ORIENTATIONAL PROPERTIES
OF THE CLASSICAL
ONE-DIMENSIONAL MULTIPOLAR ARRAY*

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129

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Orientational Properties
Of The Classical
One-Dimensional Multipolar Array*

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Abstract

The static and dynamic properties of a linear array of classical free rotors with electric dipole and/or quadrupole interactions are considered. Such static properties as correlation functions and specific heat are calculated. A formalism is presented to treat the moments of the spectral function, and is applied to the pure dipole system, showing the gradual onset of the librionic excitations first treated by Frenkel. Some thoughts are given on the effects of long-range forces, on quantum effects, and on application to such real systems as N_2 and HCl .

I. Introduction

The subject of internal rotation in solids (as well as in liquids and in large molecules) has been of interest for several decades. Smyth¹, in a 1935 review, listed over seventy substances as candidates for molecular rotation. Included in this list were H_2 , N_2 , the hydrogen halides, and the methanes.

Pauling² in 1930 proposed a one-dimensional model as a means of achieving at least qualitative insight into the properties of such systems. Pauling treated each particle as rotating in an effective potential $V(\theta) = V_0(1 - \cos 2\theta)$ for quadrupoles, or $V_0(1 - \cos \theta)$ for dipoles. The system would be ordered if the particles lacked sufficient thermal energy to surmount the potential barrier, and free-rotor-like at higher temperatures. He was thus able to make crude estimates of transition temperatures for several systems.

Frenkel³ stressed the cooperative nature of the model. He treated the phase transition for the dipolar case using Bragg-Williams theory, and discussed the nearly-harmonic low-temperature excitations which today we would call librions. However, Frenkel was led by erroneous arithmetical manipulation to neglect the existence of a free-rotor-like phase.⁴

The purpose of this paper is to present some "exact" results for the static and dynamic properties of such one-dimensional models. While we understand today the dangers

of applying one-dimensional results to three-dimensional systems and vice-versa, the methods and results are at least of pedagogical and historical interest, and some of the methods may be generalized to perturbative calculations on three-dimensional systems. By "exact" we mean that the problem can be reduced to a simple integral equation which can be easily solved numerically, and results for physical properties may be obtained by doing some numerical integrations.

This introduction would be very much incomplete without reference to other work on rotation and libration in solids. Fowler⁵ elaborated on the treatment of Pauling, attempting to apply it to real solids. Further work along these lines was done by Kirkwood.⁶ An early application of nuclear magnetic resonance to the study of rotation in hydrogen halides was done by Alpert.⁷ These systems were studied using mean field theory by Krieger and James.⁸ Many more recent references to work on hydrogen halides may be found in Niimura et al.⁹ The canonical example of a classical quadrupolar system is N_2 ; some recent studies are those of Goodings and Henkelman,¹⁰ and of Raich and Etters.¹¹ Since solid H_2 is a system of highly quantum-mechanical quadrupolar rotators, it is somewhat outside the scope of this work. Some references are those by Harris, Berlinsky, Nakamura, and co-workers.¹²⁻¹⁶ Some recent calculations on one-dimensional models using anharmonic phonon theory were done by Raich and Etters.¹⁷

In section II the model is described and the formalism

to be used for its solution is presented. Section III gives some results for the static properties of dipolar, quadrupolar, and mixed systems. In section IV a formalism is presented to treat the dynamics of multipolar systems, and results for the pure dipole system are given and discussed. Section V deals with phase transitions due to long-range forces, and section VI discusses quantum effects. Summary and conclusions are given in section VII.

II. Formalism

We wish to consider the properties of a linear array of $N+1$ classical free rotors having electric multipole interactions. The hamiltonian is

$$H = \sum_{i=1}^N T_i + U(\underline{\Omega}_1, \dots, \underline{\Omega}_{N+1}) \quad (2.1)$$

with kinetic energy

$$T_i = \frac{p_{\theta(i)}^2}{2I} + \frac{p_{\phi(i)}^2}{2I \sin^2 \theta_i} \quad (2.2)$$

To find the static properties of a classical system the kinetic energy may be neglected. We will postpone discussion of dynamic effects to later chapters.

