P \int_0^{\infty} \frac{x \chi_{\alpha\alpha}''(x)}{x^2 - \omega^2} dx. \quad (4.34)$$

It is clear that the correlation function $\langle P_\alpha(\underline{k})P_\alpha(-\underline{k}) \rangle_\omega$ may be written as a sum of (fourier transformed) advanced and retarded Green's functions, plus terms of the form $\langle d^\dagger d^\dagger + \text{h.c.} \rangle_\omega$ which may be assumed small.

The binding energy is given by

$$B = N\langle h_1 \rangle_0 - \langle H \rangle. \quad (4.35)$$

In the first term the average is to be taken over the ensemble of the non-interacting system; this may be calculated by elementary methods. The second term consists of Green's functions evaluated at $t=0^+$ plus other terms which we assume to be small. For bosons this method is equivalent (at zero temperature) to finding the change in zero-point energy of the elementary excitations; this calculation was done by Lucas (1967)(in boson approximation) to find the van der Waals energy of rare gas solids.

E. Comments

We offer some comments on the application of the formalism of this chapter to multidimensional systems. The basic steps of this formalism are (1) write the hamiltonian in fourier space; (2) for each $\underline{k}$, solve an eigenvalue problem for the approximate temperature-dependent normal modes; (3) treat the anharmonic effects.

The first step may involve computation of a slowly or conditionally converging lattice sum; in particular, the dipole-dipole interaction is conditionally convergent. Such sums may be performed by the method of Nijboer and De Wette (1957). In the case of the three-dimensional dipolar array the long-range nature of the interaction leads to a splitting between longitudinal and transverse modes at $\underline{k}=0$. Other properties, such as the van der Waals binding energy, depend on the density of states of the excitations, which is independent of the long-range nature of the interaction.

In order to perform the second step we needed the values of certain commutators $[c_{\alpha\beta}(\underline{k}), c_{\gamma\delta}^\dagger(\underline{k})] = [c_{\alpha\beta}(\underline{r}_1), c_{\gamma\delta}^\dagger(\underline{r}_1)]$. If the interaction is weak the non-interacting values of these commutators serve fairly well, the next correction to the normal mode energies being of

order J^3 . If the interaction is not weak one may prefer to demand that a sum rule be satisfied, for example, in the singlet-triplet case we may require

$$\sum_{\alpha} \langle \frac{1}{3} c_{\alpha} c_{\alpha}^{\dagger} + c_{\alpha}^{\dagger} c_{\alpha} \rangle = 1. \quad (4.36)$$

When written in terms of Green's functions using 4.29 and 4.30, condition 4.36 is sufficient to frustrate a soft mode in a one-dimensional system for finite range interaction.

The anharmonic effects become much more difficult to treat in three dimensions, since the eigenvalue transformation for $J_{\alpha\beta}$ is, in general, $\underline{k}$ -dependent. Some insight might be gained by trying to solve 4.1 for a quasi-continuum model with isotropic interaction.

V. Calculations on Model Quantum Systems

This chapter consists of three model calculations. The first is an attempt to treat a one-dimensional array of free-rotor dipoles by the method of temperature dependent Green's functions (Abrikosov et al, 1965). The second deals with the singlet-triplet system using the method of chapter IV. Results are presented for the linear dipolar array. The last outlines the beginning of a calculation on a model hamiltonian for hydrogen-bonded ferroelectrics.

A. Calculation Using Temperature-Dependent Green's Functions

This subchapter is a report of a calculation undertaken early in my graduate career. The object is to calculate temperature-dependent Green's functions for a one-dimensional dipolar array using a self-consistent equation of motion technique. Unfortunately, rather few conclusions could be drawn from the results.

Define Green's functions

$$G(i-j; l, l'; m, m'; \tau) = -e^{\beta \Omega} \times \langle e^{-\beta H} T_{\tau} c_{lm,0}(i, \tau) c_{l'm',0}^{\dagger}(j, 0) \rangle \quad (5.1)$$

where T_{τ} is an ordering operator

$$T_{\tau} c(\tau) c^{\dagger}(0) = \begin{cases} c(\tau) c^{\dagger}(0) & \tau > 0 \\ c^{\dagger}(0) c(\tau) & \tau < 0 \end{cases} \quad (5.2)$$

the operators $c_{lm,0}$ cause transitions between the single-particle ground state and the state with total angular momentum l and projection m , and

$$c(\tau) = e^{H\tau} c e^{-H\tau}. \quad (5.3)$$

The Green's functions may be written as a fourier series

$$G(\tau) = T \sum_{n=-\infty}^{\infty} e^{-i\omega_n \tau} G(\omega_n), \quad \omega_n = 2\pi nT$$

$$G(\omega_n) = \int_0^{\beta} e^{i\omega_n \tau} G(\tau) d\tau, \quad (5.4)$$

and satisfy the equation of motion

$$\frac{\partial G}{\partial \tau} = \delta(\tau) (G(\epsilon) - G(\beta - \epsilon)) \quad (5.5)$$

$$= e^{\beta H} \langle e^{-\beta H} e^{H\tau} [H, c_{\ell m, 0}(i)] e^{-H\tau} c_{\ell', m', 0}^\dagger(j) \rangle$$

where $0 \leq \tau \leq \beta$, ϵ is a positive infinitesimal, and we note that $G(\tau) = G(\beta + \tau)$ for $\tau < 0$. The hamiltonian is given by

$$H = H_0 + V \quad (5.6)$$

$$H_0 = \sum_{i, \ell, m} \ell(\ell+1) c_{\ell m}^\dagger(i) c_{\ell m}(i)$$

$$V = -\frac{1}{2} \Gamma^2 \sum_{i, j} \sum_{\ell \ell'} \sum_{mm'} \{ 2A(\ell, m; \ell', m') O_1(\ell, m, i) \\ \times O_1(\ell', m', j) - B(\ell, m; \ell', m') \times \\ \times O_2(\ell, m, i) O_2^\dagger(\ell', m', j) \}$$

where

$$A(\ell, m; \ell', m') = \left(\frac{(\ell^2 - m^2)(\ell'^2 - m'^2)}{(4\ell^2 - 1)(4\ell'^2 - 1)} \right)^{\frac{1}{2}}$$

$$B(\ell, m; \ell', m') = \left[\frac{(\ell - m)(\ell' - m')(\ell - m + 1)(\ell' - m' + 1)}{(4\ell^2 - 1)(4\ell'^2 - 1)} \right]^{\frac{1}{2}}$$

$$O_1(\ell, m, i) = (c_{\ell m, 0}^\dagger(i) c_{\ell-1, m, 0}(i) \\ + c_{\ell-1, m, 0}^\dagger(i) c_{\ell m, 0}(i)) \quad (5.7)$$

$$O_2(\ell, m, i) = (c_{\ell-1, m, 0}^\dagger(i) c_{\ell, m-1, 0}(i) \\ - c_{\ell, 1-m, 0}^\dagger(i) c_{\ell-1, -m}(i))$$

Noting that $[H_0, c_{\ell m, 0}(i)] = -\ell(\ell+1) c_{\ell m, 0}(i)$ gives

$$-i\omega_n G(\omega_n) = (G(\epsilon) - G(\beta - \epsilon)) - \ell(\ell+1)G(\omega_n) \\ - \int_0^\beta e^{i\omega_n \tau} e^{\beta H} < e^{-\beta H} e^{H\tau} \\ \times [V, c_{\ell m, 0}(i)] e^{-H\tau} c_{\ell', m', 0}^\dagger(j) >$$
(5.8)

or

$$G(\omega_n) = \{\ell(\ell+1) - i\omega_n\}^{-1} \times \{(G(\epsilon) - G(\beta - \epsilon)) - \Pi(\omega_n)\}$$
(5.9)

where $\Pi(\omega_n)$ is the last term in (5.8). The non-inter-acting Green's functions are given by

$$z_0^{(0)}(i-j; \ell, \ell'; m, m'; \omega_n) = \delta_{ij} \delta_{\ell\ell'} \delta_{mm'} \\ \times (1 - e^{-\beta\ell(\ell+1)}) / (i\omega_n - \ell(\ell+1))$$

$$z_0 = \sum_{J=0}^{\infty} (2J+1) \exp\{-\beta J(J+1)\} .$$
(5.10)

We write the equation of motion for Π , and seek a self-consistent solution by iteration, requiring the τ -dependence of the most complicated function be consistent with re-normalized energies given by

$$\epsilon_{lm} = T \log \frac{G(0;l,l;m,m;0)}{G(0;l,l;m,m;\beta)} \quad (5.11)$$

These computations were done largely on the CDC 6600 at New York University. To extract some information from the Green's functions thus obtained, transform from site space to fourier space, and concentrate on $G(k;l,l;0,0;\omega_n)$ ($-\pi \leq k \leq \pi$), which may be expected to have (approximately) the form

$$G(k;l,l;0,0;\omega_n) = \frac{A(\beta, \Gamma)}{i\omega_n - \epsilon(k)} \quad (5.12)$$

where $\epsilon(k)$ is, in general, complex. A measure of the bandwidth of the excitations represented by this Green's function may be defined by

$$\Delta(n) = \frac{\text{Re} \{G(0;l,l;0,0;\omega_n) - G(\pi;l,l;0,0;\omega_n)\}}{\text{Re} G(\pi/2;l,l;0,0;\omega_n)} \quad (5.13)$$

becoming more accurate for large n . Using $n = 5$, we get the set of bandwidths shown in figure 5.1. (For $\Gamma \leq 0.8$ the convergence was poor at low temperatures.) We may compare these results with the harmonic case (dashed lines) and a renormalized harmonic case (dot-dash lines) given by

$$\Gamma^2 \rightarrow \Gamma^2 \frac{1 - e^{-2\beta}}{1 + 3e^{-2\beta}} \quad (5.14)$$

Figure 5.1. Bandwidths for soft mode of interacting free-rotor system. Solid lines: equation 5.13; dashed lines: harmonic approximation; dot-dash curves: renormalized harmonic approximation. Upper curves: $\Gamma=0.8$; middle curves: $\Gamma=0.6$; lower curves: $\Gamma=0.4$.

