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Phonons in Quantum Solids With Defects

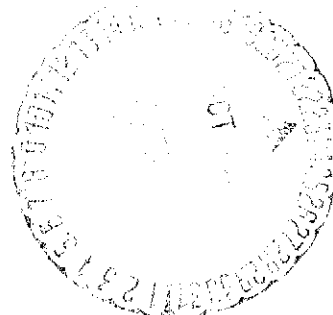
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PREFACE

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Dr. Jacobi is a NASA-NRC Senior Resident Research Associate.

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ABSTRACT

A formalism is developed for temperature-dependent, self-consistent phonons in quantum solids with defects. Lattice vacancies and interstitials in solid helium and metallic hydrogen, as well as electronic excitations in solid helium, are treated as defects that modify properties of these systems. The information to be gained from the modified phonon spectrum is discussed.

I. INTRODUCTION

In this report we are concerned with phonon properties of quantum solids with defects. We shall mainly be interested in two substances: (1) electronically excited solid helium, and (2) metallic hydrogen. The class of defects that will be considered consists of electronic excitations in solid helium and lattice imperfections (vacancies and interstitials) in both solid helium and metallic hydrogen. The two substances considered here are of great current interest, both scientifically and because of potential practical applications. In particular, the long lifetime (~ 2.3 h) and the high excitation energy (~ 20 eV) of the metastable 2^3S state of atomic helium suggest the possibilities that high concentrations of these states might be achieved, under suitable circumstances, in the liquid and solid phases of helium, and that they could be utilized for storing energy (Ref. 1). The collisional quenching of the excited 2^3S state is expected to be less severe in the solid than in the liquid, thereby singling out solid helium for primary consideration.

The existence of metallic hydrogen was first proposed by Wigner and Huntington (Ref. 2). It is presently believed that the bulk of the interior of Jupiter is metallic hydrogen, most likely in the liquid phase. An added impetus for the study of metallic hydrogen is the expectation that it is a high-temperature (100 to 300 K) superconductor (Refs. 3 and 4).

Quantum solids are characterized by the fact that the zero-point motion of constituent atoms occurs over a sizeable portion of the atomic cell. It is well established that solid helium is quantum. Although metallic hydrogen has also been assumed in the past to be quantum, recent work by Caron (Ref. 5) seems to indicate that this assumption is not entirely proper. It appears that metallic hydrogen falls somewhere in between classical and quantum solids; we shall refer to it as semiquantum. Special techniques have been developed to treat the highly anharmonic quantum solids, since standard approaches for classical solids, which are based on the harmonic approximation, simply break down for quantum solids, as manifested by phonon frequencies becoming imaginary (Ref. 6). Although classical methods may be marginally valid for metallic hydrogen, it is felt safer to treat it by quantum-solid techniques, as we shall do in this report.

As a result of the large zero-point motion of atoms in quantum solids, ~~certain lattice defects, such as vacancies and interstitials, are easily~~ excited, even at zero temperature. These defects are expected to have a marked effect on various physical properties of a quantum solid, especially on those that depend on the lattice structure. In particular, the phonon properties are expected to be strongly influenced by the defects. It is the primary purpose of this report to discuss phonons in quantum solids with defects, in the context of solid helium and metallic hydrogen. In the case of metallic hydrogen, the important defects we shall consider are vacancies and interstitials. In the case of solid helium, our primary interest is electronic excitations, treated as lattice imperfections; however, our discussion will be sufficiently general to include also the "normal" lattice defects, vacancies and interstitials.

Most of the work on defects in lattices has been done for classical solids (Ref. 7). Theoretical studies of defects in quantum solids were initiated around 1970, and have been mostly concerned with two problems. The first, in analogy to the classical case, is concerned with determining the modifications to the phonon spectrum due to various types of defects. Varma (Ref. 8) considered a single isotopic substitution, and Aksenov (Ref. 9) studied finite concentrations of static vacancies. Our intent is to generalize the approaches of these papers to treat situations relevant to electronically excited helium and metallic hydrogen at finite temperatures. The second problem that has been studied in the past is concerned with using a collective-excitation approach to treat lattice defects and their motion in quantum solids (Refs. 10 through 13). In this report we shall not treat this problem.

II. SELF-CONSISTENT PHONONS IN A PERFECT QUANTUM SOLID

To find the phonon spectrum of a system with a not too high defect concentration it is very convenient to use the phonon spectrum of the corresponding perfect and undistorted crystal. The periodicity of the latter can be used advantageously to define normal coordinates and greatly reduce the diagonalization problem. We review here the basic results on self-consistent phonons (for exhaustive reviews, see Refs. 14 through 16) in a

form that will be convenient for treating the defect problem. To introduce the notation we first briefly summarize the derivation of phonons in a perfect, classical system (Ref. 17).

A. CLASSICAL LATTICE DYNAMICS

The basic assumption of small vibrational amplitudes allows one to perform a series expansion of the potential in the displacements and to truncate the series after the dominant, quadratic terms. The original Hamiltonian is then replaced by the approximate, harmonic Hamiltonian

$$H_h = \frac{1}{2} \sum_{i\alpha} M_i \dot{u}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha, j\beta} \Phi_{j\beta}^{i\alpha} u_{i\alpha} u_{j\beta} \quad (1)$$

where

$$\Phi_{j\beta}^{i\alpha} = \left(\frac{\partial^2 V}{\partial u_{i\alpha} \partial u_{j\beta}} \right)_{\text{eq.}}$$

are the force constants derived from the original potential, and $\alpha, \beta = x, y, z$. The classical equations of motion of this Hamiltonian are, of course, linear:

$$M_i \ddot{u}_{i\alpha} = - \sum_{j\beta} \Phi_{j\beta}^{i\alpha} u_{j\beta} \quad (2)$$

The index i (or j) counts the atoms and is shorthand for the pair $m\mu$ (or $n\nu$), where the Roman letter denotes the unit cell and the Greek letter a site in the cell (allowing for more generality than a Bravais lattice). The system shown in Eqs. (2) can be greatly uncoupled by assuming the following space and time dependence of the displacements:

$$u_{m\mu\alpha} = \frac{U_{\mu\alpha}(\mathbf{k})}{\sqrt{M_\mu}} e^{i[\mathbf{k} \cdot \mathbf{R}_{m\mu} - \omega(\mathbf{k})t]} \quad (3)$$

where the wave vector \mathbf{k} reflects the lattice periodicity. Note that masses M_μ do not depend on the cell index m . The system shown in Eqs. (2) now becomes

$$\omega^2(\mathbf{k}) U_{\mu\alpha}(\mathbf{k}) = \sum_{\nu\beta} D_{\nu\beta}^{\mu\alpha}(\mathbf{k}) U_{\nu\beta}(\mathbf{k}) \quad (4)$$

where

$$D_{\nu\beta}^{\mu\alpha}(\mathbf{k}) \equiv \frac{1}{\sqrt{M_\mu M_\nu}} \sum_n \Phi_{n\nu\beta}^{m\mu\alpha} e^{i\mathbf{k} \cdot (\mathbf{R}_{n\nu} - \mathbf{R}_{m\mu})} \quad (5)$$

the so-called dynamic matrix, is the spatial Fourier transform of the force constant matrix. Let r denote the number of sites per unit cell. Comparing Eqs. (2) and (4), we see that the explicit introduction of lattice periodicity has greatly simplified the problem: while Eqs. (2) are a system of $3rN$ coupled equations (N being the number of unit cells in the system, practically infinity), Eqs. (4) consist of N systems (one for each \mathbf{k}) of only $3r$ coupled equations each. To each \mathbf{k} there correspond $3r$ roots, denoted by $\lambda = 1, \dots, 3r$. The corresponding eigenvectors of the dynamic matrix, $e_{\mu\alpha}(\mathbf{k}\lambda)$, the so-called polarization vectors, fulfill the orthogonality and closure relations

$$\left. \begin{aligned} \sum_{\mu\alpha} e_{\mu\alpha}^*(\mathbf{k}\lambda) e_{\mu\alpha}(\mathbf{k}\lambda') &= \delta_{\lambda\lambda'} \\ \sum_{\lambda} e_{\mu\alpha}^*(\mathbf{k}\lambda) e_{\nu\beta}(\mathbf{k}\lambda) &= \delta_{\mu\nu} \delta_{\alpha\beta} \end{aligned} \right\} \quad (6)$$