To solve this system we restrict the potential to an interaction between nearest neighbors

$$U = \sum_{i=1}^N h(\underline{\Omega}_i, \underline{\Omega}_{i+1})$$

If we take an isotropic interaction

$$h(\underline{\Omega}_i, \underline{\Omega}_j) \propto \underline{\Omega}_i \cdot \underline{\Omega}_j$$

we have the classical Heisenberg model whose solution was presented by Fisher.¹⁸ The key to this solution is to focus attention not on the $N+1$ particles, but on the N bonds between the particles. Each bond is independent and may be characterized by the orientation $\underline{u}_i$ of particle $i+1$ relative to particle i . The orientational partition function is then given by

$$Z = 4\pi \left\{ \int d^2 \underline{u} e^{-\beta h(\underline{u})} \right\}^N \quad (2.3)$$

For multipolar interactions, however, it is necessary to measure all angles relative to the interparticle axis, giving

$$H = \sum_{i=1}^N h(u_i, u_{i+1}, \alpha_i) \quad (2.4)$$

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

$$\begin{aligned} Z(N+1) P(u_i, u_{i+1}) &= 2\pi \int d\Omega_i \dots \int d\Omega_{i-1} \int d\alpha_i \\ &\times \int d\Omega_{i+2} \dots \int d\Omega_{N+1} e^{-\beta H} \\ &= 2\pi \int d\alpha_i e^{-\beta h_i} \{ Z(i) p_i^{(end)}(u_i) \} \\ &\times \{ Z(N+1-i) p_{N+1-i}^{(end)}(u_{i+1}) \} \end{aligned} \quad (2.5)$$

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

$$\begin{aligned} P(u_i, u_{i+1}) &= C(\beta) \int d\alpha_i p^{(end)}(u_i) p^{(end)}(u_{i+1}) \\ &\times \exp \{ -\beta h(u_i, u_{i+1}, \alpha_i) \} \end{aligned} \quad (2.6)$$

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

$$p^{(end)}(u) = C'(\beta) \int du' \int d\alpha p^{(end)}(u') e^{-\beta h(u, u', \alpha)} \quad (2.7)$$

Equation 2.7 is a Fredholm equation of the second kind for $p^{(end)}$ which may be solved numerically. Knowing $p^{(end)}$ allows

the use of 2.6 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. Some computational details are given in Appendix A.

III. Static Properties

(A) Pure Dipole Interaction

The dipole interaction is given by

$$h(u_1, u_2, \alpha) = -V \left\{ 2u_1 u_2 - \left\{ (1-u_1^2)(1-u_2^2) \right\}^{\frac{1}{2}} \cos \alpha \right\} \quad (3.1)$$

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 1.

(B) Pure Quadrupole Interaction

The interaction hamiltonian for a pair of cylindrically symmetric quadrupoles is

$$h = \left(\frac{20\pi}{9} \right) (70\pi)^{\frac{1}{2}} \sum_{mn} C(224; mn) \times r Y_4^{m+n}(\underline{\Omega}_{12}) Y_2^m(\underline{\Omega}_1) Y_2^n(\underline{\Omega}_2) \quad (3.2)$$

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

$$h(u_1, u_2, \alpha) = A \cos 2\alpha + B \cos \alpha + C$$

$$A = .995 (1-u_1^2) (1-u_2^2)$$

$$B = -15.9 u_1 u_2 \{(1-u_1^2)(1-u_2^2)\}^{\frac{1}{2}}$$

$$C = 5.96 (3u_1^2 - 1)(3u_2^2 - 1). \quad (3.3)$$

The C-term is most important, so that the low temperature configuration is as shown in figure 2b. To determine the low-temperature specific heat, note that the "vertical" 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 3.

(C) Mixed Interaction

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

$$h(u_1, u_2, \alpha) = h^{\text{dipole}} + h^{\text{quadrupole}} + h^{\text{d-q}} \quad (3.4)$$

$$h^{\text{d-q}} = G (u_2 - u_1) (2u_1 u_2 - s_1 s_2 \cos \alpha)$$

where $s_i = (1-u_i^2)^{\frac{1}{2}}$, and

$$G = 1.53 (V\Gamma)^{\frac{1}{2}} (\text{sgn } Q). \quad (3.5)$$

If the quadrupole interaction is not extremely weak, i.e., if $\Gamma \gtrsim .05V$, the low temperature orientation (figure 2c) will show quadrupole effects. Furthermore, the dipole-quadrupole hamiltonian causes an effective antiferroelectric interaction between second neighbors. The argument suggested by figure 4

leads to

$$\langle u_{i-1} \cdot u_{i+1} \rangle = - \tanh^2 2G \langle u_i^2 \rangle \quad (3.6)$$

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 5.