At high temperatures the renormalized theory works fairly well, and has the physical interpretation that thermally excited particles are effectively removed from the system. It is difficult to conclude very much from the low temperature results, due both to poor convergence and to the fact that the basis of the Green's functions is rather poor.

It may also be noted that higher excited states are coherently populated at low temperatures due to the interaction. However, this effect is sufficiently small to be unimportant in non-pathological regimes. This smallness is attributable to the large distance in energy between the $l=1$ and $l=2$ multiplets in free-rotor systems, and suggests that the singlet-triplet system is a good approximation in the low-temperature regime if the interaction is not too strong.

B. The Singlet-Triplet System

In this subchapter it is shown how the formalism of chapter IV may be applied to particles having singlet ground state and triplet excited state. Such systems have been treated previously by Pink (1968), by Cooper (1967), by Hsieh and Blume (1972), and others. None of these treatments considers the damping of the excitations, as is done in this work. One may begin by treating the single-particle states with two spin one-half operators as done by Pink and others, and from these construct the bare exciton operators of chapter IV, and derive the commutators needed for the random phase approximation. Departures from this approximation may be expressed in terms of a Dyson-like equation, which in lowest order leads to scattering of the excitations, and thence to damping and energy corrections. The results of a crude calculation for excitations of a one-dimensional system with nearest-neighbor dipolar interactions are given.

(i) Formalism

(a) Single-Site Operators

We associate with each site two spin one-half Heisenberg operators $\underline{S}_i$ and $\underline{T}_i$ having the commutation relations

$$[\underline{S}_i, \underline{T}_j] = 0$$

$$\begin{aligned}
 [\underline{S}_i, \underline{S}_j] &= 0 \text{ for } i \neq j \\
 [\underline{S}_{i\alpha}, \underline{S}_{i\beta}] &= i \underline{S}_{i\gamma} \text{ for } \alpha\beta\gamma \text{ cyclic}
 \end{aligned}
 \quad (5.15)$$

and the unperturbed hamiltonian

$$\begin{aligned}
 H_0 &= \Delta \sum_i \underline{S}_i \cdot \underline{T}_i \\
 &= \Delta \sum_i \left(\frac{1}{2} J_i^2 - 3/4 \right).
 \end{aligned}
 \quad (5.16)$$

For the moment we consider a single site, suppressing the site index. Define for each site an operator

$$\underline{P} = \frac{2}{\sqrt{3}} \underline{S} \times \underline{T}$$

so that

$$P_\alpha = \frac{2}{\sqrt{3}} (S_\beta T_\gamma - S_\gamma T_\beta) \quad (\alpha\beta\gamma \text{ cyclic}). \quad (5.17)$$

Denoting the ground state by $|0\rangle$ and defining the angular momentum $\underline{J} = \underline{S} + \underline{T}$ and the operator $\underline{L} = \underline{S} - \underline{T}$, it is straightforward to show that

$$P_\alpha |0\rangle = \frac{1}{\sqrt{3}} |\alpha\rangle \quad (\text{an excited state})$$

$$P^2 = \frac{1}{2} - 2/3 \underline{S} \cdot \underline{T}$$

$$P_\alpha P_\beta |0\rangle = 0 \quad (\alpha \neq \beta)$$

$$P_\alpha P_\beta |\beta\rangle = 1/3 |\alpha\rangle$$

$$[P_\alpha, P_\beta] = i/3 J_\gamma \quad (\alpha\beta\gamma \text{ cyclic})$$

$$[\underline{P}, H_0] = \frac{i\Delta}{\sqrt{3}} \underline{L}$$

$$[H_0, \underline{L}] = i\Delta\sqrt{3} \underline{P}$$

$$[J_\alpha, P_\beta] = iP_\gamma$$

$$[P_\alpha, L_\beta] = \begin{cases} -4i/\sqrt{3} (\underline{S} \cdot \underline{T} - S_\alpha T_\alpha) & \text{for } \alpha=\beta \\ 2i/\sqrt{3} (S_\alpha T_\beta + S_\beta T_\alpha) & \text{for } \alpha \neq \beta \end{cases} \quad (5.18)$$

etc.

We are now in a position to construct the bare exciton operators $c_\alpha, c_\alpha^\dagger$, corresponding to the "boson" operators of Cooper. We require that $[H_0, c_\alpha^\dagger] = \Delta c_\alpha^\dagger$, which is satisfied by

$$\begin{aligned} c_\alpha^\dagger &= \frac{1}{2}\sqrt{3} P_\alpha - \frac{i}{2} L_\alpha \\ c_\alpha &= \frac{1}{2}\sqrt{3} P_\alpha + \frac{i}{2} L_\alpha \end{aligned} \quad (5.19)$$

The commutation relations of these operators are

$$\begin{aligned} [c_\alpha, c_\alpha^\dagger] &= -\frac{1}{2}i\sqrt{3} [P_\alpha, L_\alpha] \\ &= -2 (S \cdot T - S_\alpha T_\alpha) \\ [c_\alpha, c_\beta] &= [c_\alpha^\dagger, c_\beta^\dagger] = 0 \\ [c_\alpha, c_\beta^\dagger] &= -c_\beta^\dagger c_\alpha. \end{aligned} \quad (5.20)$$

Note that these operators act as boson operators on the single particle ground state, suggesting a boson treatment valid at low temperatures, i.e., the treatment of Cooper.

It should be noted that the singlet-triplet problem may be equally well treated either in terms of $\underline{S}$ and $\underline{T}$ or in terms of the bare exciton operators. The bare exciton operators are a better choice in the disordered phase because they represent the normal mode operators in zeroth approximation. In the ordered phase this is not the case.

For comparison, we write the interaction of Hsieh and Blume (1972) in exciton operator notation. This interaction is given by

$$J_{ij} (a\underline{S}_i + b\underline{T}_i) \cdot (a\underline{S}_j + b\underline{T}_j) \\ = J_{ij} \left\{ \left(\frac{a+b}{2} \right)^2 \underline{A}_i \cdot \underline{A}_j + \left(\frac{a-b}{2} \right)^2 \underline{P}_i \cdot \underline{P}_j \right\} \quad (5.21)$$

where

$$\underline{P}_z |0,0\rangle = |1,0\rangle \\ \underline{P}_x |0,0\rangle = 2^{-1/2} \{ |1,1\rangle - |1,-1\rangle \} \\ \underline{P}_y |0,0\rangle = i 2^{-1/2} \{ |1,1\rangle + |1,-1\rangle \}$$

$\underline{A}$ is the usual angular momentum operator restricted to the triplet states and may be represented quadratically in the exciton operators, and we have followed Hsieh and Blume (1972) in denoting single particle states by their

total angular momentum and its z-component. For simplicity we restrict what follows to the case $a+b = 0$. However we note the suggestion of Smith (1972) that it is the $\underline{A} \cdot \underline{A}$ interaction which is primarily responsible for ferromagnetism in Pr_3Tl .

(b) Interacting Particles; Bogoliubov Transformation

We will consider an interaction of the form

$$\begin{aligned} H_i &= \frac{1}{2} \sum_{i,j} \sum_{\alpha\beta} P_{i\alpha} J_{\alpha\beta} P_{j\beta} \\ &= \frac{1}{6} \sum_{\underline{k}} \sum_{\alpha\beta} \{c_{\alpha}^{\dagger}(\underline{k}) + c_{\alpha}(-\underline{k})\} \\ &\quad \times J_{\alpha\beta}(\underline{k}) \{c_{\beta}^{\dagger}(-\underline{k}) + c_{\beta}(\underline{k})\} \end{aligned} \quad (5.22)$$

where

$$\begin{aligned} c_{\alpha}^{\dagger}(\underline{k}) &= N^{-1} \sum_i e^{i\underline{k} \cdot \underline{r}_i} c_{i\alpha}^{\dagger} \\ J_{\alpha\beta}(\underline{k}) &= \sum_j e^{i\underline{k} \cdot (\underline{r}_i - \underline{r}_j)} J_{\alpha\beta}(\underline{r}_i - \underline{r}_j). \end{aligned} \quad (5.23)$$

