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## Soft Modes in Molecular Crystals\*

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The self-consistent phonon approximation is applied to study the temperature dependence of the libron and phonon modes for simple molecular crystals. Several linear chain models are studied to illustrate the soft mode behavior of these excitations near the orientational order-disorder transitions that occur in many molecular crystals. It is shown that both libron and phonon frequencies are strongly temperature dependent in the neighborhood of the transition in qualitative agreement with experimental observations. Both the cases of strong and weak orientational coupling are considered. The effects of the cubic anharmonic terms are also discussed.

### I. INTRODUCTION

The motion of diatomic molecules in molecular crystals was first described by Pauling.<sup>1</sup> It was shown by a discussion of the wave equation for a diatomic molecule in a crystal that the motion of the molecule in its dependence on the polar angles  $\theta$  and  $\phi$  may approach either one of two limiting cases, oscillation or rotation. If the intermolecular forces are strong and the moment of inertia of the molecule is large, the eigenfunctions and energy levels approach those corresponding to oscillation about certain equilibrium orientations. If they are small, the eigenfunctions and energy levels may approximate those of the free molecule.

The specific heats and other properties of a large number of molecular crystals show anomalies which are associated with orientational order-disorder transitions.<sup>2</sup> These transitions which are often accompanied by a change in the crystal structure were interpreted by Pauling as changes from a state in which most of the molecules are oscillating to one in which most of them are rotating. Today these transitions are commonly interpreted as a sudden change in the ordering of the molecular orientations as the temperature is varied, in a manner similar to the alignment of spins in ferromagnetic or antiferromagnetic materials. However, Pauling's concept of the two limiting cases is still useful in the classification of molecular crystals as either primarily rotating or oscillating.

Solid hydrogen and deuterium are examples of diatomic molecular crystals where the molecules are primarily rotating. For the case of solid orthohydrogen, the rotational kinetic energy of the molecules is much larger than the depth of the intermolecular potential. Therefore, the intermolecular potential can be treated as a perturbation on the free rotator problem. A large amount of experimental and theoretical work has been done on these very interesting materials. The reader is referred to Refs. 2-9 and the work quoted therein for a sampling of this field. It is found that for all practical purposes in solid hydrogen and deuterium the angular momentum quantum number  $J$  is a good quantum number, and the rotational wavefunctions are linear

combinations of the spherical harmonics  $Y_{JM}$  with fixed  $J$ . The orientational ordering of  $H_2$  and  $D_2$  molecules in the solid can then be described in a manner similar to the motion of spins in antiferromagnets.<sup>5,6</sup> Solid hydrogen and deuterium are examples of quantum crystals. Their translational and librational zero-point energies are large compared with most other solids. At zero temperature, except for this zero-point motion, the molecules are centered on lattice sites and aligned along certain equilibrium directions. The molecular orientations become more and more disordered as the transition temperature is approached. At the transition temperature, a discontinuous change to a state with only short range orientational order occurs. This order-disorder transition occurs at a temperature well below the melting point.

Most other diatomic or linear molecular crystals fall in the second category where the motions are primarily oscillatory. Examples are solid  $N_2$ ,  $O_2$ ,  $CO$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ ; the hydrogen and deuterium halides,  $CO_2$ ,  $N_2O$ , and more complicated molecular crystals such as naphthalene and anthracene. Again, it is found that at zero temperature the molecules are oriented along certain equilibrium directions. As the temperature is increased, this ordering decreases until a transition temperature is reached where usually a first-order transition to an orientationally disordered phase takes place. The temperature-dependent ordering of the molecules in simple molecular crystals such as  $N_2$ ,  $CO$ , and the hydrogen halides has been described by molecular field theories.<sup>10-15</sup> These theories predict one or more transitions between several types of ordered and disordered phases. The transitions are generally first-order phase changes. The molecular ordering can also be treated by cluster variation methods,<sup>16,17</sup> which are expected to be somewhat more accurate in the transition region. These descriptions, however, all neglect the zero-point motions of the molecules. Some of the molecular crystals mentioned above are bound by orientational forces so strong that the crystals melt before their orientations become disordered.

In the light of the previous discussion one can make another characterization of molecular crystals depending in general on the amount of deviation of the mo-

molecular shape from spherical symmetry. With molecules of highly nonsymmetric form, the tendency toward liquid crystalline behavior arises.<sup>18,19</sup> With such crystals the lattice periodicity breaks down before orientational correlations between neighboring molecules are lost. In the molecular crystals of the simpler diatomic molecules the ordering of molecular orientations generally occurs at temperatures below the melting point. Whether orientational or translational melting occurs first is determined by the relative strengths of the corresponding intermolecular forces.<sup>20,21</sup>

Recently, Raman and infrared scattering have become very powerful tools to investigate the vibrational and rotational modes of molecular crystals. Experimental and theoretical work in this field was recently reviewed by Schnepf<sup>22</sup> and Leroi.<sup>23</sup> The ultimate objective of these studies is to obtain a better understanding of the intermolecular forces. When a molecule is bound in a crystal, the internal vibrations are perturbed and split by the interactions with neighboring molecules. The translational and rotational degrees of freedom become hindered and are observable in the vibrational spectrum of the solid as translational and librational lattice modes. The lattice vibrations occur at much lower frequencies than the intramolecular vibrations because the intermolecular forces are correspondingly weaker.