IV. Dynamic Properties

The dynamics of multipolar arrays may be completely described by the set of functions

$$\langle Y_{\ell}^m(i, t)^* Y_{\ell'}^{m'}(j, 0) \rangle .$$

For simplicity in what follows we specialize to the case $\ell=\ell'=1$, $i=j$, $m=m'$, although the method we shall use is more generally applicable. The quantities we shall discuss are the even moments of the spectral function

$$A_{\ell m}(\omega) = \frac{\int_{-\infty}^{\infty} \langle Y_{\ell}^m(i, t)^* Y_{\ell}^m(i, 0) \rangle e^{i\omega t} dt}{2\pi \langle |Y_{\ell}^m(i, 0)|^2 \rangle} \quad (4.1)$$

$$\langle \omega^{2n} \rangle_{\ell m} = \int_{-\infty}^{\infty} \omega^{2n} A_{\ell m}(\omega) d\omega \quad (4.2)$$

These moments are calculated with the use of the Poisson bracket relation¹⁹

$$\frac{du}{dt} = [u, H] + \frac{\partial u}{\partial t} . \quad (4.3)$$

It is then straightforward to show

$$\langle \omega^2 \rangle_{\ell, m} = \frac{\langle |[H, Y_{\ell}^m]|^2 \rangle}{\langle |Y_{\ell}^m|^2 \rangle} \quad (4.4)$$

$$\langle \omega^4 \rangle_{\ell, m} = \frac{\langle | [H, [H, Y_{\ell}^m]] |^2 \rangle}{\langle | Y_{\ell}^m |^2 \rangle} \quad (4.5)$$

The calculations are simplified by several factors: (1) The spherical harmonics Y_{ℓ}^m are independent of momenta. (2) Momenta of different particles are uncorrelated. (3) The momentum averages are independent of angular averages, giving

$$\langle \frac{p_{\theta}^2}{2I} \rangle = \langle \frac{p_{\phi}^2}{2I \sin^2 \theta} \rangle = \frac{1}{2} k_B T. \quad (4.6)$$

We have applied these ideas to the pure dipole system, for which $A_{1,0}(\omega)$ is the spectral function for order-parameter fluctuations, and $A_{1,\pm 1}(\omega)$ is a libron spectral function. At high temperatures the two spectral functions should be equal and given (quantum-mechanically) by

$$A^{QM}(\omega) = \left\{ \sum_{\ell=0}^{\infty} (2\ell+1) \exp \left[\frac{-B\ell(\ell+1)}{k_B T} \right] \right\}^{-1} \\ \times \left\{ \sum_{\ell=1}^{\infty} \ell \left[e^{-B\ell(\ell-1)/k_B T} \delta(\hbar\omega - 2\ell B) + e^{-B\ell(\ell+1)/k_B T} \delta(\hbar\omega + 2\ell B) \right] \right\} \quad (4.7)$$

where $B = \hbar^2/2I$. Classically this becomes

$$A^{HT}(\omega) = \frac{|\omega| e^{-\hbar^2 \omega^2 / 4Bk_B T}}{2 \int_0^{\infty} v e^{-\hbar^2 v^2 / 4Bk_B T} dv} \\ = \frac{I}{2 k_B T} \frac{|\omega|}{e} e^{\hbar^2 \omega^2 / 4Bk_B T} \quad (4.8)$$

At low temperature the spectral functions $A_{1,\pm 1}(\omega)$ are proportional to the libronic density of states. The libronic frequencies are given by

$$\omega^2 = \frac{4V}{I} (1 + \frac{1}{2} \cos q) ; -\pi \leq q \leq \pi \quad (4.9)$$

so

$$A(\omega) \propto \frac{4x}{(8x^2 - 4x^4 - 3)^{\frac{1}{2}}} ; x = \left| \frac{\omega^2 I}{4V} - 1 \right|^{\frac{1}{2}} \quad (4.10)$$

These spectral functions are shown in figure 6. We characterize these functions by their mean square widths $\langle \omega^2 \rangle$ and a lineshape parameter $\lambda = \langle \omega^4 \rangle / \langle \omega^2 \rangle^2$. (A delta function has $\lambda=1$; a lorentzian has $\lambda=\infty$; a gaussian centered at ω_0 with width σ has $\lambda-1=2\sigma^2/(\omega_0^2+\sigma^2)$.) It is easy to show that the high-temperature function has $\langle \omega^2 \rangle = 2k_B T / I$ and $\lambda=2$; the libron function has $\langle \omega^2 \rangle = 4V/I$ and $\lambda=9/8$.