We may suppose $J_{\alpha\beta}(\underline{k})$ is diagonal for each $\underline{k}$. (The eigenvalue transformation will, in general, be $\underline{k}$ -dependent.) We wish to make a transformation to new operators

$$\begin{aligned} d_{\alpha}^{\dagger}(\underline{k}) &= \cosh \phi_{\underline{k}\alpha} c_{\alpha}^{\dagger}(\underline{k}) \\ &\quad + \sinh \phi_{\underline{k}\alpha} c_{\alpha}(-\underline{k}) \end{aligned} \quad (5.24a)$$

such that

$$[H, d_{\alpha}^{\dagger}(\underline{k})] = \epsilon_{\underline{k}\alpha}^0 d_{\alpha}^{\dagger}(\underline{k}). \quad (5.24b)$$

In terms of these operators

$$P_{\alpha}(\underline{k}) = 3^{-\frac{1}{2}} e^{-\phi \underline{k} \alpha} \{d_{\alpha}(-\underline{k}) + d_{\alpha}^{\dagger}(\underline{k})\}. \quad (5.25)$$

(For the moment we suppress the indices $\underline{k}$, α .) Equation (5.24b) now becomes

$$\begin{aligned} & \Delta \{ \cosh \phi c^{\dagger} - \sinh \phi c \} \\ & + \frac{J}{3} C_{\alpha} \{ \cosh \phi - \sinh \phi \} (c^{\dagger} + c) \\ & = \epsilon^0 (\cosh \phi c^{\dagger} + \sinh \phi c) \quad (5.26) \end{aligned}$$

where

$$C_{\alpha} = - \frac{2}{N} \sum_i (\underline{S}_i \cdot \underline{T}_{i\alpha} - S_{i\alpha} T_{i\alpha}) \quad (5.27)$$

and we have neglected terms involving other spectral branches which we will shortly resurrect. To achieve an RPA solution we replace C_{α} by $\langle C_{\alpha} \rangle$, giving

$$(\epsilon^0)^2 = \Delta^2 + \frac{2}{3} \Delta J \langle C_{\alpha} \rangle \quad (5.28a)$$

$$\phi = \frac{1}{2} \log (\epsilon^0 / \Delta). \quad (5.28b)$$

The transformed operators thus satisfy

$$\begin{aligned} [H - \epsilon^0 \underline{q} \gamma, d_Y^{\dagger}(\underline{q})] &= \frac{1}{6} J_{\gamma\gamma}(\underline{q}) e^{-\phi \underline{q} \gamma} \\ &\times \{ \{ c_Y^{\dagger}(\underline{q}) + c_Y(-\underline{q}) \}, \{ C_Y - \langle C_Y \rangle \} \}_+ \\ &+ \sum_{\underline{k} \alpha \beta} \frac{1}{6} J_{\alpha\beta}(-\underline{k}) \{ \{ c_{\alpha}^{\dagger}(\underline{k}) + c_{\alpha}(-\underline{k}) \} \\ &\times \{ \sinh \phi \underline{q} \gamma [c_{\beta}^{\dagger}(-\underline{k}), c_Y(-\underline{q})] \} \} \end{aligned}$$

$$\begin{aligned}
 & + \cosh \phi_{\underline{q}\gamma} [c_{\beta}(\underline{k}), c_{\gamma}^{\dagger}(\underline{q})] \\
 & + \{ \sinh \phi_{\underline{q}\gamma} [c_{\alpha}^{\dagger}(\underline{k}), c_{\gamma}(-\underline{q})] \\
 & - \cosh \phi_{\underline{q}\gamma} [c_{\gamma}^{\dagger}(\underline{q}), c_{\alpha}(-\underline{k})] \} \\
 & \times \{ c_{\beta}^{\dagger}(-\underline{k}) + c_{\beta}(\underline{k}) \}. \quad (5.29)
 \end{aligned}$$

The prime on the sum indicates the omission of commutators between operators with the same polarization index. We define the right-hand side of (5.29) as $R_{\underline{q}\gamma}$. The commutators appearing in $R_{\underline{q}\gamma}$ take the form of a hard-core interaction

$$[c_{\beta}^{\dagger}(-\underline{k}), c_{\gamma}(-\underline{q})] = \frac{1}{N} \sum_{\underline{p}} c_{\beta}^{\dagger}(-\underline{k}-\underline{p}) c_{\gamma}(-\underline{q}-\underline{p}) \quad (5.30)$$

leading to

$$\begin{aligned}
 R_{\underline{q}\gamma} = & \frac{1}{6N} \sum_{\underline{k}\underline{p}} \sum_{\alpha\beta} J_{\alpha\beta}(\underline{k}) e^{-\phi_{\underline{k}\alpha}} \{ (d_{\alpha}^{\dagger}(\underline{k}) + d_{\alpha}(-\underline{k})) \cdot \\
 & (\sinh \phi_{\underline{q}\gamma} \{ \cosh \phi_{\underline{k}+\underline{p}\beta} d_{\beta}^{\dagger}(-\underline{k}-\underline{p}) \\
 & - \sinh \phi_{\underline{k}+\underline{p}\beta} d_{\beta}(\underline{k}+\underline{p}) \} \\
 & \times \{ \cosh \phi_{\underline{q}+\underline{p}\gamma} d_{\gamma}(-\underline{q}-\underline{p}) \\
 & - \sinh \phi_{\underline{q}+\underline{p}\gamma} d_{\gamma}^{\dagger}(\underline{q}+\underline{p}) \} \\
 & - \cosh \phi_{\underline{q}\gamma} \{ \cosh \phi_{\underline{q}+\underline{p}\gamma} d_{\gamma}^{\dagger}(\underline{q}+\underline{p}) \\
 & - \sinh \phi_{-\underline{q}-\underline{p}\gamma} d_{\gamma}(-\underline{q}-\underline{p}) \}
 \end{aligned}$$

$$\begin{aligned} & \times \{ \cosh \phi_{\underline{k}+\underline{p}\beta} d_{\beta}(\underline{k}+\underline{p}) \\ & - \sinh \phi_{\underline{k}+\underline{p}\beta} d_{\beta}^{\dagger}(-\underline{k}-\underline{p}) \} \} \}_{+} \end{aligned} \quad (5.31)$$

if we assume $J_{\alpha\beta}(\underline{k}) = J_{\alpha\beta}(-\underline{k})$ and neglect $(C_{\alpha} - \langle C_{\alpha} \rangle)$.

(c) Green's Functions; Dyson Equation

We define retarded and advanced Green's functions by

$$\begin{aligned} G_{\alpha\beta}^R(\underline{k}_1, \underline{k}_2, t) &= -i \langle e^{iHt} d_{\alpha}(\underline{k}_1) e^{-iHt} \\ &\quad \times d_{\beta}^{\dagger}(\underline{k}_2) \rangle \theta(t) \\ G_{\alpha\beta}^A(\underline{k}_1, \underline{k}_2, t) &= -i \langle e^{iHt} d_{\alpha}^{\dagger}(\underline{k}_1) e^{-iHt} \\ &\quad \times d_{\beta}(\underline{k}_2) \rangle \theta(t) \end{aligned} \quad (5.32)$$

In what follows we restrict ourselves to $\alpha=\beta$, $k_1=k_2$. (We suppose $J_{\alpha\beta}$ to have been diagonalized as mentioned earlier. Off-diagonal Green's functions would be important in higher approximations than we shall consider in this paper.) We have

$$G_{\alpha}^R(\underline{k}, 0^+) - G_{\alpha}^A(\underline{k}, 0^+) = -i \langle C_{\alpha} \rangle. \quad (5.33)$$

In addition we may write

$$G_{\alpha}^R(\underline{k}, 0^+) = e^{\beta \epsilon_{\underline{k}\alpha}} G_{\alpha}^A(\underline{k}, 0^+)$$

where $\epsilon_{\underline{k}\alpha}$ is equal to $\epsilon_{\underline{k}\alpha}^0$ plus higher order terms.

To derive a Dyson-like equation, we write (see Appendix B)

$$\begin{aligned}
 i \frac{\partial}{\partial t} G_{\alpha}^R(\underline{k}, t) &= i \delta(t) G_{\alpha}^R(\underline{k}, 0^+) \\
 &+ i \langle e^{iHt} [H, d_{\alpha}(\underline{k})] e^{-iHt} d_{\alpha}^{\dagger}(\underline{k}) \rangle \theta(t) \\
 &= \frac{\delta(t) \langle C_{\alpha} \rangle}{1 - e^{-\beta \epsilon_{\underline{k}\alpha}}} + \epsilon_{\underline{k}\alpha}^0 G_{\alpha}^R(\underline{k}, t) \quad (5.34) \\
 &- i \langle e^{iHt} R_{\underline{k}\alpha}^{\dagger} e^{-iHt} d_{\alpha}^{\dagger}(\underline{k}) \rangle \theta(t)
 \end{aligned}$$

or, fourier transforming

$$\begin{aligned}
 (\omega - \epsilon_{\underline{k}\alpha}^0) G_{\alpha}^R(\underline{k}, \omega) &= \frac{\langle C_{\alpha} \rangle}{1 - e^{-\beta \epsilon_{\underline{k}\alpha}}} - i \theta(t) \\
 &\times \langle e^{iHt} R_{\underline{k}\alpha}^{\dagger} e^{-iHt} d_{\alpha}^{\dagger}(\underline{k}) \rangle_{\omega} \quad (5.35)
 \end{aligned}$$