The extension of the conventional theory of lattice dynamics<sup>24</sup> to calculate the dispersion spectrum for molecular crystals has been described by several authors.<sup>25-28</sup> At low temperatures the harmonic approximation can be used, except for the case of hydrogen and deuterium.<sup>6,29</sup> For diatomic molecular crystals the intermolecular interactions between molecules are usually represented by Lennard-Jones or exp-6 type potentials between molecular centers plus angularly dependent multipole-multipole interactions.<sup>22,23</sup> Alternatively, Lennard-Jones potentials between nonbonded atoms were also found to give a satisfactory fit to the Raman and infrared lattice modes.<sup>22,23</sup> In particular the atom-atom potentials were used with some success to fit the librational and translational modes at zero wave vector ( $\mathbf{k}=0$ ) for solid nitrogen,<sup>30,31</sup> carbon monoxide,<sup>32,33</sup> and oxygen.<sup>23</sup>

Although harmonic theory probably provides an adequate description of the molecular vibrations at low temperatures, it is certain to fail as one approaches the order-disorder transition which occurs in many of the diatomic molecular crystals. The temperature dependence of the librational and translational lattice modes has been studied<sup>22,34-38</sup> for solid nitrogen. The linewidths in the Raman spectrum<sup>34,35</sup> broaden rapidly as the transition temperature is approached, indicating substantial anharmonicity in the librational oscillations. The frequencies also show a temperature dependence similar to a soft-mode behavior. Measurements of thermal expansion and isothermal compressibility of solid nitrogen<sup>39</sup> also indicate that the libra-

tional modes in solid nitrogen are appreciably anharmonic. We can therefore conclude that the harmonic theory of lattice dynamics is an inadequate method for the description of phonons in many molecular crystals near their phase transitions.

The failure of the traditional approach when applied to the case of crystalline helium led the way to a self-consistent approximation for the calculation of phonon frequencies. Review papers on this subject have recently been given by Werthamer<sup>40,41</sup> and by Plakida and Siklos.<sup>42</sup> The basic idea of the theory is contained in the choice of a trial harmonic oscillator Hamiltonian. The self-consistent phonon approximation has been used successfully as a basis to calculate the phonon frequencies of rare gas solids,<sup>43-46</sup> as well as the translational lattice modes of hydrogen and deuterium.<sup>29</sup>

The self-consistent phonon approximation is perhaps a logical starting point for the calculation of the lattice dynamics of molecular crystals near phase transitions and can therefore be applied to discuss the behavior of the translational and librational modes near an orientational order-disorder transition. The present paper provides a simple model which illustrates the temperature dependence of the phonon and libron frequencies and lifetimes of a molecular crystal for the case when the molecules can be considered to be mainly oscillating rather than rotating. It is shown that both phonon and libron frequencies exhibit a soft-mode behavior.

## II. LINEAR CHAIN MODELS

It is well known that linear chain models do not provide accurate descriptions of the three-dimensional solids they attempt to approximate. However, various one-dimensional models have been found useful for more than a qualitative description of phonons in crystals.<sup>25,47-49</sup> Of course, not all results of the linear chain can be extended to three-dimensional systems. For example, it is found that for a one-dimensional solid the mean square fluctuations of the equilibrium position of a lattice particle is infinite.<sup>50</sup>

The dispersion relation for a molecular chain has been calculated in harmonic approximation by Biem and Hahn<sup>25</sup> and Sandor.<sup>47</sup> Restricting the problem to only two degrees of freedom, it was shown that the general normal modes of the chain are mixed vibrations containing both translational and librational components. The anharmonic monatomic linear chain was discussed by Pathak,<sup>51</sup> who used the harmonic approximation as a basis. An extension of that treatment, based on the self-consistent phonon approximation, has been given by Plakida and Siklos.<sup>42</sup>

In the present work we have extended the discussion of Plakida and Siklos<sup>42</sup> to discuss the phonon and libron modes of a linear chain of diatomic molecules. We have calculated the dispersion spectrum as a function of temperature to determine the behavior of the librational and translational modes near the order-disorder tran-

sition. A relationship of the soft-mode behavior of the librins with the occurrence of the phase transition is established.

### III. MODEL POTENTIAL

We have studied the following model which is essentially the model considered by Hahn and Biem<sup>25</sup>: A linear lattice of dumbell molecules are allowed to have one translational and one librational degree of freedom. The Hamiltonian of the system is

$$\mathcal{H} = - \sum_i [(2I)^{-1}(\partial^2/\partial\theta_i^2) + (2M)^{-1}(\partial^2/\partial x_i^2)] + \frac{1}{2} \sum_{i,j} V(\theta_i, \theta_j, x_i, x_j), \quad (1)$$

where  $M$  is the molecular mass,  $I$  is the moment of inertia,  $x_i$  is the instantaneous position of molecule  $i$ , and  $\theta_i$  describes its instantaneous orientation with respect to a fixed coordinate system. Units where  $\hbar=1$  are used throughout. For the present model the intermolecular potential  $V$  is assumed to depend only on the relative coordinates  $x_{ij}=x_i-x_j$  and  $\theta_{ij}=\theta_i-\theta_j$ :

$$V(\theta_i, \theta_j, x_i, x_j) = V_1(x_{ij}) + V_2(\theta_{ij}, x_{ij}). \quad (2)$$

Following Plakida and Siklos,<sup>42</sup> a Morse potential is assumed for  $V_1$ ,

$$V_1(x) = \epsilon \{ \exp[-2\alpha_l(x-x_0)] - 2 \exp[-\alpha_l(x-x_0)] \}, \quad (3)$$

where  $\epsilon$ ,  $\alpha_l$ , and  $x_0$  are Morse potential parameters. The orientational part of the interaction potential is assumed to have the form<sup>10</sup>

$$V_2(\theta, x) = \frac{1}{2} \{ B \exp[-2\alpha_l(x-x_0)] - 2A \exp[-\alpha_l(x-x_0)] \} P_2(\cos\theta), \quad (4)$$

where  $A$ ,  $B$ ,  $\alpha_l$ , and  $x_0$  parameterize the  $\theta$ -dependent part of the interaction potential.

### IV. SELF-CONSISTENT PHONON APPROXIMATION

Within the framework of the self-consistent phonon approximation the eigenvalue equations have the form<sup>40-43</sup>

$$\omega_{k\lambda}^2 e_{k\lambda}^\alpha = \sum_j \sum_{\beta=1}^2 (I_\alpha I_\beta)^{-1/2} [1 - \exp(-ikx_{ij})] \times \langle \nabla_\alpha \nabla_\beta V(\theta_{ij}, x_{ij}) \rangle e_{k\lambda}^\beta. \quad (5)$$

The eigenfrequencies are  $\omega_{k\lambda}$  and the components of the polarization vectors are  $e_{k\lambda}^\beta$ . Here  $\mathbf{k}$  is the reciprocal lattice vector, and  $\lambda$  is the polarization index. The first sum runs over all sites of the linear chain. Here we have found it convenient to introduce the dimensionless gradients  $\nabla_1 = \partial/\partial\theta_{ij}$  and  $\nabla_2 = \partial/\partial X_{ij}$ , where  $X_{ij} = \alpha_l x_{ij}$ . The quantities  $I_\alpha$  are defined by  $I_1 = I$  and  $I_2 = \alpha_l^{-2} M$ .