Once the dynamic matrix has been diagonalized (which is easily done because it is low dimensional), the harmonic Hamiltonian can be shown to be completely diagonal in the normal coordinates $Q(\mathbf{k}\lambda)$, related to the atomic displacements by

$$\left. \begin{aligned}
 u_{m\mu\alpha} &= \frac{1}{\sqrt{NM_\mu}} \sum_{\mathbf{k}\lambda} e_{\mu\alpha}(\mathbf{k}\lambda) Q(\mathbf{k}\lambda) e^{i\mathbf{k}\cdot\mathbf{R}_{m\mu}} \\
 Q(\mathbf{k}\lambda) &= \frac{1}{\sqrt{N}} \sum_{m\mu\alpha} \sqrt{M_\mu} e_{\mu\alpha}^*(\mathbf{k}\lambda) u_{m\mu\alpha} e^{-i\mathbf{k}\cdot\mathbf{R}_{m\mu}}
 \end{aligned} \right\} (7)$$

Indeed, substitution in Expansion (1) gives

$$H_h = \frac{1}{2} \sum_{\mathbf{k}\lambda} \left(\left| \dot{Q}(\mathbf{k}\lambda) \right|^2 + \omega(\mathbf{k}\lambda)^2 \left| Q(\mathbf{k}\lambda) \right|^2 \right) \quad (8)$$

which is, as expected, the Hamiltonian of uncoupled harmonic oscillators. This form is extremely important in the treatment of a quantum solid, since it allows one to write down explicitly approximate wave functions of the solid.

B. VARIATIONAL PRINCIPLE

The basic idea of self-consistent phonons in quantum solids, for which the atomic displacements are too large and hence the harmonic part of the Expansion (1) breaks down even as a zeroth-order approximation for a possible perturbation treatment, has been to use a variational approach. Instead of expanding, one is looking for the most general harmonic Hamiltonian (Expansion 1) that would best approximate the given system in some sense. The most common approach, systematically and successfully developed by Koehler (Refs. 18 and 19), has been to regard the effective force constants, or equivalent quantities, as variable parameters determined by minimizing the ground-state energy with respect to them. The energy is evaluated by averaging the given, anharmonic Hamiltonian over harmonic oscillator wave functions. Consequent minimization gives a self-consistent condition for the phonons, with the frequencies appearing not only explicitly as in Eq. (4), but also in the dynamic matrix.

Because we are interested in temperature-dependent self-consistent phonons (especially for metallic hydrogen), we have to replace the ground-state energy by the corresponding thermodynamic quantity, the free energy F , given by

$$e^{-\beta F} = \sum_n e^{-\beta E_n} = \text{Tr} e^{-\beta H}$$

where the summation is over all states of the system and $\beta = 1/kT$. The statistical operator, or density matrix, is given by

$$\rho = \frac{e^{-\beta H}}{\text{Tr} e^{-\beta H}}$$

The thermodynamic average of an operator O is

$$\langle O \rangle = \text{Tr} (\rho O) = \frac{\text{Tr} (O e^{-\beta H})}{\text{Tr} (e^{-\beta H})}$$

The extension of the zero-temperature, ground-state variational principle to finite temperatures is the thermodynamic Gibbs-Bogolyubov principle (for a proof and review see, for example, Ref. 20), which states that

$$\left. \begin{aligned} F \leq F_{\text{trial}} &= F_0 + \langle H - H_0 \rangle_0 \\ &\equiv F_0 + \frac{\text{Tr} \left[(H - H_0) e^{-\beta H_0} \right]}{\text{Tr} \left[e^{-\beta H_0} \right]} \end{aligned} \right\} (9)$$

where H_0 is a zeroth order Hamiltonian, conveniently chosen as a Hamiltonian for which the problem can be solved explicitly. For $T = 0$ the first and last terms in Eq. (9) cancel and the principle reduces to the

well-known variational principle. This variational principle will be used now to derive temperature-dependent, self-consistent phonons.

C. SELF-CONSISTENT PHONONS

To obtain the self-consistent phonons we first evaluate the trial free energy in Eq. (9) and then minimize it. The Hamiltonian is of the form

$$\begin{aligned}
 H &= T + V \\
 &= -\frac{\hbar^2}{2} \sum_{m\mu\alpha} \frac{1}{M_\mu} \frac{\partial^2}{\partial u_{m\mu\alpha}^2} + \frac{1}{2} \sum_{\substack{m\mu \\ n\nu}} v(|\mathbf{R}_{m\mu} + \mathbf{u}_{m\mu} - \mathbf{R}_{n\nu} - \mathbf{u}_{n\nu}|) \quad \left. \vphantom{\sum} \right\} \quad (10)
 \end{aligned}$$

and the zeroth order Hamiltonian, H_0 , is naturally chosen to be the harmonic Hamiltonian H_h in Eq. (1), which has the advantage that all thermodynamic quantities and averages can be evaluated explicitly. The kinetic energy terms cancel, and we are left with

$$F_{\text{trial}} = F_0 + \langle V - V_0 \rangle$$

It should be noted that in the case of solid helium the potential V appearing in Eq. (10) is not the usual interatomic potential (of the Lennard-Jones variety), but an effective potential that incorporates short-range correlation effects (Ref. 21). The point is that the potential that a pair of helium atoms in the lattice see is drastically modified by the surrounding atoms, so that the pair potential derived from gas data is a very poor description of the interatomic forces in the solid. In the case of metallic hydrogen, V is the screened ion-ion potential (Refs. 22, 5).

In terms of the normal coordinates (Eq. 7), which diagonalize the harmonic Hamiltonian (Eq. 8), the free energy is additive and the density matrix is multiplicative, and all necessary quantities are explicitly available for harmonic oscillators (see, for example, Ref. 23 or Ref. 24):

$$F_0 = \sum_{\mathbf{k}\lambda} F_{\mathbf{k}\lambda} = kT \sum_{\mathbf{k}\lambda} \ln \left(2 \sinh \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT} \right) \quad (11)$$

$$P_0 = \prod_{\mathbf{k}\lambda} \rho_{\mathbf{k}\lambda} = \prod_{\mathbf{k}\lambda} \left(\sqrt{\frac{\omega_{\mathbf{k}\lambda}}{2\pi\hbar \sinh \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT}}} e^{-\frac{\omega_{\mathbf{k}\lambda}}{\hbar} |Q(\mathbf{k}\lambda)|^2 \operatorname{tgh} \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT}} \right) \quad (12)$$

The averages of V and V_0 are given by

$$\langle V \rangle_0 = \prod_{\mathbf{k}\lambda} \left(\frac{A(\omega_{\mathbf{k}\lambda})}{\pi} \right)^{1/2} \int \prod_{\mathbf{k}\lambda} dQ_{\mathbf{k}\lambda} V e^{-\sum_{\mathbf{k}\lambda} A(\omega_{\mathbf{k}\lambda}) |Q_{\mathbf{k}\lambda}|^2} \quad (13)$$

$$\langle V_0 \rangle_0 = \frac{\hbar}{4} \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}\lambda} \operatorname{ctgh} \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT} \quad (14)$$

where

$$A(\omega_{\mathbf{k}\lambda}) = \frac{\omega_{\mathbf{k}\lambda}}{\hbar} \operatorname{tgh} \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT}$$

The result of Eq. (14) is obtained by averaging the square of the displacement of a single harmonic oscillator (see Eqs. 8 and 12). In the low-temperature limit each term gives $\hbar\omega/4$, which is the potential energy contribution to the zero-point energy. In the high-temperature limit, each term contributes $kT/2$, the expected classical result.