We may further treat the last term by writing

$$\begin{aligned}
 i \frac{\partial}{\partial t} \{ \theta(t) \langle R_{\underline{k}\alpha}^{\dagger} e^{-iHt} d_{\underline{k}\alpha}^{\dagger} e^{iHt} \rangle \} &= \quad (5.36) \\
 i \delta(t) \langle R_{\underline{k}\alpha}^{\dagger} d_{\underline{k}\alpha}^{\dagger} \rangle + \theta(t) \langle R_{\underline{k}\alpha}^{\dagger} \\
 &\times e^{-iHt} [H, d_{\underline{k}\alpha}^{\dagger}] e^{iHt} \rangle.
 \end{aligned}$$

Taking as vanishing the first term on the right, we have

$$\begin{aligned}
 (\omega - \epsilon_{\underline{k}\alpha}^0) \{ \langle R_{\underline{k}\alpha}^{\dagger} e^{-iHt} d_{\underline{k}\alpha}^{\dagger} e^{iHt} \rangle \theta(t) \}_{\omega} &= \\
 \langle e^{iHt} R_{\underline{k}\alpha}^{\dagger} e^{-iHt} R_{\underline{k}\alpha} \theta(t) \rangle_{\omega} \quad (5.37)
 \end{aligned}$$

Equation 5.35 then becomes

$$(\omega - \epsilon^0_{\underline{k}\alpha}) G^R_{\alpha}(\underline{k}, \omega) = \frac{\langle C_{\alpha} \rangle}{1 - e^{-\beta \epsilon_{\underline{k}\alpha}}} \quad (5.38)$$

$$- \frac{i}{\omega - \epsilon^0_{\underline{k}\alpha}} \{ \langle e^{iHt} R_{\underline{k}\alpha}^{\dagger} e^{-iHt} R_{\underline{k}\alpha} \rangle \theta(t) \}_{\omega}$$

which in the usual way can be written

$$\frac{\langle C_{\alpha} \rangle}{1 - e^{-\beta \epsilon_{\underline{k}\alpha}}} \{ G^R_{\alpha}(\underline{k}, \omega) \}^{-1} = \{ \omega - \epsilon^0_{\underline{k}\alpha} - \Sigma_{\underline{k}\alpha}(\omega) \} \quad (5.39)$$

where

$$\Sigma_{\underline{k}\alpha}(\omega) = (\omega - \epsilon^0_{\underline{k}\alpha})^{-1} \{ -i \langle e^{iHt} R_{\underline{k}\alpha}^{\dagger} e^{-iHt} R_{\underline{k}\alpha} \rangle \theta(t) \}_{\omega}$$

$$\times \{ G^R_{\alpha}(\underline{k}, \omega) \}^{-1}. \quad (5.40)$$

(ii) Illustrative Calculation

In this section we apply the preceding formalism to a one-dimensional dielectric having dipolar interactions between nearest neighbors. Thus (with unit lattice constant)

$$J_{xx}(q) = J_{yy}(q) = 2 J_0 \cos q$$

$$J_{zz}(q) = -4 J_0 \cos q$$

$$J_{xy}(q) = J_{yz}(q) = \dots = 0 \quad (5.41)$$

for any q . The spectrum will have a longitudinal mode which softens to zero at $q = 0$ for a sufficiently strong

interaction, and two transverse modes with minima at $q = \pi$. We restrict this calculation to the framework of perturbation theory in the parameter J_0/Δ , and henceforth set $\Delta = 1$ and measure T in units of Δ/k_B .

The value of $\langle C_\alpha \rangle$ may be reasonably well calculated by solving the two particle problem for $\langle C_\alpha \rangle^{(2)}$ and putting $\{\langle C_\alpha \rangle - \langle C_\alpha \rangle^{(1)}\}$ equal to $2\{\langle C_\alpha \rangle^{(2)} - \langle C_\alpha \rangle^{(1)}\}$. (This amounts to saying that each bond contributes independently to $\{\langle C_\alpha \rangle - \langle C_\alpha \rangle^{(1)}\}$.) We then use this value to compute the approximate Green's functions

$$G_\alpha^R(k, \omega) = \frac{\langle C_\alpha \rangle}{1 - e^{-\beta \epsilon_{k\alpha}}} \{\omega - \epsilon_{k\alpha} + i\delta\}^{-1}. \quad (5.42)$$

The largest term in $\Sigma_{q\gamma}$ is now

$$\begin{aligned} & \frac{\langle C_\alpha \rangle}{1 - e^{-\beta \epsilon_{q\gamma}}} (6N)^{-2} \sum_{kp\alpha} \sum_{k'p'\alpha'} J_{\alpha\alpha}(k) J_{\alpha'\alpha'}(k') \\ & \times \cosh^2 \phi_{q\gamma} \cosh \phi_{q+p\gamma} \cosh \phi_{k+p\alpha} \cosh \phi_{q+p\gamma} \\ & \times \cosh \phi_{k'+p'\alpha'} \times (-i) \langle \theta(t) e^{iHt} \{ \{ d_\alpha(k) + d_\alpha^\dagger(-k) \}, \\ & d_\alpha^\dagger(k+p) d_\gamma(q+p) \}_+ e^{-iHt} \{ \{ d_{\alpha'}^\dagger(k') + d_{\alpha'}(-k') \}, \\ & d_\gamma^\dagger(q+p') d_\alpha(k'+p') \}_+ \rangle_w. \end{aligned} \quad (5.44)$$

The last factor may be decoupled to give

Figure 5.2. Diagrammatic representation of the main dynamic correction to $G_\gamma(q)$. The wavy line represents a thermal excitation.

$$\begin{aligned}
 & -\pi^{-2} \int d\omega_1 \int d\omega_2 G_{\alpha}^R(k, \omega_1) G_Y^R(q+p, \omega_2) \\
 & \quad \times G_{\alpha}^A(k+p, \omega-\omega_1-\omega_2) \delta_{\alpha\alpha'} \delta(k-k') \delta(p-p') \\
 & \quad + \text{smaller terms.} \qquad (5.44)
 \end{aligned}$$

This term corresponds to scattering from a thermally excited particle, and may be diagrammatically represented as figure 5.2. This and other terms may be evaluated (using the approximate normal mode Green's functions) as described in Appendix A. The term we have represented is proportional to J^2 and vanishes exponentially at low temperatures. The expansion of Σ includes as well terms finite at low temperatures but proportional to higher powers of J .

We have performed the calculation for the longitudinal mode of the one-dimensional dielectric previously described. The integrals were done using Simpson's Rule on the Brillouin zone $-\pi < k < \pi$ divided into 40 subintervals, with the help of the Cornell University IBM 360/65. All terms were retained involving single scattering from a thermal particle. The results are shown in figures 5.3-5.4. This constitutes a rather crude calculation so that, while we believe the qualitative features to be correct, the numerical values should not be taken too seriously.

Figure 5.3. Energy (solid line) and damping ($\Gamma = \text{Im}\Sigma$; dot-dash line) for various temperatures and $J_0 = 0.4$. The dashed line is the approximate energy of equation 5.28a.

Figure 5.4. Same as figure 5.3, but for various values of J_0 at $k_B T/\Delta = 0.5$.

(iv) Discussion and Conclusions

One feature which is readily understood is that the soft mode is somewhat depressed and relatively highly damped by the scattering. These excitations scatter strongly with other low-energy excitations, and particularly with excitations in low-energy portions of other spectral branches. The intermediate states of such scatterings will be of equal or higher energy. The lowering of the group velocity and small damping near $q=\frac{1}{2}\pi$ is probably peculiar to this model, and related to the large group velocity in this region.

These dynamical effects will be particularly large in systems which interact strongly enough to exhibit phase transitions. Such a system can be disordered only if there are enough thermal excitations to prevent ordering, and furthermore scattering matrix elements will be large. Our results suggest the possibility that mode softening effects in some systems may be concentrated in a small region near $q=0$. For weak interactions the energies of small q modes are due to thermal population at finite q , but this relationship is reversed when the interaction is strong. One must be wary of any statements concerning finite wavevector behavior in the regime where it is governed primarily by the poorly understood soft modes.

The presence of higher single-particle levels will

drastically alter the scattering effects treated here. In that case, two excitations are no longer excluded from occupying the same site, but can combine to form a (virtual) heavy excitation in a higher band. This effect should tend to counteract the mode-softening effect for temperatures $T < \Delta$.

We conclude that the mean-field-like theories published thus far for excitations in the disordered regime of singlet-triplet systems cannot be expected to be very accurate unless the interaction is weak. There is room for a good deal more work along these lines.

C. Hydrogen-Bonded Ferroelectrics

The method of chapter IV may be applied to a model hydrogen-bonded ferroelectric. We present here a primitive version of a common model for KDP. (A recent reference is Stamenkovic and Novakovic (1970).)

Consider the hamiltonian

$$\begin{aligned}
 H = \epsilon_H \sum_i S^z(i) + \epsilon_{op} \sum_{\underline{k}} a^\dagger(\underline{k}) a(\underline{k}) \\
 + i \sum_{\underline{k}} J(\underline{k}) \{S^+(\underline{k}) + S^-(-\underline{k})\} \\
 \times \{a(\underline{k}) - a^\dagger(-\underline{k})\} \quad (5.45)
 \end{aligned}$$

where $S(i)$ is the pseudospin operator for a hydrogen bond at $\underline{r}_i$, $a(\underline{k})$ is an optical phonon operator, $S^+(\underline{k}) = N^{-1/2} \sum_i S^+(i) \exp\{i\underline{k} \cdot \underline{r}_i\}$, $S^-(\underline{k}) = \{S^+(\underline{k})\}^\dagger$ and $J(\underline{k})$ represents a coupling between the phonon and tunnelling modes.