For a linear chain with only nearest neighbor inter-

actions, Eq. (5) reduces to

$$\omega_{k\lambda}^2 e_{k\lambda}^\alpha = 2 \sum_{\beta=1}^2 (I_\alpha I_\beta)^{-1/2} (1 - \cos ka) \langle \nabla_\alpha \nabla_\beta V \rangle e_{k\lambda}^\beta, \quad (6)$$

where  $a$  is the nearest neighbor distance. These equations are easily solved for the eigenfrequencies and polarization vectors of the system. The frequencies are given by

$$\chi_{k\lambda}^2 = ([c_{11} + (I_1/I_2)c_{22}] + \{[c_{11} - (I_1/I_2)c_{22}]^2 + 4(I_1/I_2)c_{12}^2\}^{1/2})(1 - \cos ka), \quad (7)$$

where  $\chi_{k\lambda}$  is a reduced frequency

$$\chi_{k\lambda} = \omega_{k\lambda}/\Omega \quad (8)$$

with

$$\Omega^2 = 6A/I_1. \quad (9)$$

Here  $A$  is a parameter in the orientational part of the potential and  $I_1 = I$ , the moment of inertia of the molecules. The coefficients appearing in Eq. (7) are determined by

$$c_{11} = (1/6A) \langle \partial^2 V_2^2 / \partial \theta^2 \rangle, \quad (10)$$

$$c_{12} = (1/6A) \langle \partial^2 V_2 / \partial \theta \partial X \rangle, \quad (11)$$

$$c_{22} = (1/6A) (\langle \partial^2 V_1 / \partial X^2 \rangle + \langle \partial^2 V_2 / \partial X^2 \rangle). \quad (12)$$

Here the brackets  $\langle \rangle$  denote thermal averages, and we have put, in the nearest neighbor approximation,  $\theta = \theta_{ij}$  and  $X = X_{ij}$ . For convenience these subscripts shall be left off where they are not necessary for clarity.

The thermal averages of Eqs. (10), (11), and (12) are calculated from<sup>43</sup>

$$\langle V(\theta, x) \rangle = [(\pi)^2 \det \mathbf{D}^{ij}]^{-1} \int du_1 \int du_2 V(\theta_e + u_1, x_e + u_2) \times \exp[-\frac{1}{2} \mathbf{u} \cdot (\mathbf{D}^{ij})^{-1} \cdot \mathbf{u}], \quad (13)$$

where  $\mathbf{u} = (u_1, u_2)$  and  $\mathbf{D}^{-1}$  is the inverse of the displacement-displacement correlation  $\mathbf{D}$  with respect to the  $2 \times 2$  vector space. The quantities  $\theta_e$  and  $x_e$  are the equilibrium values of  $\theta_{ij}$  and  $x_{ij}$ , respectively. We identify the subscript 1 with the  $\theta$  components and the subscript 2 with the  $x$  components of  $\mathbf{u}$  and  $\mathbf{D}$ . The averages (10)–(12) can be calculated from Eq. (13) analytically. The useful relations are

$$\langle \exp(-\alpha_l x) \rangle = \exp(-X_e) \exp(\frac{1}{2} \mathcal{D}_{22}), \quad (14)$$

$$\langle \exp(-\alpha_l x) \rangle = \exp(-\gamma X_e) \exp(\frac{1}{2} \gamma^2 \mathcal{D}_{22}), \quad (15)$$

$$\left\langle \exp(-\alpha_l x) \frac{\cos 2\theta}{\sin} \right\rangle = \exp(-\gamma X_e) \times \exp(\frac{1}{2} \gamma^2 \mathcal{D}_{22} - 2\mathcal{D}_{11}) \frac{\cos}{\sin} (2\theta_e - 2\gamma \mathcal{D}_{12}). \quad (16)$$

Here  $\gamma = \alpha_l / \alpha_t$  and  $X_e = \alpha_l a$ , where  $a$  is the equilibrium lattice constant which is determined in a manner discussed below. The components of the matrix  $\mathcal{D}$  are related to the components of the displacement-dis-

placement correlation  $\mathfrak{D}$  by

$$\mathfrak{D}_{11} = D_{11}, \mathfrak{D}_{12} = \mathfrak{D}_{21} = \alpha_l D_{12}, \mathfrak{D}_{22} = \alpha_l^2 D_{22}. \quad (17)$$

With the help of Eqs. (14)–(17) one finds that the coefficients (10)–(12) are given by

$$\begin{aligned} c_{11} = & \frac{1}{2} \exp[-\gamma(X_e - X_0)] \exp(\frac{1}{2}\gamma^2 \mathfrak{D}_{22} - 2\mathfrak{D}_{11}) \\ & \times \cos(2\theta_e - 2\gamma \mathfrak{D}_{12}) - \frac{1}{4}(B/A) \exp[-2\gamma(X_e - X_0)] \\ & \times \exp(2\gamma^2 \mathfrak{D}_{22} - 2\mathfrak{D}_{11}) \cos(2\theta_e - 4\gamma \mathfrak{D}_{12}), \end{aligned} \quad (18)$$

$$\begin{aligned} c_{12} = & -\frac{1}{4}\gamma \exp[-\gamma(X_e - X_0)] \exp(\frac{1}{2}\gamma^2 \mathfrak{D}_{22} - 2\mathfrak{D}_{11}) \\ & \times \sin(2\theta_e - 2\gamma \mathfrak{D}_{12}) + \frac{1}{4}\gamma(B/A) \exp[-2\gamma(X_e - X_0)] \\ & \times \exp(2\gamma^2 \mathfrak{D}_{22} - 2\mathfrak{D}_{11}) \sin(2\theta_e - 4\gamma \mathfrak{D}_{12}), \end{aligned} \quad (19)$$