Using the Poisson bracket formalism with hamiltonian 2.1, 3.1, we find

$$\frac{I}{k_B T} \langle \omega^2 \rangle_{1,0} = \frac{\langle \sin^2 \theta \rangle}{\langle \cos^2 \theta \rangle} \quad (4.11)$$

$$\frac{I}{k_B T} \langle \omega^2 \rangle_{1,\pm 1} = \frac{1 + \langle \cos^2 \theta \rangle}{\langle \sin^2 \theta \rangle} \quad (4.12)$$

$$\begin{aligned} \left(\frac{I}{k_B T} \right)^2 \langle \omega^4 \rangle_{1,0} &= 8 - 8 \left(\frac{V}{k_B T} \right) \frac{T_1}{\langle \cos^2 \theta \rangle} \\ &+ 2 \left(\frac{V}{k_B T} \right)^2 \frac{T_{2c} + T_{3c}}{\langle \cos^2 \theta \rangle} \end{aligned} \quad (4.13)$$

$$\begin{aligned} \left(\frac{1}{k_B T}\right)^2 \langle w^4 \rangle_{1,\pm 1} = & 8+8 \left(\frac{v}{k_B T}\right) \frac{T_1}{\langle \sin^2 \theta \rangle} \\ & + 2 \left(\frac{v}{k_B T}\right)^2 \frac{T_{2s} + T_{3s}}{\langle \sin^2 \theta \rangle} \end{aligned} \quad (4.14)$$

where

$$\begin{aligned} T_1 = & \langle 2 \sin^2 \theta_i \cos \theta_i \cos \theta_{i+1} \\ & + \cos^2 \theta_i \sin \theta_i \sin \theta_{i+1} \cos(\varphi_i - \varphi_{i+1}) \rangle \end{aligned} \quad (4.15)$$

$$\begin{aligned} T_{2c} = & \langle \{ 2 \sin^2 \theta_i \cos \theta_{i+1} \\ & + \frac{1}{2} \sin 2\theta_i \sin \theta_{i+1} \cos(\varphi_i - \varphi_{i+1}) \}^2 \rangle \end{aligned} \quad (4.16)$$

$$\begin{aligned} T_{2s} = & \langle \{ \sin 2\theta_i \cos \theta_{i+1} + \cos^2 \theta_i \sin \theta_{i+1} \cos(\varphi_i - \varphi_{i+1}) \}^2 \\ & + \sin^2 \theta_{i+1} \sin^2(\varphi_i - \varphi_{i+1}) \rangle \end{aligned} \quad (4.17)$$

$$\begin{aligned} T_{3c} = & \langle 4 \sin^4 \theta_i \cos \theta_{i+1} \cos \theta_{i-1} \\ & + \frac{1}{4} \sin^2 2\theta_i \sin \theta_{i+1} \sin \theta_{i-1} \cos(\varphi_i - \varphi_{i+1}) \cos(\varphi_i - \varphi_{i-1}) \\ & + \sin^2 \theta_i \sin 2\theta_i \cos \theta_{i+1} \sin \theta_{i-1} \cos(\varphi_i - \varphi_{i-1}) \rangle \end{aligned} \quad (4.18)$$

$$\begin{aligned}
 T_{3s} = & \langle \sin^2 2\theta_i \cos\theta_{i-1} \cos\theta_{i+1} \\
 & + \sin 2\theta_i \cos\theta_{i-1} \cos^2 \theta_i \sin\theta_{i+1} \cos(\varphi_i - \varphi_{i+1}) \\
 & + \cos^4 \theta_i \sin\theta_{i+1} \sin\theta_{i-1} \cos(\varphi_{i+1} - \varphi_i) \cos(\varphi_i - \varphi_{i-1}) \rangle \quad (4.19)
 \end{aligned}$$

Note that the second moments involve only single-particle static properties, while the fourth moments involve not only two- but also three-particle correlations. We have plotted the second moments and the lineshape parameters for the pure dipole system in figures 7 and 8. The libron spectral function $A_{1,\pm 1}(\omega)$, as indicated by its second and fourth moments, appears to correspond to mildly anharmonic excitations at the lowest temperatures we have calculated, and should merge with similar results using standard anharmonic phonon theories. We have no simple interpretation for the spectral moments of $A_{1,0}$, except that the large value of $\langle \omega^4 \rangle / \langle \omega^2 \rangle^2$ suggests a nearly exponential decay of order parameter fluctuations.