The trial free energy is given by combining Eqs. (11), (13), and (14). The resulting expression depends on all the $\omega_{\mathbf{k}\lambda}$, which are obviously related to the effective force constants in Eq. (1). It is convenient to regard

these frequencies as variational parameters, to be determined by imposing the condition

$$\frac{\partial F_{\text{trial}}}{\partial \omega_{\mathbf{k}\lambda}} = 0 \quad (15)$$

This procedure is similar to that employed by Morley and Kliever (Ref. 25) to derive zero-temperature, self-consistent phonons. The algebra is somewhat long, but straightforward, and the result is

$$0 = \frac{\hbar}{4} \left(\text{ctgh} \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT} + \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT} \frac{1}{\sinh^2 \frac{\hbar \omega_{\mathbf{k}\lambda}}{2kT}} \right) \left(1 - \frac{1}{\omega_{\mathbf{k}\lambda}^2} \left\langle \frac{\partial^2 V}{\partial Q_{\mathbf{k}\lambda} \partial Q_{\mathbf{k}\lambda}^*} \right\rangle_0 \right)$$

or

$$\omega_{\mathbf{k}\lambda}^2 = \left\langle \frac{\partial^2 V}{\partial Q_{\mathbf{k}\lambda} \partial Q_{\mathbf{k}\lambda}^*} \right\rangle_0 \quad (16)$$

This is the basic result of the variational self-consistent phonon approach, replacing second derivatives of the potential at equilibrium by thermodynamic averages of the second derivatives over harmonic density matrices. This system has to be solved self-consistently, as the thermodynamic average depends on all the frequencies. To relate this result to the corresponding classical result, Eqs. (4) and (5), we transform from normal coordinates to atomic displacements by means of Eq. (7). The result is formally similar to Eqs. (4) and (5) except that the dynamic matrix now becomes

$$\left\langle D_{\nu\beta}^{\mu\alpha}(\mathbf{k}) \right\rangle_0 = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_n \left\langle \frac{\partial^2 V}{\partial u_{m\mu\alpha} \partial u_{n\nu\beta}} \right\rangle_0 e^{i\mathbf{k} \cdot (\mathbf{R}_{n\nu} - \mathbf{R}_{m\mu})} \quad (17)$$

Both this and the classical dynamic matrix can be written in more detail, specifying properties of acoustic and optic modes, by writing the potential as a sum of pair potentials, as follows:

$$\frac{\partial^2 V}{\partial u_{m\mu\alpha} \partial u_{n\nu\beta}} = \left\{ \begin{array}{l} \frac{\partial^2 v_{m\mu, n\nu}}{\partial u_{m\mu\alpha} \partial u_{n\nu\beta}}, \quad m\mu \neq n\nu \\ \sum_{r\rho} \frac{\partial^2 v_{m\mu, r\rho}}{\partial u_{m\mu\alpha} \partial u_{m\mu\beta}}, \quad m\mu = n\nu \end{array} \right\} \quad (18)$$

Substituting this into the dynamic matrix, we get

$$\left\langle D_{\nu\beta}^{\mu\alpha}(\mathbf{k}) \right\rangle_0 = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_{r\rho} \left(\delta_{\mu\nu} - \delta_{\rho\nu} e^{i\mathbf{k} \cdot (\mathbf{R}_{r\rho} - \mathbf{R}_{m\mu})} \right) \left\langle \frac{\partial^2 v_{m\mu, r\rho}}{\partial u_{m\mu\alpha} \partial u_{m\mu\beta}} \right\rangle_0 \quad (19)$$

D. EVALUATION OF THERMODYNAMIC AVERAGE

The last step is to evaluate the thermodynamic average of the second derivative of the pair potential, and to reduce the multidimensional integral to a form that can be calculated. This is achieved by Koehler's method (Refs. 18 and 19) of expressing the density matrix Eq. (12) in terms of atomic displacements (resulting in correlated Gaussians) and consequent reduction of the multidimensional integral appearing in the thermodynamic average to a three-dimensional one, which can be evaluated numerically. We start by substituting Eq. (7) in Eq. (12), and Eq. (12) in Eq. (19), with the result

$$\left\langle \frac{\partial^2 v_{m\mu, n\nu}}{\partial u_{m\mu\alpha} \partial u_{m\mu\beta}} \right\rangle_0 = \left(\frac{\det G}{\pi^{3rN}} \right)^{1/2} \int (\Pi du) \frac{\partial^2 v_{m\mu, n\nu}}{\partial u_{m\mu\alpha} \partial u_{m\mu\beta}} e^{-\sum_{\substack{r\rho\gamma \\ s\sigma\delta}} G_{s\sigma\delta}^{r\rho\gamma} u_{r\rho\gamma} u_{s\sigma\delta}} \quad (20)$$

where the temperature-dependent correlation function is

$$G_{s\sigma\delta}^{r\rho\gamma} = \frac{1}{N} \sum_{k\lambda} \frac{\sqrt{M_\rho M_\sigma} \omega_{k\lambda}}{\hbar} \operatorname{tgh} \frac{\hbar \omega_{k\lambda}}{2kT} e_{\rho\gamma}^*(k\lambda) e_{\sigma\delta}(k\lambda) e^{i\mathbf{k} \cdot (\mathbf{R}_{s\sigma} - \mathbf{R}_{r\rho})} \quad (21)$$

Next, since the second derivative depends on the coordinates of two particles only, we can perform the integration over all coordinates but these two. For this it is convenient to partition the matrix G and its inverse G^{-1} into a six-dimensional block involving the indices of particles m_μ , $n\nu$, and the rest:

$$G = \begin{matrix} & m_\mu & n\nu \\ \begin{matrix} m_\mu \\ n\nu \end{matrix} & \left(\begin{array}{c|c} \mathbf{g} & \\ \hline & \end{array} \right) & \end{matrix}, \quad G^{-1} = \left(\begin{array}{c|c} \mathbf{h} & \\ \hline & \end{array} \right)$$

The result of the integration is (Ref. 18)

$$\left\langle \frac{\partial^2_{\nu} m_\mu, n\nu}{\partial u_{m_\mu\alpha} \partial u_{m_\mu\beta}} \right\rangle_0 = \frac{(\det \mathbf{h}^{-1})^{1/2}}{\pi^3} \int d\mathbf{u} \frac{\partial^2_{\nu} m_\mu, n\nu}{\partial u_{m_\mu\alpha} \partial u_{m_\mu\beta}} e^{-\mathbf{u} \mathbf{h}^{-1} \mathbf{u}}$$

where \mathbf{u} is a six-dimensional vector consisting of the components of \mathbf{u}_{m_μ} and $\mathbf{u}_{n\nu}$. Since G and G^{-1} are symmetric, \mathbf{h} and \mathbf{h}^{-1} have the block structure

$$\mathbf{h} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^T & \mathbf{A} \end{pmatrix}, \quad \mathbf{h}^{-1} = \begin{pmatrix} \mathbf{C} & \mathbf{D} \\ \mathbf{D}^T & \mathbf{C} \end{pmatrix}$$

with

$$\mathbf{C} = (\mathbf{A} - \mathbf{B} \mathbf{A}^{-1} \mathbf{B}^T)^{-1}, \quad \mathbf{D} = (\mathbf{B}^T - \mathbf{A} \mathbf{B}^{-1} \mathbf{A})^{-1}$$

For central force potentials the integral can be further reduced by introducing relative and center of mass coordinates

$$\mathbf{u}_{m\mu} = \mathbf{R} + \frac{1}{2} \mathbf{r}, \quad \mathbf{u}_{n\nu} = \mathbf{R} - \frac{1}{2} \mathbf{r}$$

$$\mathbf{u} \mathbf{h}^{-1} \mathbf{u} = 2 \mathbf{R}(\mathbf{C} + \mathbf{D}) \mathbf{R} + \frac{1}{2} \mathbf{r}(\mathbf{C} - \mathbf{D}) \mathbf{r}$$

The integration over \mathbf{R} is readily performed:

$$\left\langle \frac{\partial^2_{\mathbf{v}}}{\partial \mathbf{u}_{m\mu\alpha} \partial \mathbf{u}_{m\mu\beta}} \right\rangle_0 = \left(\frac{\det(\mathbf{C} - \mathbf{D})}{(2\pi)^3} \right)^{1/2} \int d\mathbf{r} \frac{\partial^2_{\mathbf{v}}(|\mathbf{R}_{m\mu} - \mathbf{R}_{n\nu} + \mathbf{r}|)}{\partial r_{\alpha} \partial r_{\beta}} e^{-\frac{1}{2} \mathbf{r}(\mathbf{C} - \mathbf{D}) \mathbf{r}} \quad (22)$$