$$\begin{aligned} c_{22} = & \frac{1}{3}(\epsilon/A) \exp[-(X_e - X_0)] \{2 \exp[-(X_e - X_0)] \\ & \times \exp(2\mathfrak{D}_{22}) - \exp(\frac{1}{2}\mathfrak{D}_{22})\} \\ & - (1/24)\gamma^2 e \exp[-\gamma(X_e - X_0)] \\ & \times [3 \exp(\frac{1}{2}\gamma^2 \mathfrak{D}_{22} - 2\mathfrak{D}_{11}) \cos(2\theta_e - 2\gamma \mathfrak{D}_{12}) \\ & + \exp(\frac{1}{2}\gamma^2 \mathfrak{D}_{22}) + \frac{1}{12}\gamma^2(B/A) \exp[-2\gamma(X_e - X_0)] \\ & \times [3 \exp(2\gamma^2 \mathfrak{D}_{22} - 2\mathfrak{D}_{11}) \cos(2\theta_e - 4\gamma \mathfrak{D}_{12}) \\ & + \exp(2\gamma^2 \mathfrak{D}_{22})], \end{aligned} \quad (20)$$

where  $X_0 = \alpha_l x_0$ .

Finally, the dimensionless displacement-displacement correlation is given by<sup>43</sup>

$$\begin{aligned} \mathfrak{D}_{\alpha\beta}^{ij} = & (1/N) \sum_{k,\lambda} [1 - \exp(ikx_{ij})] e_k^\alpha e_{k\lambda}^\beta (I_\alpha I_\beta)^{-1/2} \\ & \times \omega_{k\lambda}^{-1} \coth(\omega_{k\lambda}/2kT), \quad \beta = 1, 2. \end{aligned} \quad (21)$$

For a linear chain the nearest neighbor displacement-displacement correlation reduces to

$$\begin{aligned} \mathfrak{D}_{\alpha\beta} = & (I_1 Q/N) \sum (1 - \cos ka) e_{k\lambda}^\alpha e_{k\lambda}^\beta (I_\alpha I_\beta)^{-1/2} X_{k\lambda}^{-1} \\ & \times \coth(X_{k\lambda}/2\tau), \quad \beta = 1, 2, \end{aligned} \quad (22)$$

where

$$Q = (I_1 \Omega)^{-1} \quad (23)$$

and

$$\tau = kT/\Omega, \quad (24)$$

with  $\Omega$  defined by Eq. (9). It will be shown that large values of  $Q$  indicate that the molecules are primarily rotating, while small values of  $Q$  indicate oscillatory motion. For diatomic molecular crystals  $Q$  ranges from about 10 for the light molecular species to less than 0.1 for the heavier ones like  $N_2$ . The quantity  $\tau$  is a reduced temperature. The reduced phonon and libron frequencies  $X_{k\lambda}$  are given by Eq. (7).

The equilibrium lattice constant  $a$  at zero pressure is determined by requiring that the average force acting on a molecule vanish:

$$\langle \partial V / \partial X | X_e \rangle = 0, \quad (25)$$

$$\langle \partial V / \partial \theta | \theta_e \rangle = 0. \quad (26)$$

These conditions are equivalent to minimizing the free energy with respect to the parameters  $X_e$  and  $\theta_e$ .

The numerical calculation of the phonon frequencies now involves the iteration of equations (7), (18), (19), (20), and (22) together with the equilibrium conditions (25) and (26). These equations are iterated in the order listed. The results are shown in Sec. VI.

## V. ANHARMONIC CORRECTIONS

The cubic anharmonic energy shifts and lifetimes of the phonons and librations can be calculated in the manner discussed by Plakida and Siklos<sup>42</sup> for the monatomic linear chain. The corrected self-consistent frequencies  $\epsilon_{k\lambda}$  are found from Eq. (31) of Ref. 42:

$$\epsilon_k^2 = \omega_k^2 + 2\omega_k \Delta_k(\epsilon_k), \quad (27)$$

where

$$\Delta_k(\epsilon_k) = \text{Re}[\pi_k(\epsilon_k)]. \quad (28)$$

We have used the notation of Plakida and Siklos where  $k = (\mathbf{k}, \lambda)$ . The self-energy operator is given by

$$\pi_k(\omega) = \sum_{p,q} |\tilde{V}_3(-k, p, q)|^2 \frac{1}{2} \left( (N_p + N_q) \frac{\omega_p + \omega_q}{\omega^2 - (\omega_p + \omega_q)^2} - (N_p - N_q) \frac{\omega_p - \omega_q}{\omega^2 - (\omega_p - \omega_q)^2} \right). \quad (29)$$

Here

$$N_p = (\omega_p / \epsilon_p) \coth(\frac{1}{2}\beta\epsilon_p), \quad (30)$$

where  $\beta = 1/kT$  and, from Eq. (21) of Ref. 42.

$$\begin{aligned} \tilde{V}_3(k_1, k_2, k_3) = & N^{-3/2} \Delta(k_1 + k_2 + k_3) \sum_{l,m,n} \sum_{\alpha,\beta,\gamma} \exp(ik_1 l + ik_2 m + ik_3 n) e_{k_1}^\alpha e_{k_2}^\beta e_{k_3}^\gamma (8M_\alpha M_\beta M_\gamma \omega_{k_1} \omega_{k_2} \omega_{k_3})^{-1/2} \\ & \langle \nabla_\alpha^l \nabla_\beta^m \nabla_\gamma^n U \rangle. \end{aligned} \quad (31)$$

The quantity  $\Delta(k)$  is defined by

$$\begin{aligned} \Delta(\mathbf{k}) = & 1, \quad \text{if } \mathbf{k} = 0, \text{ or a reciprocal lattice vector,} \\ & 0, \quad \text{otherwise.} \end{aligned} \quad (32)$$

The indices  $l, m, n$  indicate lattice positions, and we let  $\nabla_1^m = \partial/\partial\theta_m$  and  $\nabla_2^m = \partial/\partial x_m$ . The quantities  $M$  are defined by  $M_1 = I = I_1$  and  $M_2 = M = \alpha_l^2 I_2$ . Here  $U$  is the total potential energy of the system. We have again used the notation  $k_1 = (\mathbf{k}_1, \lambda_1)$ . The imaginary part of the self-energy (29) gives the half-widths of the phonons and librons:

$$\Gamma_k(\epsilon_k) = -\text{Im}[\pi_k(\epsilon_k + i\delta)], \quad \delta = 0+. \quad (33)$$