V. 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

$$H^{LR} = \sum_{i=1}^N \sum_{j=i+2}^N \frac{2 u_i u_j}{|i-j|^x} \quad (5.1)$$

Ordinary mean field theory consists of solving the equation

$$P = P_0 (E + 4\zeta(x)P; T), \quad (5.2)$$

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 5.2 has a non-zero solution for P at $E = 0$. A better mean field theory is given by

$$P = P_1(E + 4(\zeta(x)-1)P; T) \quad (5.3)$$

where P_1 is calculated using the nearest-neighbor pair hamiltonian

$$h^{(E)} = h^{(0)}(u_1, u_2, \alpha) - \frac{1}{2}E(u_1 + u_2). \quad (5.4)$$

This gives critical points for the pure dipole case as shown in figure 9. The portion of the figure for $x > 2$ is meaningless, as no true phase transitions occur.

Equation 5.3 gives a first order transition if $\frac{\partial^3}{\partial E^3} P(E; T) > 0$ for $E=0$, as shown in figure 10. This derivative is always negative for the pure dipole case, but becomes positive upon the addition of a sufficient quadrupole interaction.

VI. Quantum Effects

For high temperatures quantum effects can be expressed as an expansion in the parameter

$$\sigma = \frac{\hbar^2}{2Ik_B T}.$$

For concreteness we will deal with quantum corrections to the specific heat. One such correction arises purely from the difference between the quantum and classical kinetic energy operators and leads to²⁰

$$C^{\text{kinetic}} = C^{\text{kinetic}}_{\text{classical}} \left(1 + \frac{\sigma^2}{45} + \frac{\sigma^3}{945} + \dots \right) \quad (6.1)$$

A more interesting correction comes from the non-commutativity of the kinetic and potential energy operators. To find this effect we look for corrections to

$$z = \left\{ \text{Tr} \exp (-\beta H) \right\}^{1/N}. \quad (6.2)$$

Using $\text{Tr} U = 0$, we find

$$z = z_{\text{classical}} - \frac{\beta^3}{6} \frac{\hbar^2}{2I} \text{Tr} [U, L_1^2] U \quad (6.3)$$

where L_1^2 is the square of the single-particle angular momentum operator. Since U consists of terms of the form $Y_\ell^m(i) Y_\ell^{m'}(i+1)$ with $\ell=1$ for dipole, 2 for quadrupole, etc., and the Y_ℓ^m 's are eigenfunctions of L^2 , we find

$$z = z_{\text{classical}} + \frac{\ell(\ell+1)}{3} \sigma \text{Tr} (\beta V)^2 / N + \dots \quad (6.4)$$

For a pure dipole interaction

$$\text{Tr} \frac{U^2}{N} = \frac{8V^2}{9}. \quad (6.5)$$

The specific heat is given by

$$\frac{C}{Nk_B} = \beta^2 \frac{\partial^2 \ln z}{\partial \beta^2} \quad (6.6)$$

so the correction is

$$\frac{\Delta C}{Nk_B} = \frac{16}{9} \sigma \left(\frac{V}{k_B T} \right)^2 \quad (6.7)$$

It must be realized that the convergence of these series is very poor, so that 6.7 should be applied only when both σ and $V/k_B T$ are small. If $V \gg \hbar^2/2I$, the quantum effects at low temperatures are best treated in terms of the nearly harmonic librations (for example, in solid N_2). If $V \ll \hbar^2/2I$, we have a slightly perturbed quantum free-rotor system (as in solid H_2 , or in solid rare gases). For $V \sim \hbar^2/2I$ the problems encountered are similar to those in crystal field magnets.²¹

VII. Summary and Conclusions

We have shown that finding the properties of a linear array of classical multipolar rotors can be reduced to the numerical solution of a simple integral equation, followed by some numerical integrations. Various properties were calculated for pure dipole, pure quadrupole, and mixed cases. In particular, specific heat maxima occur at $k_B T \approx \frac{1}{2} V = p^2 / 2a^3$ and at $k_B T \approx 4\Gamma$ for the pure quadrupole system. For the common case of particles having both types of moments, a small quadrupole moment can have substantial effects. For the hydrogen halides the ratios V/Γ are about 26, 5, 2.6, 0.3 for HF, HCl, HBr, and HI respectively²², so that only for HF are quadrupole effects relatively unimportant. Dipolar effects will always dominate at sufficiently low temperatures due to the long-range nature of the dipole interaction.