This form is useful if the three-dimensional matrix $(\mathbf{C} - \mathbf{D})$ can be related to the correlation matrix \mathbf{G} (Eq. 21). Some matrix manipulation shows that $\mathbf{C} - \mathbf{D} = (\mathbf{A} - \mathbf{B})^{-1}$. \mathbf{A} and \mathbf{B} are the diagonal and off-diagonal blocks of the inverse of the correlation matrix \mathbf{G} . Fortunately, the latter can be inverted (despite its practically infinite dimension) by using the orthogonality and closure properties of the polarization vectors. It is readily verified that

$$(\mathbf{G}^{-1})_{n\nu\beta}^{m\mu\alpha} = \frac{1}{N} \sum'_{k\lambda} \frac{\hbar}{\sqrt{M_{\mu} M_{\nu}} \omega_{k\lambda}} \operatorname{ctgh} \frac{\hbar \omega_{k\lambda}}{2kT} e_{\mu\alpha}^*(k\lambda) e_{\nu\beta}(k\lambda) e^{i\mathbf{k} \cdot (\mathbf{R}_{n\nu} - \mathbf{R}_{m\mu})} \quad (23)$$

Defining the matrix $\mathbf{F} = (\mathbf{C} - \mathbf{D})^{-1} = \mathbf{A} - \mathbf{B}$ with elements $F(m\mu, n\nu)_{\alpha\beta} = (\mathbf{G}^{-1})_{m\mu\beta}^{m\mu\alpha} - (\mathbf{G}^{-1})_{n\nu\beta}^{m\mu\alpha}$ and collecting all the results, we obtain the self-consistent phonon scheme

$$\omega_{k\lambda}^2 e_{\mu\alpha}(k\lambda) = \sum_{\substack{r\rho \\ \nu\beta}} \frac{1}{\sqrt{M_{\mu} M_{\nu}}} \left(\delta_{\mu\nu} - \delta_{\rho\nu} e^{i\mathbf{k} \cdot (\mathbf{R}_{r\rho} - \mathbf{R}_{m\mu})} \right) \left\langle \frac{\partial^2_{\mathbf{v}}}{\partial \mathbf{u}_{m\mu\alpha} \partial \mathbf{u}_{m\mu\beta}} \right\rangle_0 e_{\nu\beta}(k\lambda) \quad (24)$$

$$\left\langle \frac{\partial^2 v_{m\mu, r\rho}}{\partial u_{m\mu\alpha} \partial u_{m\mu\beta}} \right\rangle_0 = \frac{1}{\sqrt{(2\pi)^3 \det F(m\mu, r\rho)}} \int d\mathbf{r} \frac{\partial^2 v(|\mathbf{R}_{m\mu, r\rho} + \mathbf{r}|)}{\partial r_\alpha \partial r_\beta} e^{-\frac{1}{2} \mathbf{r} F^{-1} \mathbf{r}} \quad (25)$$

$$F(m\mu, r\rho)_{\alpha\beta} = \frac{1}{N} \sum_{\mathbf{k}\lambda} \frac{\hbar}{\sqrt{M_\mu M_\rho}} \operatorname{ctgh} \frac{\hbar\omega_{\mathbf{k}\lambda}}{2kT} e_{\mu\alpha}^*(\mathbf{k}\lambda) \times \left(e_{\mu\beta}(\mathbf{k}\lambda) - e_{\rho\beta}(\mathbf{k}\lambda) e^{i\mathbf{k}\cdot(\mathbf{R}_{r\rho} - \mathbf{R}_{m\mu})} \right) \quad (26)$$

This is the self-consistent harmonic approximation in a form equivalent to that of Gillis (Ref. 26), and will be used as a basis for treating the defect problem.

III. SELF-CONSISTENT PHONONS IN AN IMPERFECT QUANTUM SOLID

We formulate a scheme for computing self-consistent phonons in quantum solids with defects in the expectation of applying it to systems such as solid helium and metallic hydrogen, in which electronic excitations and lattice imperfections are regarded as defects. The first system is of interest in connection with the possibility of energy storage in metastable excited states (Ref. 1). The phonon spectrum for metallic hydrogen was evaluated (Ref. 5) for a perfect crystal at zero temperature. It is important to obtain the temperature-dependent phonon spectrum, including vacancies and interstitials that set in with temperature, and to see how the defects modify the phonon spectrum and affect the lattice stability and, possibly, melting of metallic hydrogen. Moreover, lattice defects are expected to influence the superconducting properties of metallic hydrogen, as will be discussed in Section V. For solid helium the problem is similar to the passage from perfect to imperfect classical solids (for an exhaustive summary see Ref. 7), only that now a quantum solid is being considered. The two types of defects, electronic excitations and lattice imperfections, differ

greatly in their activation energy (20 eV and fraction of an eV, respectively) and hence deserve to be treated differently: The fact that lattice imperfections have low activation energies means that their concentration is greatly temperature-dependent and so requires a statistical-mechanical treatment. This is not so in the case of electronic excitations, which cannot be thermally excited because their effective temperatures are of the order of 10^5 K, enormous compared to the solid-helium temperatures of ≤ 10 K. For this reason we shall treat electronic excitations as fixed, temperature-independent impurities with a random distribution in the solid, characterized only by an average concentration.

A. VARIATIONAL PRINCIPLE

The variational principle for the free energy (Eq. 9) was stated for the canonical ensemble, in which the number of particles was fixed. To allow for a variable number of defects we have to use the grand-canonical ensemble, in which the number of particles (defects in our case) is allowed to vary. The statistical quantities we need are defined as follows (Ref. 27). The grand partition function is

$$Z_G = \text{Tr} e^{-\beta(H - \mu_v N_v - \mu_i N_i)} \quad (27)$$

where Tr means summation over the states as well as over the number of vacancies and interstitials, and μ_v and μ_i are the chemical potentials associated with these defects. The analog to the free energy is the thermodynamic potential Ω

$$\Omega = -kT \ln Z_G \quad (28)$$

while the density matrix, or statistical operator, is given by

$$\begin{aligned} \rho_G &= \frac{1}{Z_G} e^{-\beta(H - \mu_v N_v - \mu_i N_i)} \\ &= e^{\beta(\Omega - H + \mu_v N_v + \mu_i N_i)} \end{aligned}$$

The average number of vacancies, for example, is given by

$$\begin{aligned}
 \langle N_v \rangle = \text{Tr} (N_v \rho_G) &= \frac{\text{Tr} \left[N_v e^{-\beta (H - \mu_v N_v - \mu_i N_i)} \right]}{\text{Tr} \left[e^{-\beta (H - \mu_v N_v - \mu_i N_i)} \right]} \\
 &= \frac{1}{\beta} \frac{\partial}{\partial \mu_v} \ln \text{Tr} e^{-\beta (H - \mu_v N_v - \mu_i N_i)} \\
 &= - \frac{\partial \Omega}{\partial \mu_v}
 \end{aligned}
 \tag{29}$$

and, similarly

$$\langle N_i \rangle = - \frac{\partial \Omega}{\partial \mu_i}
 \tag{30}$$

A variational principle will now be derived by relating the grand canonical to the canonical quantities and using the variational principle for the latter. For a system of N particles we have (Eq. 9):

$$F_N \leq F_{N, \text{trial}} = F_{0, N} + \langle H_N - H_{0, N} \rangle_{0, N}$$

and

$$Z_N = e^{-\beta F_N}$$

The grand partition function is related to the canonical partition function Z_N by

$$e^{-\beta \Omega} = Z_G = \sum_N e^{\beta \mu N} Z_N = \sum_N e^{\beta (\mu N - F_N)}$$

Using the variational upper bound on F_N we have

$$e^{-\beta\Omega} \geq \sum_N e^{-\beta(F_{N, \text{trial}} - \mu N)} \equiv e^{-\beta\Omega_{\text{trial}}}$$

This defines the variational principle for the thermodynamic potential:

$$\begin{aligned} \Omega \leq \Omega_{\text{trial}} &\equiv -\frac{1}{\beta} \ln \sum_N e^{-\beta(F_{N, \text{trial}} - \mu N)} \\ &= -\frac{1}{\beta} \ln \sum_N e^{-\beta \left(F_{0, N} + \langle H_N - H_{0, N} \rangle_{0, N} - \mu N \right)} \end{aligned} \quad (31)$$

In the case of our defect problem, N is the set of numbers of vacancies and interstitials, $N = \{N_v, N_i\}$, and $\mu N = \mu_v N_v + \mu_i N_i$. In what follows Ω_{trial} will be differentiated with respect to phonon frequencies to obtain self-consistent phonons, with respect to effective equilibrium positions to find the lattice relaxation due to defects, and with respect to the chemical potentials to find the defect concentration (Eq. 29).