The results for the diatomic molecular chain are

$$\frac{\Delta_{k\lambda}(\chi_{k\lambda})}{\Omega} = \frac{Q}{9N} \mathcal{P} \sum_{\lambda', \lambda''} \sum_{k'} \sin^2 \frac{1}{2}(ka) \sin^2 \frac{1}{2}(k'a) \sin^2 \frac{1}{2}(k''a) \left( (N_{k'\lambda'} + N_{k''\lambda''}) \frac{\chi_{k'\lambda'} + \chi_{k''\lambda''}}{\chi_{k\lambda}^2 - (\chi_{k'\lambda'} + \chi_{k''\lambda''})^2} \right. \\ \left. - (N_{k'\lambda'} - N_{k''\lambda''}) \frac{\chi_{k'\lambda'} - \chi_{k''\lambda''}}{\chi_{k\lambda}^2 - (\chi_{k'\lambda'} - \chi_{k''\lambda''})^2} \right) (\chi_{k\lambda} \chi_{k'\lambda'} \chi_{k''\lambda''})^{-1} [F_3(-k, \lambda; k', \lambda'; k'', \lambda'')]^2, \quad (34)$$

where  $\mathcal{P}$  denotes the principal part,  $k'' = k - k' + K$ , with  $K$  equal to zero or a reciprocal lattice vector. The sums  $F_3$  are found from

$$F_3(-k, \lambda; k', \lambda'; k'', \lambda'') = I^{3/2} A^{-1} \sum_{\alpha, \beta, \gamma} e_{-k\lambda}^\alpha e_{k'\lambda'}^\beta e_{k''\lambda''}^\gamma (M_\alpha M_\beta M_\gamma)^{-1/2} \langle \nabla_\alpha \nabla_\beta \nabla_\gamma V \rangle, \quad \alpha, \beta, \gamma = 1, 2, \quad (35)$$

where the gradients are taken with respect to the relative coordinates  $\theta$  and  $x$ , and  $V$  is the two-body interaction potential (2).

Similarly, the linewidths are given by

$$\Gamma_{k\lambda}(\chi_{k\lambda}) = (4\pi Q/9N) \sum_{\lambda, \lambda'} \sum_{k'} [F_3(-k, \lambda; k', \lambda'; k'', \lambda'')]^2 [N_{k'\lambda'} \chi_{k'\lambda'} + N_{k''\lambda''} \chi_{k''\lambda''} + \eta(\chi_{k\lambda}^2 - \chi_{k'\lambda'}^2 - \chi_{k''\lambda''}^2) \\ \times (N_{k'\lambda'} \chi_{k'\lambda'} + N_{k''\lambda''} \chi_{k''\lambda''})] \chi_{k\lambda}^{-1} \sin^2 \frac{1}{2}(ka) \sin^2 \frac{1}{2}(k'a) \sin^2 \frac{1}{2}(k''a) \\ \times \delta[\chi_{k\lambda}^4 - 2\chi_{k\lambda}^2(\chi_{k'\lambda'}^2 + \chi_{k''\lambda''}^2) + (\chi_{k'\lambda'}^2 - \chi_{k''\lambda''}^2)^2], \quad (36)$$

where  $\eta$  is a step function defined by

$$\eta(\omega) = \begin{cases} 1, & \omega > 0, \\ -1, & \omega < 0. \end{cases} \quad (37)$$

Here  $k''$  is defined as for Eq. (34), and  $F_3$  is given by Eq. (35).

The first-order corrections to the energy shifts and linewidths are then given by Eqs. (34)–(37). In the present work we have limited ourselves to the first-order corrections. Renormalized frequencies can in principle be obtained from Eq. (27) if one replaces  $\omega_{k\lambda}$  by  $\epsilon_{k\lambda}$  in the iterative equations of Sec. IV in the manner indicated by Plakida and Siklos.<sup>42</sup> The phonon frequencies are usually identified as the poles of the displacement-displacement function. The effect of the cubic anharmonic terms will be considered in the next section.

## VI. RESULTS

We discuss three cases. The first one corresponds to diatomic molecules with one rotational degree of freedom but with their centers fixed on rigid lattice points. For the second case the parameters of the potentials (3) and (4) were chosen to reflect the intermolecular potential of a simple diatomic molecular crystal such as solid nitrogen. The third case represents the case of a molecular crystal with very strong orientational coupling.

### A. Rigid Lattice Model

For the rigid lattice model we have chosen  $\epsilon = 0$ ,  $\alpha_l = 0$ ,  $B = 0$ , and  $\alpha_t = 0$ . The interaction potential then has the same form as the one chosen by Krieger and James<sup>10</sup>:

$$V(\theta_{ij}) = -AP_2(\cos\theta_{ij}). \quad (38)$$

The iterative equations of Sec. IV are then no longer a function of the relative translational coordinate  $X_{ij}$ .

The equilibrium value for  $\theta_{ij}$  is found to be zero for the potential (38). The iterative equations (7) and (18)–(22) are then solved with the potential parameters as specified by the potential in (38). The results are shown in Fig. 1. Shown there is reduced libron frequency  $\mathfrak{X}_{k1}$  for  $k = \pi/2a$  is plotted versus temperature for several values of  $Q$ . It can be seen that if  $Q$ , which describes the rotational or oscillatory nature of the motion, becomes larger than some critical  $Q_c$ , libration will no longer occur and all molecules will rotate. The critical value of  $Q$  is  $Q_c = \pi/2\sqrt{2}e = 0.4086$ .