Defining approximate normal mode operators by

$$\begin{aligned}
 d^\dagger(\underline{k}) = \alpha_1 S^+(\underline{k}) + \alpha_2 S^-(-\underline{k}) \\
 + \alpha_3 a^\dagger(\underline{k}) + \alpha_4 a(-\underline{k}) \quad (5.46)
 \end{aligned}$$

gives

$$\begin{aligned}
 [H, d^\dagger(\underline{k})] &= \alpha_1 \epsilon_H S^+(\underline{k}) - \alpha_2 \epsilon_H S^-(\underline{k}) \\
 &+ \alpha_3 \epsilon_{op} a^\dagger(\underline{k}) - \alpha_4 \epsilon_{op} a(-\underline{k}) \\
 &+ i \sum_{\underline{q}} J(\underline{q}) \{ (\alpha_1 [S^-(\underline{q}), S^+(\underline{k})] \\
 &\quad + \alpha_2 [S^+(\underline{q}), S^-(\underline{k})]) \\
 &\quad \times (a(\underline{q}) - a^\dagger(-\underline{q})) \\
 &\quad + (\alpha_3 + \alpha_4) \delta(\underline{k} - \underline{q}) (S^+(\underline{k}) + S^-(\underline{k})) \} \\
 &= (\alpha_1 \epsilon_H + i(\alpha_3 + \alpha_4) J(\underline{k})) S^+(\underline{k}) \\
 &\quad - (\alpha_2 \epsilon_H - i(\alpha_3 + \alpha_4) J(\underline{k})) S^-(\underline{k}) \\
 &\quad - (\alpha_4 \epsilon_{op} - i(\alpha_2 - \alpha_1) J(\underline{k}) \langle S^z \rangle) a(-\underline{k}) \\
 &\quad + (\alpha_3 \epsilon_{op} + i(\alpha_1 - \alpha_2) J(\underline{k}) \langle S^z \rangle) a^\dagger(\underline{k}) \\
 &\quad + i \sum_{\underline{q} \neq -\underline{k}} J(\underline{q}) \{ \alpha_1 [S^-(\underline{q}), S^+(\underline{k})] \\
 &\quad + \alpha_2 [S^+(\underline{q}), S^-(\underline{k})] \} \\
 &\quad \times (a(\underline{q}) - a^\dagger(-\underline{q})). \quad (5.47)
 \end{aligned}$$

Here $S^z = \frac{1}{N} \sum_i S^z(i)$, the first four terms give the quasi-harmonic normal modes, and the last term represents interactions among quasi-particles. The energies of the normal modes are given by the eigenvalues $E(\underline{k})$ of

$$\underline{M} = \begin{pmatrix} \epsilon_H & 0 & iJ(\underline{k}) & iJ(\underline{k}) \\ 0 & -\epsilon_H & iJ(\underline{k}) & iJ(\underline{k}) \\ iJ(\underline{k})\langle S^z \rangle & -iJ(\underline{k})\langle S^z \rangle & \epsilon_{op} & 0 \\ -iJ(\underline{k})\langle S^z \rangle & iJ(\underline{k})\langle S^z \rangle & 0 & -\epsilon_{op} \end{pmatrix} \quad (5.48)$$

which are

$$E(\underline{k})^2 = \frac{1}{2}(\epsilon_H + \epsilon_{op})^2 \pm \left\{ \frac{1}{4}(\epsilon_H^2 - \epsilon_{op}^2)^2 - 4J(\underline{k})^2 \langle S^z \rangle \epsilon_H \epsilon_{op} \right\}^{\frac{1}{2}} \quad (5.49)$$

The temperature-dependent parameter $\langle S^z \rangle$ may be found self-consistently using

$$\langle S^z \rangle = \frac{1}{N} \sum_{\underline{k}} [S^+(\underline{k}), S^-(\underline{k})]. \quad (5.50)$$

To do this, express S^+ , S^- in terms of the d 's using the inverse eigenvalue transformation. The commutators $[d, d^\dagger]$ will have a very complicated dependence on $\langle S^z \rangle$.

One may then proceed to find the damping and further corrections to the energy using the Dyson-like equation analogous to 5.39-5.40. As hydrogen-bonded ferroelectrics exhibit phase transitions at fairly high temperatures, these corrections may be considerable. In addition, cubic and quartic anharmonicities in the phonon spectrum may be important.

VI. Calculations on Model One-Dimensional Classical Systems

Classical systems are simpler than quantum systems because the partition function

$$Z = \int d^N \underline{p} \int d^N \underline{q} \exp\{-\beta H(\underline{p}, \underline{q})\} \quad (6.1)$$

may be factored into configurational and dynamic parts. The static properties may then be computed independently of dynamic effects, and these results used in treating the dynamics.'

A system may be considered classical if the temperature is large compared with the energy level spacing, or, equivalently, if the thermal motion is larger than the quantum zero-point motion. However, such a system is not necessarily lacking in quantum effects. In particular, the evenly spaced optical absorption bands characteristic of free rotor dipoles are readily observable at fairly high temperatures. While it is intriguing to speculate about what happens to these bands as the rotation becomes hindered, for the purposes of this chapter we suppose our resolution sufficiently coarse that quantum effects are unobservable.

In the first subchapter we show how Fisher's solution

(Fisher, 1964) to the classical Heisenberg model may be extended to a more general one-dimensional classical system. We apply this method to systems having dipolar, quadrupolar, or mixed interactions, thus solving the problem considered by Pauling, Fowler, Frenkel and others. In the second subchapter we discuss two methods for treating the dynamics of such systems: first, a method analogous to that used for hcp hydrogen (chapter VII of this thesis), and second, a method we have used in a previous publication for systems in which viscosity is important. An improved computational method for the viscous interacting case is presented.

A. Orientational Order in One-Dimensional Free-Rotor Systems with Multipolar Interactions

Fisher's solution to the classical Heisenberg model rests on the fact that $N+1$ Heisenberg particles may be regarded as a system of N independent bonds connecting the particles, giving

$$H = \sum_{i=1}^N h(\underline{\Omega}_{i+1} - \underline{\Omega}_i) \quad (6.2)$$

$$Z = 4\pi \{ \int d\underline{\Omega} e^{-\beta h(\underline{\Omega})} \}^N. \quad (6.3)$$

For multipolar interactions, however, it is necessary to quantize along the interparticle axis, giving

$$H = \sum_{i=1}^N h(u_i, u_{i+1}, \alpha_i) \quad (6.4)$$

where α_i is the azimuthal angle difference $\phi_{i+1} - \phi_i$, and $u_i = \cos \theta_i$. Let us consider the joint probability density $P(u_i, u_{i+1})$, which satisfies

$$\begin{aligned} Z(N+1) P(u_i, u_{i+1}) &= 2\pi \int d\underline{\Omega}_1 \cdots \int d\underline{\Omega}_{i-1} \int d\alpha_1 \\ &\quad \times \int d\underline{\Omega}_{i+2} \cdots \int d\underline{\Omega}_{N+1} e^{-\beta H} \quad (6.5) \\ &= 2\pi \int d\alpha_i e^{-\beta h_i} \{ Z(i) p_i^{(end)}(u_i) \} \\ &\quad \times \{ Z(N+1-i) p_{N+1-i}^{(end)}(u_{i+1}) \} \end{aligned}$$

where $Z(m)$ is the partition function for a chain of m particles, and $p_m^{(end)}(u)$ is the probability density for a

particle at the end of a chain of length m . (If $h(u_1, u_2, \alpha) \neq h(u_2, u_1, \alpha)$ it is necessary to consider whether the particle is on the right or left end.) We then have

$$P(u_i, u_{i+1}) = C(\beta) \int d\alpha_1 p^{(end)}(u_i) p^{(end)}(u_{i+1}) \times \exp\{-\beta h(u_i, u_{i+1}, \alpha_1)\} \quad (6.6)$$

where $C(\beta)$ is a constant and $N \gg 1$, $i \gg 1$, $N-i \gg 1$, and

$$P(u_1, u_2) = C'(\beta) \int d\alpha_1 p^{(end)}(u_2) e^{-\beta h(u_1, u_2, \alpha_1)},$$

so

$$p^{(end)}(u) = C'(\beta) \int du' \int d\alpha p^{(end)}(u') e^{-\beta h(u, u', \alpha)}. \quad (6.7)$$

Equation 6.7 is a Fredholm equation of the second kind for $p^{(end)}$ which may be solved numerically. Knowing $p^{(end)}$ allows the use of 6.6 to find the joint probability for two interior particles, and thence various correlation functions and other properties. The method may be generalized to find joint probabilities for further neighbors.