B. DEFECT HAMILTONIAN

The first step in evaluating the thermodynamic potential is to write down the Hamiltonian of the system in the presence of defects. The Hamiltonian of a perfect crystal is

$$H = \sum_i t_i + \frac{1}{2} \sum_{ij} v_{ij} \quad (i \neq j \text{ in the summation})$$

In the presence of the defects enumerated above (electronic excitations and/or vacancies and interstitials) the Hamiltonian will be modified in two important ways. First, the presence of electronic excitations drastically

changes the interatomic potential between two atoms, one of which at least is excited. The excited sites will be characterized by

$$\sigma_i^{(x)} = \begin{cases} 1 & \text{site } i \text{ excited} \\ 0 & \text{site } i \text{ normal} \end{cases}$$

The modified potential becomes

$$u_{ij} = v_{ij} + \delta v_{ij} \left(\sigma_i^{(x)} + \sigma_j^{(x)} - 2\sigma_i^{(x)} \sigma_j^{(x)} \right) + \delta' v_{ij} \sigma_i^{(x)} \sigma_j^{(x)} \quad (32)$$

where

$$\delta v_{ij} = v_{ij}^{gx} - v_{ij}$$

$$\delta' v_{ij} = v_{ij}^{xx} - v_{ij}$$

v^{gx} is the potential between two atoms, one of which is electronically excited, and v^{xx} is the potential between two electronically excited atoms. For helium, for example, both v^{gx} and v^{xx} are available from extensive quantum-chemical calculations (Refs. 28 and 29). The potential u_{ij} was constructed in such a manner that when one atom is excited $u_{ij} = v_{ij}^{gx}$, and when both are excited $u_{ij} = v_{ij}^{xx}$.

To describe the effect of missing or superfluous atoms we similarly introduce

$$\rho_i^{(v)} = \begin{cases} 1 & i \text{ occupied} \\ 0 & i \text{ vacant} \end{cases}$$

$$\rho_{i'}^{(i)} = \begin{cases} 1 & i' \text{ vacant} \\ 0 & i' \text{ occupied} \end{cases}$$

$$\sigma_i^{(v)} = 1 - \rho_i^{(v)} = \begin{cases} 0 & i \text{ occupied} \\ 1 & i \text{ vacant} \end{cases}$$

$$\sigma_{i'}^{(i)} = 1 - \rho_{i'}^{(i)} = \begin{cases} 0 & i' \text{ vacant} \\ 1 & i' \text{ occupied} \end{cases}$$

The superscripts (v) and (i) stand for vacancies and interstitials, and the primed index runs over interstitial sites. The modified Hamiltonian can be written as

$$H = \sum_i t_i \rho_i^{(v)} + \sum_{i'} t_{i'} \sigma_{i'}^{(i)} + \frac{1}{2} \sum_{ij} u_{ij} \rho_i^{(v)} \rho_j^{(v)}$$

$$+ \frac{1}{2} \sum_{i'j'} u_{i'j'} \sigma_{i'}^{(i)} \sigma_{j'}^{(i)} + \frac{1}{2} \sum_{ij'} u_{ij'} \rho_i^{(v)} \sigma_{j'}^{(i)} + \frac{1}{2} \sum_{i'j} u_{i'j} \sigma_{i'}^{(i)} \rho_j^{(v)}$$

The first two terms are the kinetic energies of the occupied regular sites and of the interstitial sites, respectively. The third term is the potential energy between the regular sites and the fourth term between two interstitials. The last two terms describe the potential between one regular site and an interstitial, and are obviously equal to each other. This way of writing the Hamiltonian is very similar to that of Aksenov (Ref. 9), who treats vacancies in quantum solids. Our work differs from his in three important aspects. First, he considers vacancies only, and no interstitials. Secondly, he uses the canonical distribution throughout, while it seems to us essential to use the grand-canonic ensemble when the number of particles varies. Third, Aksenov does not include lattice relaxation around defects that can be incorporated in our formalism. Such lattice relaxation effects are expected to be very important in solid helium.

We next express the ρ 's in the Hamiltonian in terms of the corresponding σ 's and partition the Hamiltonian into lattice and defect parts:

$$H = H_{\text{latt}} + H_{\text{def}} \quad (33)$$

$$H_{\text{latt}} = \sum_i t_i + \frac{1}{2} \sum_{ij} u_{ij} \quad (34)$$

$$H_{\text{def}} = \sum_{i'} t_{i'} \sigma_{i'}^{(i)} - \sum_i t_i \sigma_i^{(v)} + \frac{1}{2} \sum_{i'j'} u_{i'j'} \sigma_{i'}^{(i)} \sigma_{j'}^{(i)} \\ + \sum_{ij'} u_{ij'} \left(1 - \sigma_i^{(v)} \right) \sigma_{j'}^{(i)} - \frac{1}{2} \sum_{ij} u_{ij} \left(\sigma_i^{(v)} + \sigma_j^{(v)} - \sigma_i^{(v)} \sigma_j^{(v)} \right) \quad (35)$$

The defect Hamiltonian is the σ -dependent part of the Hamiltonian and obviously vanishes for $\sigma = 0$, i. e., in the absence of defects.

In the variational principle (Eq. 31) we choose as H_0 the harmonic part of the lattice Hamiltonian, so that

$$\langle H - H_0 \rangle_0 = \langle H_{\text{latt}} - H_0 \rangle_0 + \langle H_{\text{def}} \rangle_0 \quad (36)$$

The "perturbation" Hamiltonian consists of two parts, the effective anharmonicity of the perfect crystal and the average defect Hamiltonian. As we will see, the first term contains the self-consistent phonons previously derived, as well as the modification due to electronic excitations (through the modification of the potential, Eq. 32). The second term contains the effect of vacancies and interstitials. The average in $\langle H_{\text{def}} \rangle$ consists of two parts, the average of the kinetic and potential energy operators over the density matrix of harmonic oscillators, and the summations of the linear and quadratic terms in the σ 's over N_v and N_i . As a result we have

$$\langle H_{\text{def}} \rangle = (\sigma^{(i)} - \sigma^{(v)}) \langle T \rangle + \frac{1}{2} \sigma^{(i)2} \sum_{i'j'} \langle u_{i'j'} \rangle + \sigma^{(i)} (1 - \sigma^{(v)}) \sum_{ij'} \langle u_{ij'} \rangle - \frac{1}{2} \sigma^{(v)} (2 - \sigma^{(v)}) \sum_{ij} \langle u_{ij} \rangle \quad (37)$$

where $\sigma^{(v)}$ and $\sigma^{(i)}$ are the average vacancy and interstitial concentrations.