The dynamic properties have been treated by using a Poisson bracket formalism to calculate moments of certain spectral functions. In particular, we have shown how the incoherent spectral function for Y_1^m in a pure dipole system changes from a non-harmonic free-rotor function at high temperatures to mildly anharmonic librations and order parameter relaxation as the temperature is lowered. These effects should be observable in the vibration-rotation spectrum or other infrared absorption experiments.

We have also used a modified mean field theory to treat phase transitions due to long-range dipole interactions. The transition is second order for the pure dipole system, but first

order when sufficient quadrupole interaction is mixed in.

Real three-dimensional solids such as N_2 or HCl cannot be as neatly treated as one-dimensional models. However, it is possible to develop high-temperature expansions for the quantities treated here. This has been done for the quantum crystals H_2 and D_2 , and met with considerable success in treating specific heat¹⁶, nuclear magnetic relaxation^{13,14}, and Raman scattering²³. It should be possible to treat N_2 this way as well. The hydrogen halides are complicated by having both dipole and quadrupole moments as well as hydrogen bonding effects.²⁴ Nonetheless, it should be possible to get good results for these systems at least in the region immediately below the melting point.

Appendix A

The computations of this paper involve integrals of the form

$$I = \int_{-1}^{+1} g(u) du \int_0^{2\pi} d\alpha \exp\left\{\sum_{n=0}^l f_n(u) \cos n\alpha\right\}. \quad (\text{A.1})$$

The integral over α is treated first, using the identity

$$\int_0^{2\pi} e^{p \cos x} dx = 2\pi I_0(p), \quad (\text{A.2})$$

where I_0 is the Bessel function for imaginary argument. For $l > 1$ it is necessary to treat cross-terms among different values of n , as can be seen by expanding the exponential.

The integrals over u are done numerically using Simpson's Rule. For the pure dipole case the mesh size used was $\Delta u = 0.1$. This was sufficient to obtain accuracy of a few percent at the lowest temperatures considered. For quadrupole and mixed systems the mesh size was $\Delta u = 0.05$. The computations were done on the Cornell University IBM 360/65.

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$$p^2/a^3 = (10^{-18})^2/(3 \times 10^{-8})^3$$
$$\approx 3 \times 10^{-12} \text{ ergs} = 2 \times 10^4 \text{ }^\circ\text{K},$$
suggesting that HCl has nearly harmonic librations at all ordinary temperatures.
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Figure Captions

- Figure 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 2. Low temperature arrangement for (a) pure dipole interaction; (b) pure quadrupole interaction; (c) mixed interaction.
- Figure 3. Orientational specific heat (solid curve, in units of k_B per particle), $\langle 3u^2 - 1 \rangle$ (dashed curve), and $\langle 3u_i^2 - 1 \rangle \langle 1 - 3u_{i+1}^2 \rangle$ (dot-dash curve) for pure quadrupole interaction.
- Figure 4. Anti-ferroelectric coupling between second neighbors induced by dipole-quadrupole interaction.
- Figure 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 $\Gamma=0.25$.
- Figure 6. Spectral functions in the high temperature (free rotor) limit (solid line) and the low temperature (harmonic libron) limit (dot-dash line). The unit of frequency is $(k_B T/I)^{1/2}$ at high temperatures, and $(4V/I)^{1/2}$ at low temperatures.

- Figure 7. Solid curves: second moment of spectral function for Y_1^0 (lower curve) and $Y_1^{\pm 1}$ (upper curve) for pure dipole system. Dot-dash curves: same with added quadrupole interaction $\Gamma=0.10V$. Dashed curve: harmonic limit $\langle \omega^2 \rangle = 4V/I$.
- Figure 8. Lineshape parameter $\lambda = \langle \omega^4 \rangle / \langle \omega^2 \rangle^2$ for Y_1^0 (upper curve) and $Y_1^{\pm 1}$ (lower curve) for pure dipole system. The dashed line is the low temperature limit $\lambda=1.125$.
- Figure 9. 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 10. Condition for a first order phase transition. The solid line is $P=P_1(E, T_c)$; the dashed line is $E=4\{\zeta(x)-1\}P$.

Figure 1

Figure 2

Figure 3

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

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10