(i) Pure Dipole Interaction

The dipole interaction is given by

$$h(u_1, u_2, \alpha) = -V \{ 2u_1 u_2 - \{(1-u_1^2)(1-u_2^2)\}^{1/2} \cos \alpha \} \quad (6.8)$$

where $V = p^2/2a^3$. At low temperatures all dipoles align

parallel (or antiparallel) to the quantization axis. The low temperature orientational specific heat per particle approaches that of a two-dimensional harmonic oscillator. (There is a constant dynamic specific heat of k_B per particle.) The specific heat maximum occurs at $k_B T = V/2$. Various quantities of interest are plotted (as a function of inverse temperature) in figure 6.1.

(ii) Pure Quadrupole Interaction

The interaction hamiltonian for a pair of cylindrically symmetric quadrupoles is

$$h = \left(\frac{20\pi}{9} \right) (70\pi)^{\frac{1}{2}} \sum_{mn} C(224;mn) \times \Gamma Y_4^{m+n}(\underline{\Omega}_{12}) Y_2^m(\underline{\Omega}_1) Y_2^n(\underline{\Omega}_2) \quad (6.9)$$

with $\underline{\Omega}_{12}$ the direction of the interparticle vector and $\Gamma = 6Q^2/25R^5$. For the one-dimensional case this reduces to

$$\begin{aligned} h(u_1, u_2, \alpha) &= A \cos 2\alpha + B \cos \alpha + C \\ A &= .995 (1-u_1^2)(1-u_2^2) \\ B &= -15.9 u_1 u_2 \{ (1-u_1^2)(1-u_2^2) \}^{\frac{1}{2}} \\ C &= 5.96 (3u_1^2-1)(3u_2^2-1). \end{aligned} \quad (6.10)$$

The C-term is most important, so that the low temperature configuration is as shown in figure 6.2b. To determine the low-temperature specific heat, note that the "vertical"

Figure 6.1. Orientational specific heat (solid curve, in units of k_B per particle); $\langle 3u^2 - 1 \rangle$ (dashed curve); nearest-neighbor correlation function $\langle u_i \cdot u_{i+1} \rangle$ (upper dot-dash curve) and second neighbor correlation function $\langle u_{i-1} \cdot u_{i+1} \rangle$ (lower dot-dash curve) for pure dipole interaction.

Figure 6.2. Low temperature arrangement for (a) pure dipole interaction; (b) pure quadrupole interaction; (c) mixed interaction.

molecules act as one-dimensional harmonic oscillators, while the "horizontal" particles are two-dimensional oscillators, giving an average configurational specific heat per particle of $.75k_B$. (For three dimensions all particles would be two-dimensional oscillators, giving $1.0 k_B$.) Various properties are shown in figure 6.3.

(iii) Mixed Interaction

Physical particles having dipole moments generally have non-negligible quadrupole moments as well, so that

$$h(u_1, u_2, \alpha) = h^{\text{dipole}} + h^{\text{quadrupole}} + h^{\text{d-q}} \\ h^{\text{d-q}} = G (u_2 - u_1) (2u_1 u_2 - s_1 s_2 \cos \alpha) \quad (6.11)$$

where $s_1 = (1 - u_1^2)^{1/2}$, and

$$G = 1.53 (VF)^{1/2} (\text{sgn } Q). \quad (6.12)$$

If the quadrupole interaction is not extremely weak, i.e., if $\Gamma \geq .05V$, the low temperature orientation (figure 6.2c) will show quadrupole effects. Furthermore, the dipole-quadrupole hamiltonian causes an effective antiferroelectric interaction between second neighbors. The argument suggested by figure 6.4 leads to

$$\langle u_{i-1} \cdot u_{i+1} \rangle = - \tanh^2 2G \langle u_1^2 \rangle \quad (6.13)$$

if we neglect h^{dipole} , and if (i-1) and (i+1) are horizontal particles. Some correlation functions for mixed systems are shown in figure 6.5.

Figure 6.3. Orientational specific heat (solid curve, in units of k_B per particle), $\langle 3u^2 - 1 \rangle$ (dashed curve), and $\langle (3u_i^2 - 1)(1 - 3u_{i+1}^2) \rangle$ (dot-dash curve) for pure quadrupole interaction.

$i-1$	i	$i+1$	$\langle h^{d-q} \rangle$
0
$4G u_i^2$
$-4G u_i^2$
0

Figure 6.4. Anti-ferroelectric coupling between second neighbors induced by dipole-quadrupole interaction.

Figure 6.5. Solid curves: nearest neighbor correlation function $\langle u_i \cdot u_{i+1} \rangle$ for $V=2.0$ and various values of Γ . Dashed curve: Second neighbor correlation function $\langle u_{i-1} \cdot u_{i+1} \rangle$ for $V=2.0$ and $\Gamma=0.25$.

(iv) Phase Transitions due to Long-Range Forces

By considering their free energy $F = E - TS$ it may be readily shown that one-dimensional systems will exhibit phase transitions in the presence of an interaction $J_{ij} \propto |i-j|^{-x}$ for $1 < x < 2$. We may consider this case by mean field theory, adding to the nearest neighbor interaction a long-range dipolar hamiltonian

$$H^{LR} = \sum_{i=1}^N \sum_{j=i+2}^N \frac{2 u_i u_j}{|i-j|^x} . \quad (6.14)$$

Ordinary mean field theory consists of solving the equation

$$P = P_0(E + 4\zeta(x)P; T), \quad (6.15)$$

where $P_0(E; T)$ is $\langle u_i \rangle$ computed at temperature T for the noninteracting case, and $\zeta(x)$ is the Riemann zeta function. A phase transition occurs when 6.15 has a non-zero solution for P at $E = 0$. A better mean field theory is given by

$$P = P_1(E + 4(\zeta(x)-1)P; T) \quad (6.16)$$

where P_1 is calculated using the nearest-neighbor pair hamiltonian

$$h(E) = h^{(0)}(u_1, u_2, \alpha) - \frac{1}{2}E(u_1 + u_2). \quad (6.17)$$

This gives critical points for the pure dipole case as shown in figure 6.6. The portion of the figure for $x > 2$

Figure 6.6. Phase transition line β_c vs. exponent x in mean field theory for pure dipole system using equations 6.15 (dashed line) and 6.16 (solid line).

Figure 6.7. Condition for a first order phase transition.
 The solid line is $P=P_1(E, T_c)$; the dashed line is
 $E=4[\zeta(x)-1]P$.

is meaningless, as no true phase transitions occur.

Equation 6.16 gives a first order transition if $\frac{\partial^3}{\partial E^3} P_1(E;T) > 0$ for $E=0$, as shown in figure 6.7. This derivative is always negative for the pure dipole case, but may be positive in some regime for the mixed case.

B. Dynamics of Classical Systems

When classical multipolar systems are sufficiently well ordered they exhibit nearly harmonic normal modes known as librions. We shall focus on the opposite regime, in which the multipoles are largely disordered and no harmonic modes exist. The dynamics may be described by the set of functions

$$F(\ell m; \underline{i}, \underline{j}; t) = \frac{\langle Y_{\ell}^m(\underline{i}, t)^* \cdot Y_{\ell}^m(\underline{j}, 0) \rangle}{\langle |Y_{\ell}^m(\underline{i}, 0)|^2 \rangle} \quad (6.18)$$

or the fourier transform

$$F(\ell m; \underline{k}; \omega) = \frac{\langle |Y_{\ell}^m(\underline{k}, \omega)|^2 \rangle}{\int_{-\infty}^{\infty} d\omega \langle |Y_{\ell}^m(\underline{k}, \omega)|^2 \rangle} \quad (6.19)$$

The even moments of F may be found using the Poisson bracket relation

$$\frac{du}{dt} = [u, H] + \frac{\partial u}{\partial t} \quad (6.20)$$

and the hamiltonian

$$H = \sum_i \left[\frac{P_{\theta_i}^2}{2I} + \frac{P_{\phi_i}^2}{2I \sin^2 \theta_i} \right] + V. \quad (6.21)$$

For example, $\langle \omega^2 Y_{\ell}^{m*}(\underline{i}, \omega) Y_{\ell}^m(\underline{j}, \omega) \rangle$ is given by

$$\frac{1}{I} \left\langle \left[P_{\theta_i} \frac{\partial Y_{\ell}^{m*}(\underline{i})}{\partial \theta_i} + \frac{P_{\phi_i}}{\sin^2 \theta_i} \frac{\partial Y_{\ell}^{m*}(\underline{i})}{\partial \phi} \right] \times \left[P_{\theta_j} \frac{\partial Y_{\ell}^m(\underline{j})}{\partial \theta_j} + \frac{P_{\phi_j}}{\sin^2 \theta_j} \frac{\partial Y_{\ell}^m(\underline{j})}{\partial \phi} \right] \right\rangle. \quad (6.22)$$

This idea is applied to the quantum case in chapter VII, but I have not yet applied this formalism to a classical multipolar system.