It should be pointed out that in passing from H_{def} to $\langle H_{\text{def}} \rangle$ one obtains a translationally invariant defect Hamiltonian, thereby suppressing all information about the localized nature of the defect. A more rigorous description of a finite defect concentration would be provided by a scheme such as the coherent potential approximation. The discussion in Subsection C below is kept general in that translational invariance of the lattice is not assumed. Calculations will be carried out in the low-defect concentration approximation when only linear terms in $\sigma^{(v)}$ and $\sigma^{(i)}$ are retained

$$\left. \begin{aligned} \langle H_{\text{def}} \rangle &\cong (\sigma^{(i)} - \sigma^{(v)}) \langle T \rangle + \sigma^{(i)} \sum_{ij'} \langle u_{ij'} \rangle - \sigma^{(v)} \sum_{ij} \langle u_{ij} \rangle \\ &= \frac{N_i - N_v}{N} \langle T \rangle + \frac{N_i}{N} \sum_{ij'} \langle u_{ij'} \rangle - \frac{N_v}{N} \sum_{ij} \langle u_{ij} \rangle \end{aligned} \right\} \quad (38)$$

This form is next substituted in the variational principle, Eq. (31), resulting in

$$\begin{aligned}
 \Omega_{\text{trial}} &= -\beta^{-1} \ln \sum_{N_v, N_i} e^{-\beta(F_0 + \langle H_{\text{latt}} - H_0 \rangle)} e^{-\beta N_i \left(\frac{\langle T \rangle}{N} + \frac{1}{N} \sum \langle u_{ij} \rangle - \mu_i \right)} \\
 &\quad \times e^{\beta N_v \left(\frac{\langle T \rangle}{N} + \frac{1}{N} \sum_{ij} \langle u_{ij} \rangle + \mu_v \right)} \\
 &= F_0 + \langle H_{\text{latt}} - H_0 \rangle + \beta^{-1} \ln \left[1 - e^{-\beta \left(\frac{\langle T \rangle}{N} + \frac{1}{N} \sum_{ij'} \langle u_{ij'} \rangle - \mu_i \right)} \right] \\
 &\quad + \beta^{-1} \ln \left[1 - e^{\beta \left(\frac{\langle T \rangle}{N} + \frac{1}{N} \sum_{ij} \langle u_{ij} \rangle + \mu_v \right)} \right]
 \end{aligned} \tag{39}$$

This derivation seems somewhat inconsistent. On the one hand, only linear terms in N_v and N_i were retained due to the assumption of few defects. On the other hand, the summation was performed over all values, from 0 to ∞ , using the well-known sum of a geometric progression. In the Appendix we start from the total defect Hamiltonian Eq. (37) rather than Eq. (38), derive an integral representation for the trial thermodynamic potential, and show that in cases of interest to us the result reduces to Eq. (38).

The first two terms in Eq. (38) describe the variational free energy of a crystal with some fixed, localized electronic excitation, and will be considered in the next subsection. The last two terms are the contribution of interstitials and vacancies, and will be considered later.

C. ELECTRONIC EXCITATIONS AS DEFECTS

The first two terms in Eq. (39),

$$F_{\text{trial}} = F_0 + \langle U - U_0 \rangle$$

are of the same form as the variational free energy of a perfect crystal.

Denoting the normal modes by ω_ν , we obtain from the previous section, by minimizing the free energy with respect to the normal mode frequencies, the basic equation of lattice dynamics

$$M\omega_\nu^2 = \left\langle \frac{\partial^2 U}{\partial q_\nu \partial q_\nu^*} \right\rangle \quad (40)$$

Despite the formal similarity, Eq. (40) differs from the equation for a perfect crystal in that the potential U is modified close to electronically excited sites, as described by Eq. (32). As a result of different potentials between different pairs of atoms, there is lattice relaxation around the defects. The lattice loses its periodicity, and we can no longer use the translational symmetry to simplify Eq. (40). The normal modes ω_ν differ from those of the perfect crystal, both in their values and in the appearance of localized frequencies not present in the perfect crystal.

The most convenient approach to Eq. (40) is to write U as the perfect crystal potential V plus a correction term, thus enabling one to use the well-known solution of the perfect crystal as a basis for the defect problem (Ref. 7). As we shall shortly see, the correction terms in the resulting equation for the normal modes can be characterized by a defect matrix, consisting of deviations in mass and in force constants (i. e., interatomic forces) from the corresponding values of a perfect crystal. For a quantum solid the first type of defect has been discussed by Varma (Ref. 8), who considered a single isotopic substitution, while we consider here a change in the interatomic potential. Although we expect more drastic effects due to electronic excitations (not unlike bubbles in liquid helium with electronic excitations) than due to an isotopic substitution, the formal approach to both problems is rather similar, as we now proceed to show.

Looking at electronic excitations, we can consider either a single excitation at the origin or a finite concentration of randomly distributed electronic excitations. In the first case the formulation becomes practically

identical to that of Varma (Ref. 8). Of considerably greater practical interest is the second case, which we now examine. By Eq. (32) we can rewrite Eq. (40) in the form

$$M\omega_{\nu}^2 - \left\langle \frac{\partial^2 V}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle = 2\sigma(1 - \sigma) \left\langle \frac{\partial^2 \delta V}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle + \sigma^2 \left\langle \frac{\partial^2 \delta' V}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle \quad (41)$$

where σ is the concentration of electronic excitations. The left-hand side looks like the expression appearing in the perfect crystal equation, but this is not quite the case. The potential is evaluated at relaxed lattice positions, $R_0 + \delta R + u$, where the R_0 are the equilibrium positions of atoms in the undistorted lattice, δR are the lattice relaxation displacements due to the defects considered, and u are the phonon displacements. We can write

$$\begin{aligned} V(R_0 + \delta R + u) &= V(R_0 + u) + V(R_0 + \delta R + u) - V(R_0 + u) \\ &= V(R_0 + u) + \Delta V = V_{nd} + \Delta V \end{aligned}$$

where ΔV is the distortion potential due to lattice relaxation, and V_{nd} is the undistorted lattice potential. Equation (41) can now be written in the form

$$M\omega_{\nu}^2 - \left\langle \frac{\partial^2 V_{nd}}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle = \left\langle \frac{\partial^2 \Delta V}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle + 2\sigma(1 - \sigma) \left\langle \frac{\partial^2 \delta V}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle + \sigma^2 \left\langle \frac{\partial^2 \delta' V}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle \quad (42)$$

It is convenient to transform from normal modes to atomic displacements

$$u_{i\alpha} = \sum_{\nu} T_{i\alpha\nu} q_{\nu}$$

Because of the lattice distortion the $T_{i\alpha\nu}$ do not possess translational symmetry and we cannot introduce polarization vectors, as we did for perfect crystals. The $T_{i\alpha\nu}$ have the orthogonality and closure properties

$$\sum_{i\alpha} T_{i\alpha\nu} T_{i\alpha\nu'}^* = \delta_{\nu\nu'}$$

$$\sum_{\nu} T_{i\alpha\nu} T_{j\beta\nu}^* = \delta_{ij} \delta_{\alpha\beta}$$

The second derivatives in Eq. (42) become

$$\frac{\partial^2}{\partial q_{\nu}^* \partial q_{\nu}} = \sum_{i\alpha, j\beta} T_{i\alpha\nu} T_{j\beta\nu}^* \frac{\partial^2}{\partial u_{i\alpha} \partial u_{j\beta}}$$

Using the orthogonality, Eq. (42) can be rearranged to read

$$-M\omega_{\nu}^2 T_{i\alpha\nu} + \sum_{j\beta} \left\langle \frac{\partial^2 V_{nd}}{\partial u_{i\alpha} \partial u_{j\beta}} \right\rangle T_{j\beta\nu} = \sum_{j\beta} C_{j\beta}^{i\alpha} T_{j\beta\nu} \quad (43)$$

where C is the defect matrix for the problem

$$C_{j\beta}^{i\alpha} = \left\langle \frac{\partial^2}{\partial u_{i\alpha} \partial u_{j\beta}} \left\{ 2\sigma(\sigma - 1) \delta V - \sigma^2 \delta' V - \Delta V \right\} \right\rangle \quad (44)$$

For a vanishing defect matrix the problem reduces to that of a perfect crystal. The defect matrix consists of two parts, one due to the modified interatomic potentials, and the second due to the deviation of the distorted lattice potential from the undistorted one.