Previous descriptions of the temperature dependence of the properties of molecular crystals have been given in terms of the molecular field approximation.<sup>10–14</sup> However, the molecular field approximation is not a limiting case of the self-consistent libron theory. For the libron theory the average kinetic energy is always equal to the average potential energy, whereas for the molecular field theories<sup>10–14</sup> there is no kinetic energy term. However, the two theories can be compared in the region where they can both be applied, that is, the

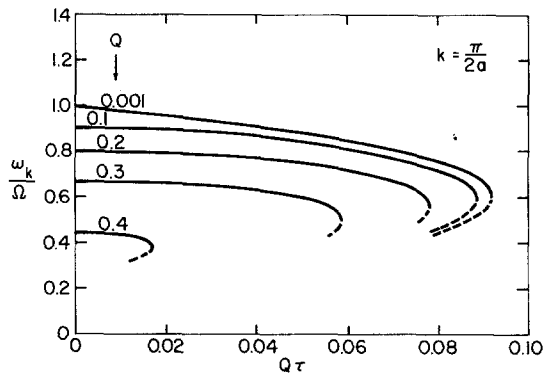


FIG. 1. The temperature dependence of the libron frequency for a linear chain of diatomic molecules on a rigid lattice with  $P_2$  coupling for a range of values of  $Q$ . The quantities  $Q$ ,  $\Omega$ , and  $\tau$  are defined by Eqs. (9), (23), and (24), respectively. The stable solutions are shown by the solid lines, a part of the unstable solutions by the dashed lines.

case when the molecules are primarily oscillating and  $Q$  is small.

For a potential of the form (38), Krieger and James<sup>10</sup> find a first-order phase transition at  $kT^* = 0.2228 Az$ , where  $z$  is the number of nearest neighbors. For  $z=2$  the molecular field theory would predict an orientational order-disorder transition at  $kT^*/A = 0.4456$ . In the limit as  $Q$  approaches zero the iterative equations in Sec. IV can be solved analytically. For small  $Q \geq 0$ , one finds that the librons become unstable above a temperature given by  $kT_c \leq 3/(2e) = 0.5518$ . For small  $Q$  the ordering temperature predicted by the molecular field theory is thus of the same order of magnitude as the temperature at which the librational oscillations cease to exist. For nonzero  $Q$  this critical temperature is reduced until the value  $Q_c = 0.4086$  is reached where  $kT_c$  is zero, and librational motions can no longer occur.

The above calculations can be repeated for  $P_1$  coupling<sup>10</sup> where the interaction potential has the form

$$V(\theta) = -AP_1(\cos\theta). \quad (39)$$

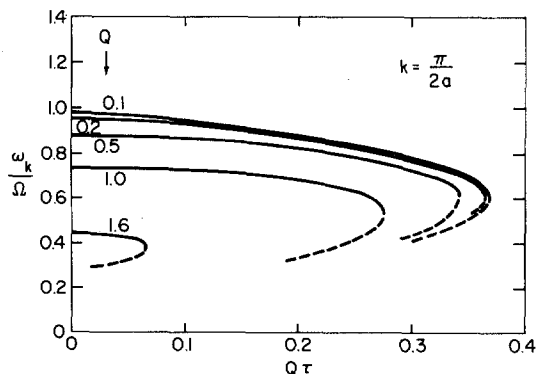


FIG. 2. The temperature dependence of the libron frequency for a linear chain of diatomic molecules on a rigid lattice with  $P_1$  coupling for a range of values of  $Q$ . The quantities  $Q$ ,  $\Omega$ , and  $\tau$  are defined by Eqs. (9), (23), and (24), respectively. The stable solutions are shown by the solid lines, a part of the unstable solutions by the dashed lines.

The results are similar to the case of  $P_2$  coupling and are shown in Fig. 2. For  $P_1$  coupling,  $Q_c = \sqrt{2} \pi/e = 1.634$ . The Krieger and James<sup>10</sup> molecular field critical temperature is  $kT^*/A = 2/3$  and the libron critical temperature is  $kT_c/A \leq 6/e$  for the case of  $Q \geq 0$ .

The above examples illustrate the approximate nature of the self-consistent phonon theory. In contrast to models B and C discussed below, model A is a one-dimensional system. It is well known that one-dimensional systems should not exhibit phase transitions.<sup>52</sup> The general model discussed in this paper has two degrees of freedom, one translational and one librational. The internal librational degree of freedom can

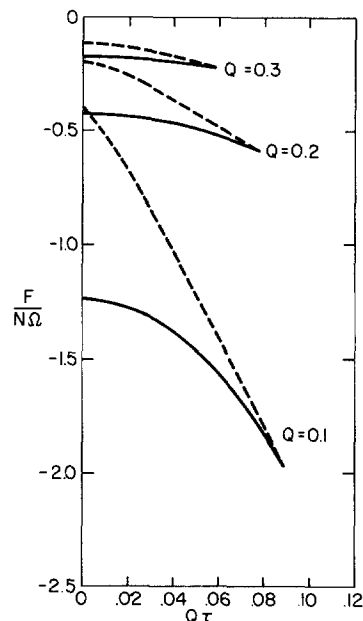


FIG. 3. The temperature dependence of the free energy per molecule of a linear chain of diatomic molecules on a rigid lattice with  $P_2$  coupling for several values of  $Q$ . The quantities  $Q$ ,  $\Omega$ , and  $\tau$  are defined by Eqs. (9), (23), and (24), respectively. The stable solutions are indicated by the solid lines, the unstable solutions by the dashed lines.

assume an infinite number of values, as in this case of a continuous variable, and the model becomes a two-dimensional one. This fact is easy to see for lattice models; the configurations of a horizontal row of a two-dimensional lattice can be put in correspondence with internal states of one site of a vertical one-dimensional array.

In Figs. 1 and 2 we have indicated the fact that two possible solutions to the iterative equations of Sec. IV exist, giving two possible solutions for the libron frequencies  $\omega_{kl}$ . The stable libron frequency can be determined by calculating the free energy of the system, as given by Eq. (17) of Ref. 43. The free energy per molecule for the case of  $P_2$  coupling is shown in Fig. 3 for several values of  $Q$ . The stable solution is shown by the solid line, and the unstable solution by the dashed

line. The corresponding stable and unstable solutions for the libron frequencies for  $P_2$  and  $P_1$  coupling are shown in the same manner in Figs. 1 and 2, respectively.