If viscous effects are important it is easier to calculate directly the susceptibility to an external field, $\chi(\omega)$. In (Mandell, 1972) it was shown that, for a system with one rotational degree of freedom per particle,

$$\frac{\chi}{N} = (2\pi IT)^{N/2} \int d^N \underline{p} f(\underline{p}) \exp\{-\underline{p} \cdot \underline{p} / 2IT\} \quad (6.23)$$

where f can be expanded in a high-temperature series

$$f = f_0(x_0) + 2(v/2T)f_1(x_0, x_1) + \dots, \quad (6.24)$$

and each f_i satisfies a linear inhomogeneous equation involving the previous f 's. In (Mandell, 1972) f_1 was found using a relaxation method which proved moderately unsatisfactory. An improved method can be found by noting the form of 6.23. If f_1 is decomposed in Hermite polynomials according to

$$f_1 \exp\{\frac{1}{2} \sum_j x_j^2\} = \sum_{\{n\}} A_{\{n\}}^{(i)} \prod_j H_{n_j}(x_j) \quad (6.25)$$

then, since

$$\int_{-\infty}^{\infty} e^{-x^2} H_k(x) H_l(x) dx = \delta_{kl} 2^k k! \pi^{1/2} \quad (6.26)$$

the susceptibility to this order depends only on $A_{\{0\}}^{(1)}$.

The equation for f_i may be rewritten as a matrix equation for the coefficients A , and, in practice, may be truncated to a matrix of reasonable size to get good values of $A_{\{0\}}$. Using this method, susceptibilities have been calculated to second order in $(v/2T)$ (Selgrade, 1972), and for off-diagonal viscosity (viscous force proportional to the momentum of neighboring particles)(M. J. Mandell, unpublished). No interesting results were found.

VII. On the Transport of Angular Momentum in Solid Hydrogen

Solid H_2 , as is well known, may be treated to an excellent approximation as an array of freely rotating molecules. In the $J=1$ (orthohydrogen or paradeuterium) species, however, quadrupolar interactions (Harris, 1970a, Lee and Raich, 1972) between members of the triply-degenerate ground state cause a phase transition at $2.8^\circ K$ ($4^\circ K$ for paradeuterium) from a high-temperature hcp phase to an fcc phase exhibiting well-defined angular momentum excitations (librons) which have been studied extensively. (Berlinsky and Coll, 1972 and references therein.)

In this work we are concerned with the high-temperature precursors of the librons, which for brevity we call paralibrons. These excitations are seen in Raman scattering (Silvera et al, 1972) and neutron scattering (Stein et al, 1972) and have important effects in NMR relaxation (Harris, 1970b; Hama and Nakamura, 1970; Amstutz et al., 1969; Weinhaus et al, 1971). The second and fourth moments of the spectral function for angular momentum fluctuations of a single particle have been previously calculated (Harris, 1970b; Hama and Nakamura, 1970); this spectral function is the reciprocal-space average of paralibron spectral functions.

Let us quantize along the c-axis of the hcp lattice and consider excitations consisting of one unit of angular momentum propagating along this axis. The creation operator for such an excitation is

$$c^{\dagger}(q) = \sum_{i=1}^2 \alpha_i(q\hat{e}_z) J_i^{\dagger}(q\hat{e}_z) \quad (7.1)$$

where $0 \leq |q| \leq \sqrt{3/8}\pi$,

$$J_i^{\dagger}(q) = N^{-1/2} \sum_{\underline{r}} J_i^{\dagger}(\underline{r}) e^{iq \cdot \underline{r}}, \quad (7.2)$$

$\underline{r}$ runs over the sites of a hexagonal lattice with unit nearest neighbor distance, and the subscript indicates which sublattice is to be operated upon. We define the second and fourth moments by

$$\langle c(q)c^{\dagger}(q) \rangle \langle \omega_q^2 \rangle = \langle | [H, c^{\dagger}(q)] |^2 \rangle \quad (7.3a)$$

$$\langle c(q)c^{\dagger}(q) \rangle \langle \omega_q^2 \rangle = \langle | [H, [H, c^{\dagger}(q)]] |^2 \rangle \quad (7.3b)$$

where angle brackets denote a thermal average. To first order in reciprocal temperature it is straightforward to show that these moments are given by the eigenvalues of a matrix

$$\langle \omega_q^2 \rangle_{ij} = \begin{pmatrix} \Omega_q^n & \Lambda_q^n \\ \Lambda_q^{n*} & \Omega_q^n \end{pmatrix} \quad (7.4)$$

where

$$\begin{aligned}
 \langle J_1^- J_1^+ \rangle_{\underline{q}}^2 &= \langle | [H, J_1^+(\underline{q})] |^2 \rangle \\
 \langle J_1^- J_1^+ \rangle_{\underline{q}}^2 &= \langle [J_2^(-\underline{q}), H] [H, J_1^+(\underline{q})] \rangle \\
 \langle J_1^- J_1^+ \rangle_{\underline{q}}^4 &= \langle | [H, [H, J_1^+(\underline{q})]] |^2 \rangle \quad (7.5) \\
 \langle J_1^- J_1^+ \rangle_{\underline{q}}^4 &= \langle [[J_2(-\underline{q}), H], H] [H, [H, J_1^+(\underline{q})]] \rangle
 \end{aligned}$$

The moments are thus

$$\langle \omega_{\underline{q}}^n \rangle = \Omega_{\underline{q}}^n \pm |\Lambda_{\underline{q}}^n| \quad (7.6)$$

The relevant part of the hamiltonian may be written

$$\begin{aligned}
 H &= (20\pi/9)(70\pi)^{\frac{1}{2}} \sum_{m,n=-2}^2 C(224;mn) \quad (7.7) \\
 &\times \Gamma \sum_{\underline{k}} \{ Y_{4,I}^{m+n}(\underline{k}) \}^* \{ \frac{1}{2} \sum_i Y_{2,i}^m(\underline{k}) Y_{2,i}^n(-\underline{k}) \} \\
 &\quad + \{ Y_{4,II}^{m+n}(\underline{k}) \}^* Y_{2,1}^m(\underline{k}) Y_{2,2}^n(-\underline{k}) \}.
 \end{aligned}$$

Here $C(224;mn)$ is a Clebsch-Gordan coefficient, $\underline{k}$ runs over the Brillouin zone of a hexagonal lattice, Γ is the nearest-neighbor quadrupole interaction constant ($\Gamma=6Q^2/25r^5$), and the Y 's are spherical harmonics given by

$$Y_{2,i}^m(\underline{k}) = \sum_{\underline{r}} e^{i\underline{k} \cdot \underline{r}} Y_{2,i}^m(\underline{r})$$

$$Y_{4,I}^m(k) = \sum_{\underline{r} \neq 0} e^{i\mathbf{k} \cdot \underline{r}} Y_4^m(\underline{r}) / |\underline{r}|^5 \quad (7.8)$$

$$Y_{4,II}^m(k) = \sum_{\underline{r}} e^{i\mathbf{k} \cdot \underline{r}} Y_4^m(\underline{r} + \underline{1}) / |\underline{r} + \underline{1}|^5.$$

Here $\underline{1}$ is the vector between the two sublattices, and i denotes a given sublattice. Also, Y_2^m is to be construed as an operator on the particle at a given site, while the Y_4 's are numbers. The operators $\underline{J}$ and Y_2^m are treated as 3×3 matrices acting on the $J=1$ subspace. The effect of working in this restricted space is to exclude those (high energy) portions of the spectral function involving transitions between the $J=1$ and $J=3$ multiplets. This exclusion brings $\langle |Y_2^m|^2 \rangle$ to $(10\pi)^{-1}$ from its classical value $(4\pi)^{-1}$.

The expectation values may be written as a high-temperature expansion

$$\langle \dots \rangle = \langle \dots \rangle_{T=\infty} - \beta \langle \dots H \rangle_{T=\infty} + O(\beta^2) \quad (7.9)$$

leading to

$$\langle \omega_{\underline{q}}^2 \rangle = \langle \omega_{\underline{q}}^2 \rangle_{T=\infty} - B_2 t + O(t^2) \quad (7.10a)$$

$$\begin{aligned} \langle \omega_{\underline{q}}^4 - \langle \omega_{\underline{q}}^2 \rangle^2 \rangle &= \langle \omega_{\underline{q}}^4 - \langle \omega_{\underline{q}}^2 \rangle^2 \rangle_{T=\infty} \\ &\quad - B_4 t + O(t^2) \end{aligned} \quad (7.10b)$$

where $t = \beta \Gamma$. The quantities appearing in equations 7.10 may be computed in a straightforward, though very tedious,

manner (with the help of the Cornell University IBM 360/65) by performing the indicated commutations and decoupling the resulting product of Y_2 's and J^α 's. The main contributions come from terms in which this decoupling is done pairwise. These terms involve the maximal number of distinct particles, and are most easily evaluated in reciprocal space; working in reciprocal space has the additional advantage that the usual restriction to nearest neighbor interactions is easily lifted. Terms involving less than the maximal number of particles make relatively small contributions to 7.10b, and have been omitted; B_2 contains a substantial contribution from terms involving two particles.