Equation (43) is conveniently solved in terms of classical Green functions, defined as solutions to Eq. (43) with the right-hand side replaced by a δ -inhomogeneity,

$$-M\omega_{\nu}^2 g_{l\gamma}^{i\alpha}(\omega_{\nu}) + \sum_{j\beta} \left\langle \frac{\partial^2 v_{nd}}{\partial u_{i\alpha} \partial u_{j\beta}} \right\rangle g_{l\gamma}^{j\beta}(\omega_{\nu}) = \delta_{l\gamma}^{i\alpha}$$

It can be seen, by direct substitution, that the Green functions are given by

$$g_{j\beta}^{i\alpha}(\omega_{\nu}) = \sum_{\mathbf{k}\lambda} \frac{T_{i\alpha}(\mathbf{k}\lambda) T_{j\beta}^*(\mathbf{k}\lambda)}{\omega_{\mathbf{k}\lambda}^2 - \omega_{\nu}^2} \quad (45)$$

where $\omega_{\mathbf{k}\lambda}$ are the normal modes of the perfect crystal, and $T_{i\alpha}(\mathbf{k}\lambda)$ are the corresponding eigenvectors, related to the polarization vectors by

$$T_{i\alpha}(\mathbf{k}\lambda) = \frac{1}{\sqrt{NM}} e_{\alpha}^*(\mathbf{k}\lambda) e^{-i\mathbf{k}\cdot\mathbf{R}}$$

Knowing the Green functions, it can again be verified by direct substitution that the solution to Eq. (43) can be written as

$$T_{i\alpha\nu} = \sum_{\substack{j\beta \\ l\gamma}} g_{j\beta}^{i\alpha}(\omega_{\nu}) C_{l\gamma}^{j\beta} T_{l\gamma\nu}$$

This can be regarded as the matrix equation

$$(1 - g C) T = 0$$

solved by diagonalizing the product of the Green and defect matrices

$$\det \left| \delta_{l\gamma}^{i\alpha} - \sum_{j\beta} g_{j\beta}^{i\alpha}(\omega_{\nu}) C_{l\gamma}^{j\beta} \right| = 0 \quad (46)$$

Unlike the secular equation of a perfect crystal, whose size is determined geometrically by the number of vibrational degrees of freedom per unit cell, the size of this equation is determined physically by the number of neighbors affected by the defect.

Finally, the lattice distortion δR can be determined by varying the free energy with respect to δR :

$$F_{\text{trial}} = F_0 - \langle H_0 \rangle_0 + \langle H_{\text{latt}}(R_0 + \delta R + u) + H_{\text{def}}(R_0 + \delta R + u) \rangle_0$$

Only the last two terms include the lattice distortion, and imposing the condition $\partial F_{\text{trial}} / \partial \delta R = 0$ results in an equation similar to that derived by Varma (Ref. 8).

D. VACANCIES AND INTERSTITIALS

For this problem we have to include the last two terms in Eq. (38) that were not considered so far. The self-consistent phonons will be determined from the condition

$$\frac{\partial \Omega_{\text{trial}}}{\partial \omega_\nu} = 0$$

We conveniently define

$$E_i = e^{-\beta \left(\frac{\langle T \rangle}{N} + \frac{1}{N} \sum_{ij'} \langle u_{ij'} \rangle - \mu_i \right)}$$

$$E_\nu = e^{\beta \left(\frac{\langle T \rangle}{N} + \frac{1}{N} \sum_{ij} \langle u_{ij} \rangle + \mu_\nu \right)}$$

Differentiation gives

$$\begin{aligned} \frac{\partial \Omega_{\text{trial}}}{\partial \omega_{\nu}} &= \frac{\partial F_{\text{trial}}}{\partial \omega_{\nu}} + \frac{E_i}{1 - E_i} \cdot \frac{1}{N} \left(\frac{\partial \langle T \rangle}{\partial \omega_{\nu}} + \frac{\partial}{\partial \omega_{\nu}} \sum_{ij'} \langle u_{ij'} \rangle \right) \\ &\quad - \frac{E_{\nu}}{1 - E_{\nu}} \cdot \frac{1}{N} \left(\frac{\partial \langle T \rangle}{\partial \omega_{\nu}} + \frac{\partial}{\partial \omega_{\nu}} \sum_{ij} \langle u_{ij} \rangle \right) \end{aligned}$$

The derivatives required here are all available in the previous section for the perfect crystal. They are

$$\frac{\partial F_{\text{trial}}}{\partial \omega_{\nu}} = \frac{\hbar}{4} \left(\text{ctgh} \frac{\beta \hbar \omega_{\nu}}{2} + \frac{\beta \hbar \omega_{\nu}}{2} \frac{1}{\sinh^2 \frac{\beta \hbar \omega_{\nu}}{2}} \right) \left(1 - \frac{1}{M \omega_{\nu}^2} \left\langle \frac{\partial^2 U}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle \right)$$

$$\frac{\partial \langle T \rangle}{\partial \omega_{\nu}} = \frac{\hbar}{4} \left(\text{ctgh} \frac{\beta \hbar \omega_{\nu}}{2} - \frac{\beta \hbar \omega_{\nu}}{2} \frac{1}{\sinh^2 \frac{\beta \hbar \omega_{\nu}}{2}} \right)$$

$$\frac{\partial}{\partial \omega_{\nu}} \left\{ \begin{array}{l} \sum_{ij} \langle u_{ij} \rangle \\ \sum_{ij'} \langle u_{ij'} \rangle \end{array} \right. = - \frac{\hbar}{2M \omega_{\nu}^2} \left(\text{ctgh} \frac{\beta \hbar \omega_{\nu}}{2} + \frac{\beta \hbar \omega_{\nu}}{2} \frac{1}{\sinh^2 \frac{\beta \hbar \omega_{\nu}}{2}} \right) \left\langle \frac{\partial^2}{\partial q_{\nu} \partial q_{\nu}^*} \right\rangle \left\{ \begin{array}{l} U \\ U_{\text{int}} \end{array} \right.$$

U_{int} denotes the interaction between regular lattice sites and interstitial sites. Defining the function $\text{sinhc } x = (\sinh x)/x$, we collect and rearrange

all terms. The resulting self-consistent phonon equation in the presence of defects is

$$m\omega_v^2 = \frac{\left\langle \frac{\partial^2 U}{\partial q_v \partial q_v^*} \right\rangle + \frac{2}{N} \left[\frac{E_i}{1 - E_i} \left\langle \frac{\partial^2 U_{\text{int}}}{\partial q_v \partial q_v^*} \right\rangle - \frac{E_v}{1 - E_v} \left\langle \frac{\partial^2 U}{\partial q_v \partial q_v^*} \right\rangle \right]}{1 + \frac{1}{N} \frac{\sinh \beta \hbar \omega_v - 1}{\sinh \beta \hbar \omega_v + 1} \left(\frac{E_i}{1 - E_i} - \frac{E_v}{1 - E_v} \right)} \quad (47)$$

We next evaluate the average number of defects from relations Eqs. (29) and (30):

$$\langle N_v \rangle = - \frac{\partial \Omega_{\text{trial}}}{\partial \mu_v} = \frac{E_v}{1 - E_v} \quad (48)$$

$$\langle N_i \rangle = - \frac{\partial \Omega_{\text{trial}}}{\partial \mu_i} = \frac{E_i}{1 - E_i} \quad (49)$$

Substituting these results into Eq. (47), we can write the self-consistent phonon equation in terms of the vacancy and interstitial concentrations:

$$M\omega_v^2 = \frac{\left\langle \frac{\partial^2 U}{\partial q_v \partial q_v^*} \right\rangle + 2 \left(\sigma^{(i)} \left\langle \frac{\partial^2 U_{\text{int}}}{\partial q_v \partial q_v^*} \right\rangle - \sigma^{(v)} \left\langle \frac{\partial^2 U}{\partial q_v \partial q_v^*} \right\rangle \right)}{1 + (\sigma^{(i)} - \sigma^{(v)}) \frac{\sinh \beta \hbar \omega_v - 1}{\sinh \beta \hbar \omega_v + 1}} \quad (50)$$

$$\approx \left\langle \frac{\partial^2 U}{\partial q_v \partial q_v^*} \right\rangle + \sigma^{(i)} \left[2 \left\langle \frac{\partial^2 U_{\text{int}}}{\partial q_v \partial q_v^*} \right\rangle - \left\langle \frac{\partial^2 U}{\partial q_v \partial q_v^*} \right\rangle \frac{\sinh \beta \hbar \omega_v - 1}{\sinh \beta \hbar \omega_v + 1} \right]$$

$$- \sigma^{(v)} \left[1 + \frac{2}{\sinh \beta \hbar \omega_v + 1} \right] \left\langle \frac{\partial^2 U}{\partial q_v \partial q_v^*} \right\rangle$$

This equation can be treated by the classical Green function technique described in the previous subsection. The quantities appearing here, particularly the defect concentration, depend on the chemical potentials μ_i and μ_v that are not yet determined. One way to determine then is to compare Eq. (48) and Eq. (49) with

$$\langle N_v \rangle = e^{-\Delta E_v/kT}, \quad \langle N_i \rangle = e^{-\Delta E_i/kT}$$

where ΔE_v , ΔE_i are the activation energies of vacancies and interstitials, and thus relate the chemical potentials to the activation energies.