### B. Weak Orientational Coupling

This second model is intended to represent a molecular crystal with relatively weak orientational coupling, as, for example, solid nitrogen. We have chosen the case  $Q=0.1$ ,  $\epsilon/A=3.0$ ,  $I_1/I_2=0.6$ ,  $\gamma=1.0$  and  $B=0$ . The equations (7), (18)–(20), and (22) are again iterated numerically starting with an initial guess for the coefficients  $c_{11}$ ,  $c_{12}$ , and  $c_{22}$ . One proceeds with the iteration of these equations until successive values for the reduced frequencies are consistent within one part in  $10^5$ . The temperature dependence of the phonon and libron frequencies is shown in Fig. 4. This figure shows

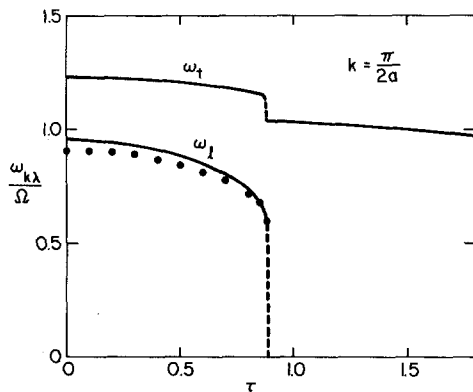


FIG. 4. The temperature dependence of the phonon ( $\omega_t$ ) and libron ( $\omega_l$ ) frequencies for model B (weak orientational coupling) at  $k=\pi/(2a)$  is given by the solid lines. The points indicate the corresponding libron frequencies for the rigid lattice model A with  $P_2$  coupling. The potential parameters are  $Q=0.1$ ,  $\epsilon/A=3.0$ ,  $I_1/I_2=0.6$ ,  $\gamma=1.0$ , and  $B=0$ . The quantities  $\Omega$  and  $\tau$  are defined by Eqs. (23) and (24).

$\omega_{k1}$  and  $\omega_{k2}$  for  $k=\pi/(2a)$ . Very similar results are found for all other values of the reciprocal lattice vector  $k$ ; the  $k$  dependence of  $\omega_{k\lambda}$  is shown explicitly by Eq. (7). It is seen that the librations are only stable below a critical temperature  $T_c$ . The behavior the libron frequencies for model B is qualitatively similar to the rigid lattice model A. For comparison the libron frequencies for model A with  $P_2$  coupling is shown by the dots in Fig. 4. It is seen, that although for the present model the coupling between phonons and librations is weak, the libron frequencies are affected somewhat by the presence of phonons. For this model the effect is to raise the libron frequencies slightly from their rigid lattice values. Figure 4 also shows a discontinuous change in the phonon frequencies at the transition temperature  $T_c$ .

Similar changes in the positional and orientational order parameters were also predicted by Pople and Karasz,<sup>20</sup> who applied the Bragg-Williams approximation to the problem of translational and orientational ordering in molecular crystals. First-order transitions

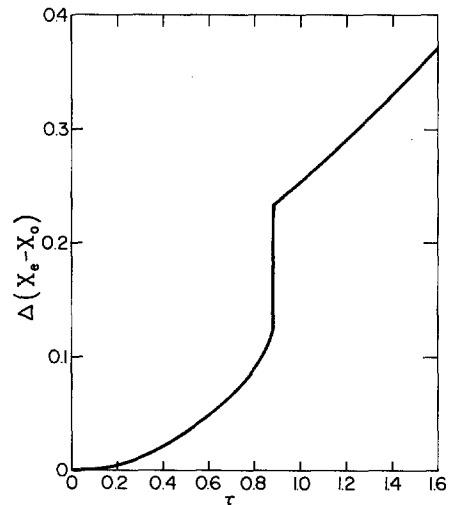


FIG. 5. The change in the lattice constant  $X_e - X_0$  from its value at zero temperature is plotted versus temperature for model B. Here  $X_e$  is the dimensionless equilibrium lattice constant defined in Sec. IV,  $X_0$  is a dimensionless Morse potential parameter also defined in Sec. IV, and  $\tau$  is given by Eq. (24). The potential parameters are the same as in Fig. 4.

are also obtained with the one-dimensional model for correlated molecular rotation of Casey and Runnels.<sup>48</sup> The temperature dependence of the libron and phonon frequencies is qualitatively the same as observed by Raman and infrared scattering.<sup>34–38</sup>

The change in the lattice constant is plotted versus temperature in Fig. 5. The qualitative behavior of the thermal expansion is the same as measured for solid nitrogen. The free energy, specific heat, and other ther-

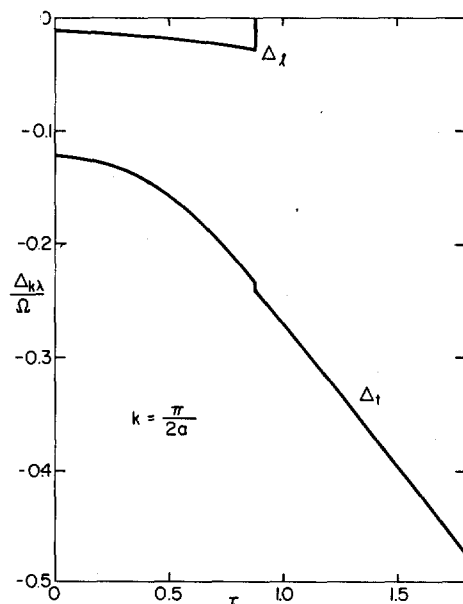


FIG. 6. The temperature dependence of the cubic anharmonic energy shift for the librations ( $\Delta_l$ ) and the phonons ( $\Delta_t$ ) at  $k=\pi/(2a)$  for model B. The quantities  $\Omega$  and  $\tau$  are defined by Eqs. (23) and (24). The potential parameters are the same as in Fig. 4.