The results are given in figure 7.1 and table 7.1. The energy scale is set by $\langle \omega_{\underline{q}}^2 \rangle_{T=\infty}$, which may be compared with libron energies of $\sim 20\Gamma$. The temperature dependence is given by $\delta\Xi = \partial(\log \langle \omega_{\underline{q}}^2 \rangle) / \partial t$, noting that a phase transition occurs at $t \sim 0.3$. The parameter $\eta \equiv \langle \omega_{\underline{q}}^4 - \langle \omega_{\underline{q}}^2 \rangle^2 \rangle / \langle \omega_{\underline{q}}^2 \rangle^2$ characterizes the lineshape: $\eta=2$ would suggest a gaussian centered at the origin; $\eta < 2$ suggests gaussians symmetrically placed about the origin, for which $\eta = 2\sigma^2 / (\omega_0^2 + \sigma^2)$; $\eta > 2$ suggests a narrow lineshape with substantial wings. The derivative $\partial\eta / \partial t$ is given by

$$-\frac{\partial\eta}{\partial t} = \langle \omega_{\underline{q}}^2 \rangle_{T=\infty}^{-2} \times \{ B_4 - 2B_2 \frac{\langle \omega_{\underline{q}}^4 - \langle \omega_{\underline{q}}^2 \rangle^2 \rangle_{T=\infty}}{\langle \omega_{\underline{q}}^2 \rangle_{T=\infty}} \}. \quad (7.11)$$

Figure 7.1. Mean square linewidth (in units of Γ^2) as a function of wavevector for $T=\infty$ (solid lines) and $t=3\Gamma=0.25$ (dashed lines) to linear order in t .

$q/q_{\max}$	Upper Branch				Lower Branch			
	$\frac{\langle \omega^2 \rangle_{T=\infty}}{\Gamma^2}$	δ	η	$\frac{\partial \eta}{\partial t}$	$\frac{\langle \omega^2 \rangle_{T=\infty}}{\Gamma^2}$	δ	η	$\frac{\partial \eta}{\partial t}$
0.0	476	1.71	0.91	1.7	217	1.47	2.8	3.8
0.4	451	1.69	0.98	1.8	241	1.51	2.3	3.3
0.8	385	1.66	1.16	2.0	305	1.60	1.6	2.5

Table 7.1. Computed linewidth and lineshape parameters for various values of q : mean square linewidth $\langle \omega_q^2 \rangle_{T=\infty}/\Gamma^2$; temperature dependence $\delta \equiv \partial \{\log \langle \omega_q^2 \rangle\} / \partial t|_{T=\infty}$; lineshape parameter $\eta \equiv \{\langle \omega_q^4 \rangle - \langle \omega_q^2 \rangle^2\} / \langle \omega_q^2 \rangle^2|_{T=\infty}$; and $\partial \eta / \partial t$ at $T=\infty$.

The last term in the braces is dominant, so that η increases somewhat as the phase transition is approached from above.

We have compared these results with the published data of Silvera et al (1972) for para-deuterium at 4.2°K. Harris (1970b) suggests that the appropriate value for Γ_{eff} is $.74 \text{ cm}^{-1}$, which leads to $t=.25$, $\langle \omega^2 \rangle = 272\Gamma^2$, and $\eta=1.33$. Assuming the lineshape to be two symmetrically placed gaussians

$$S(0, \omega) = A \sum_{\pm} \exp[-(\omega \pm \omega_0)^2 / 2\sigma^2], \quad (7.12)$$

our theory gives $\omega_0/\sigma=0.7$. We have digitized the published Raman curve and fit it in the least squares sense (Cornell University Mathematical Subroutine Package (CORMAT), Subroutine NLLS), giving $\omega_0/\sigma=0.8$ and $\langle \omega^2 \rangle = 256\Gamma^2$. (Symmetrically placed Lorentzians fit the data rather poorly.) We consider this to be impressive agreement between theory and experiment.

It must be pointed out, however, that the operator J^+ which couples to the modes we have calculated is a magnetic dipole operator, whereas Raman scattering couples to orthohydrogen via the electric quadrupole operator Y_2^m . At finite temperatures these two operators are coupled via intermolecular correlations, and may have similar spectra, but at high temperatures their spectra will be different. One might hope to couple to these modes via microwave absorption, the matrix element being given by the rotational

magnetic moment of .88 nuclear magnetons. Unfortunately, this gives a small absorption coefficient of $10^{-6} \omega_p(\omega) \text{ cm}^{-1}$.

We hope to calculate spectral parameters for the quadrupole operators in the near future, but preliminary considerations lead to the following results:

- (1) The high temperature second moment will have a wave-vector independent value of about 172 r^2 .
- (2) The high-temperature fourth moment should be wave-vector dependent.
- (3) We expect the zeroth moment $\langle Y_1^1(\underline{q}) Y_1^1(\underline{q})^* \rangle$ to increase as the temperature is lowered for $\underline{q}$ along the c-axis, this increase being least for the Raman active mode. If this is the most important wave-vector dependence, then the Raman active mode will have the widest spectrum as before.

It is instructive to compare this calculation to the specific heat calculation of Berlinsky and Harris (1970). The specific heat can be represented in the form

$$C = \sum_{n=2}^{\infty} \sum_{m=2}^n A_{mn} x^m t^n \quad (7.13)$$

where x is the concentration of orthohydrogen and $t = \beta T$, and the terms contributing to A_{mn} can be represented diagrammatically. We may also represent diagrammatically (in site space) the terms calculated in this paper; these are shown in figure 7.2. Here each line represents a

$$\langle \omega^2 \rangle$$

$$\frac{\partial}{\partial (\beta \Gamma)} \langle \omega^2 \rangle$$

$$\langle \omega^4 - \langle \omega^2 \rangle^2 \rangle$$

$$\frac{\partial}{\partial (\beta \Gamma)} \langle \omega^4 - \langle \omega^2 \rangle^2 \rangle$$

Figure 7.2. Diagrams which are important in calculating the spectral moments. These are also the important diagrams for the specific heat.

factor of the two particle hamiltonian H_{1j} , which may appear in a commutator or may come from the expansion of $e^{-\beta H}$. Comparison with Berlinsky and Harris (1970) shows that these are exactly the diagrams which make important contributions to the specific heat, while diagrams we have ignored are also unimportant in the specific heat. We may thus conclude that the apparent rapid convergence of this calculation and the slow convergence of the specific heat are consistent.

In principle the parameters of the two spectral branches may be split at the zone edge. While we have not specifically searched for such a splitting, our results suggest any such splitting will be fairly small.

For comparison we have also calculated the second-moment parameters for an fcc lattice quantized along the $\langle 111 \rangle$ direction. While there is negligible difference in $\langle \omega^2 \rangle_{T=\infty}$ or in the two-particle contribution to δ , the three-particle contribution is significantly larger in hcp than in fcc. The result is that δ_{hcp} exceeds δ_{fcc} by about 4% at the zone center (highest energy mode), this difference decreasing toward the zone edge (lowest energy mode). This suggests that there may be sufficient difference in the orientational free energy to explain the structural transition. (This idea has been studied by Lee and Raich (1972)).

We conclude that there is a substantial amount of information in angular momentum excitations in hcp orthohy-

drogen. The zone-center Raman-active paralibrons are less than completely damped, and have already been seen. Elsewhere in the Brillouin zone one may find rather interesting temperature-dependent lineshapes. Furthermore, these excitations play a significant rôle in the binding energy and phonon spectra of solid hydrogen, as well as providing a tool for the study of the structural phase transition.

Appendix A

To evaluate $-\frac{1}{\pi^2} \int d\omega_1 \int d\omega_2 G^0 R(\omega_1, \underline{k}_1) G^0 R(\omega_2, \underline{k}_2) G^0 R(\omega - \omega_1 - \omega_2, \underline{k}_3)$

The quantity desired may be written

$$Q(\omega) = \frac{1}{\pi^2} \int d\omega_1 \int d\omega_2 \frac{A_1}{\omega_1 - \epsilon_1 + i\delta} \times \frac{A_2}{\omega_2 - \epsilon_2 + i\delta} \times \frac{A_3}{\omega - \omega_1 - \omega_2 - \epsilon_3 + i\delta}. \quad (A.1)$$

We close the contours for ω_1 and ω_2 in the upper half-plane, giving

$$Q(\omega) = \frac{4A_1 A_2 A_3}{\omega \epsilon_3 \epsilon_2 \epsilon_1 \delta} \quad (A.2)$$

$$= 4A_1 A_2 A_3 \left\{ P \frac{1}{\omega + \epsilon_2 - \epsilon_1 - \epsilon_3} - i\pi \delta(\omega + \epsilon_2 - \epsilon_1 - \epsilon_3) \right\}. \quad (A.3)$$

This may then be integrated over $\underline{k}_1$, $\underline{k}_2$, and $\underline{k}_3$ by usual methods to find $\Sigma_{\alpha}(\underline{q}, \omega = \epsilon_{\alpha}^0(\underline{q}))$, the real part of Σ giving an energy shift and the imaginary part a damping.

Appendix B

This derivation uses the standard equation of motion technique. To make this method work, we need not write the hamiltonian in terms of the operators, provided we can write the commutators of the hamiltonian with the operators.

If the quasi-particles were bosons, we would have

$$\langle C_{\alpha} \rangle = 1$$

$$H = \sum_{\underline{k}\alpha} \epsilon_{\alpha}(\underline{k}) d_{\alpha}^{\dagger}(\underline{k}) d_{\alpha}(\underline{k}) + V$$

$$R_{\underline{k}\alpha}^{\dagger} = [d_{\alpha}(\underline{k}), V]$$

and the calculation would lead to the standard result.

Appendix C

"Dynamic Susceptibility of a Model Polymer in Several Limits -- Theory and Calculations." M. J. Mandell, J. Chem. Phys. 57, 4858 (1972).

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