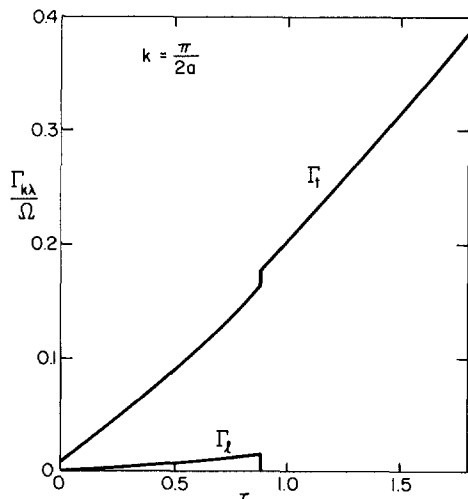


FIG. 7. The temperature dependence of the cubic anharmonic linewidths for the librons ( $\Gamma_l$ ) and the phonons ( $\Gamma_p$ ) at  $k = \pi/(2a)$  for model B. The quantities  $\Omega$  and  $\tau$  are defined by Eqs. (23) and (24). The potential parameters are the same as in Fig. 4.

modynamic properties of the system can be calculated in the same manner as outlined for potential model A. They also show an anomaly at the libron instability temperature which is assumed to correspond to the observed order-disorder transition.

The cubic anharmonic energy shifts of the librons and phonons are shown versus temperature in Fig. 6. These energy shifts are calculated from Eqs. (34) and (35). Because of our choice of the orientational coupling (4), the libron energy shifts are very small. This effect is due to the symmetry of the  $P_2(\cos\theta)$  term; the libron energy shifts arise only from their coupling to the phonons. This behavior of the energy shifts is due to our choice of the orientational interaction and does not occur for more realistic potentials. The linewidths are shown in Fig. 7 as a function of temperature. Figures 6 and 7 show  $\Delta_{k\lambda}$  and  $\Gamma_{k\lambda}$  for  $\lambda = 1, 2$  and  $k = \pi/(2a)$ . The energy shifts and linewidths have strong  $k$  dependence with  $\Delta_{k\lambda}$  and  $\Gamma_{k\lambda}$  generally increasing as  $k$  is increased.

To obtain the renormalized frequencies  $\epsilon_{k\lambda}$ , as discussed in Sec. V, one needs to reiterate Eqs. (7), (18)–(20), and (21) substituting  $\epsilon_{k\lambda}$  for  $\omega_{k\lambda}$  in the manner shown by Plakida and Siklos.<sup>42</sup> When this is done, the calculated frequencies change considerably from their values predicted by the self-consistent phonon approximation, especially at the higher temperatures. The calculation of the renormalized frequencies will be described elsewhere.

### C. Strong Orientational Coupling

The third model was chosen to represent a molecular crystal with strong orientational forces. An example of such a molecular crystal is the solid phase of a liquid crystal. The calculations follow in the same manner as

outlined for model B. The choice of parameters for model C is  $Q=0.1$ ,  $\epsilon/A=0.3$ ,  $I_1/I_2=1.0$ ,  $\gamma=0.2$ , and  $B/A=1.0$ . In addition we have added a crystalline field term of the form

$$V_c = -C \sum_i P_2(\cos\theta_i) \quad (40)$$

to the total Hamiltonian (1). For the present example we have chosen  $C/A=1/2$ . The present formalism is easily extended to include the potential (40) into the Hamiltonian (1). The results for the temperature-dependent phonon and libron frequencies are shown in Fig. 8. For model C both librons and phonons become unstable at the same temperature  $T_c$ . Lattice periodicity is lost above the temperature  $T_c$ . We have therefore not attempted to describe the librational excitations in the liquid crystalline phase. A description of the liquid crystalline state can be given by averaging the interaction (2) over intermolecular separations.<sup>15</sup>

## VII. CONCLUSIONS

The linear chain models examined in the present paper all show that the librational modes of a molecular crystal become unstable above a critical temperature  $T_c$ . It is found that molecular crystals can be classified according to Pauling's limits, that is, as either primarily oscillating or rotating. Only the oscillatory or librational motion can be described by the self-consistent phonon approximation. We have introduced the parameter  $Q$  to measure the amount of rotation. For small values of  $Q$ , when the motion is primarily oscillatory, we have compared our results with those of the molecular field approximations which also treat the orientational ordering of molecules on rigid lattices. For small values of  $Q$  the libron instability temperature is roughly the same as the orientational ordering temperature predicted

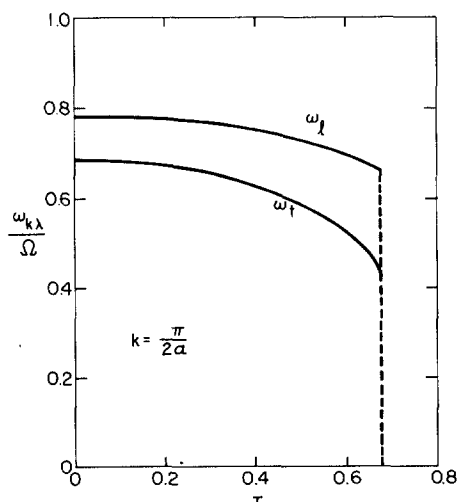


FIG. 8. The temperature dependence of the phonon ( $\omega_p$ ) and libron ( $\omega_l$ ) frequencies for model C (strong orientational coupling) at  $k = \pi/(2a)$ . The potential parameters are  $Q=0.1$ ,  $\epsilon/A=0.3$ ,  $B/A=1.0$ ,  $I_1/I_2=1.0$ ,  $\gamma=0.2$ , and  $C/A=0.5$ . The quantities  $\Omega$  and  $\tau$  are defined by Eqs. (23) and (24).

by the molecular field theory.<sup>10-15,20</sup> Within the framework of the self-consistent phonon approximation, the present models are in qualitative agreement with the observed temperature-dependent behavior of diatomic molecular crystals. It is hoped that this paper will point the way towards more realistic calculations of the thermodynamic properties of molecular crystals using the self-consistent phonon approximation. At this point it is difficult to judge the accuracy of the self-consistent phonon approximation until a detailed comparison with experiment can be made.

A detailed calculation of the temperature dependence of the libron and phonon frequencies, using the self-consistent phonon approximation, would therefore be a valuable addition to the understanding of the thermodynamic properties of the simple diatomic molecular crystals. Detailed measurements of the phonon and libron frequencies and intensities in the neighborhood of the orientational ordering temperatures of these crystals would shed additional light on the soft-mode behavior of these vibrational excitations. A comparison of theory and experiment must of course depend on the accuracy of the chosen intermolecular potentials.

#### ACKNOWLEDGMENT

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