IV. SOLID HELIUM

In this section we discuss the relevance of phonons to the study of electronic excitations in solid helium. Our attention will be exclusively devoted to the 2^3S metastable excitations of helium because only they have a sufficiently long lifetime to be studied conveniently experimentally. In fact, as noted in the Introduction, the long lifetime and the high excitation energy of the $\text{He}(2^3S) \equiv \text{He}^*$ state provide the major motivation for the study of electronically excited helium, for eventual energy-storage applications.

A. MEASUREMENT OF He^* CONCENTRATIONS

An excited atom in the solid-helium lattice can be regarded as a defect or an impurity. As such, it produces a static lattice distortion in its immediate neighborhood and thereby leads to a modification of the phonon spectrum. The lattice distortion is expected to be quite substantial, in analogy to the case of liquid helium where "bubbles" or cavities around excited atoms are known to exist, with estimated bubble radii of the order of 7 \AA , as compared to the mean interatomic distances of about 3.5 \AA (Ref. 30). Both the static lattice distortions and the vibration of normal and excited helium atoms about the distorted equilibrium positions are treated self-consistently, at any temperature, by the formalism of the last section. Knowledge of the phonon spectrum of an imperfect solid-helium crystal,

together with sound attenuation measurements in the crystal, may provide a viable technique for determining the concentration of He* atoms in solid helium, as we shall now discuss.

It is known that the presence of impurities in an otherwise perfect crystal leads to scattering and attenuation of sound waves propagating in the lattice. For sufficiently low-impurity concentrations, attenuation of sound waves is essentially proportional to the impurity concentration, although nonlinearities are expected to complicate matters at higher concentrations. Analogously, by measuring the attenuation characteristics of sound waves in an electronically excited solid-helium crystal, one is expected to obtain information about the excited-state concentration. Experimental techniques for making such measurements on ordinary crystals with impurities are well established. There appear no major obstacles in applying them to solid helium. To interpret sound-attenuation experiments, one must know the effect of excited-state impurities on the propagation of sound waves in solid helium. The work on the phonon properties of solid helium, reported here, is being extended to deal with this problem.

Present experimental techniques for measuring sound attenuation in imperfect crystals are quite accurate and the errors in determining percentage impurity concentrations are of the order of 0.01, for concentrations not exceeding 10%. It is expected that comparable accuracies can be achieved in the solid-helium case. It should be stressed that at present there is no reliable method of estimating excited-state concentrations in solid helium (Ref. 31) and that therefore sound-attenuation techniques are expected to find an important application in this area.

B. DEEXCITATION PROCESSES

According to theoretical estimates (Refs. 32 and 33), an isolated He* atom has a lifetime of some 2.3.h. In a solid-helium crystal, the lifetime of the He* atom is generally expected to be shorter in view of various perturbations acting on the atom that tend to facilitate its transitions to the ground state. A case where an analysis of lattice perturbation effects has been performed is that of the excited $N^* \equiv N(2p^3 \ ^2D)$ state in a lattice of N₂ molecules (Ref. 34). The results of this analysis show that indeed a rather

drastic reduction of the N^* lifetime is caused by lattice perturbations. The case of solid helium is sufficiently different to require independent considerations, although one might a priori expect lifetime shortening effects here, too.

The mechanisms by means of which an He^* atom may lose its excitation are quite numerous. Some of the more important ones are:

(1) increased spin-orbit mixing (and thereby enhanced radiative decay) caused by the presence of neighboring atoms, (2) He^* migration in the crystal and subsequent "collisional" He^*-He^* deexcitation, (3) formation of He^*-He molecules or other complexes having shorter lifetimes, (4) radiationless deexcitation into phonons, and (5) loss of electronic energy in exciting vacancies and interstitials in solid helium.

To be able to discuss these various processes quantitatively, one must know how electronic excitations modify the static solid-helium lattice and how they couple to the lattice vibrations, i. e., phonons. The formalism presented in Section III has been developed for the purpose of supplying this information. Here we shall briefly outline how the static and dynamic properties of the lattice enter into the calculations of some of the above decay processes.

The fact that an He^* atom has spin 1 and that, apart from spin-orbit terms, the Hamiltonian is spin independent means that the only way He^* in a solid-helium lattice can decay is either by the action of spin-orbit forces or by mutual deexcitation with another He^* atom. Spin-orbit perturbations lead to both radiative and radiationless decays. In the case of radiationless decays the electronic excitation energy of an He^* atom is dumped into phonons to appear ultimately as heat. For energy-storage applications, it is extremely important that such radiationless He^* decays have very low probability. Estimates of matrix elements for these decays, at various temperatures, will be made on the basis of numerical calculations of self-consistent phonons.

Although radiative decays seem to represent another clear-cut loss mechanism of He^* atoms, it must be borne in mind that phonons emitted by the decay of He^* atoms may become trapped or reabsorbed as they propagate through the crystal, so that, effectively, energy is retained in a useful

form. In fact, the photon concept may lose its meaning in a crystal, since photons are known to couple to electronic excitations (or excitons) in crystals to generate new types of excitations, the polaritons (Refs. 35 and 36). To study the various possibilities, a knowledge of the thermally-averaged dielectric properties of solid helium is essential. A calculation of the dielectric constant of solid helium, based on the self-consistent phonon formalism, is being undertaken for this reason.

It is well known that electronic excitations, even the well localized ones, are able to migrate in crystals (see a discussion in Ref. 37). The mechanism for this migration is provided by resonant electronic interaction between neighboring excited and normal atoms. It is expected that in solid helium the migration of 2^3S excitations can well be represented by an effective hopping Hamiltonian with parameters determined by evaluating thermally-averaged matrix elements of the He^*-He exchange interaction. Using this effective Hamiltonian, one should be able to compute the probability of He^*-He^* collisions, for given He^*/He concentration, and thus to estimate the collisional loss rate of He^* atoms, on the assumption that a near-neighbor collision of two He^* atoms is certain to lead to their deexcitation. In experiments with liquid helium, it has been found (Ref. 38) that activation of rotons and the presence of impurities independently tend to inhibit excited bubble collisions and so to lengthen the lifetimes of excited bubbles. It is interesting to speculate about possible ways of inhibiting "bubble" collisions in solid helium.

V. METALLIC HYDROGEN

In all cases where metallic hydrogen is believed to exist, i. e. , in the interior of Jupiter and in shock-wave experiments (Ref. 39), it is found at elevated temperatures, close to or above the melting temperature. Thus, from an experimental point of view, it is important to undertake studies to understand the physical properties of metallic hydrogen at finite, nonzero temperatures. These studies would also constitute a first step for future considerations of liquid metallic hydrogen. In view of the semiquantum nature of metallic hydrogen (Ref. 5), vacancies and interstitials are expected to have a dramatic effect on such properties of metallic hydrogen as lattice stability, melting, and superconductivity, to be discussed next.

A. LATTICE STABILITY AND MELTING

The effect of static vacancies was considered by Aksenov (Ref. 9) who performed some simple model calculations for quantum solids. He obtained phonon softening due to vacancies. Also, in some of his calculations, lattice instability, characterized by at least one of the lattice frequencies becoming imaginary, occurred at vacancy concentrations as low as 5 to 10%. We intend to perform more realistic and complete calculations for metallic hydrogen, including also interstitials and their effect on lattice relaxation. It is known that in some cases (Ref. 40) interstitials cause a much larger lattice relaxation than vacancies, and therefore are of crucial importance in the study of defect effects. Not much is known about the relative importance of vacancies and interstitials in metallic hydrogen, and this will be one of the first questions to be investigated in our studies.

In many solids the lattice instability due to defects occurs at temperatures well above the melting temperature, and so is of no particular consequence. However, in metallic hydrogen there are indications that the situation is quite different. In a recent study of metallic hydrogen, Caron (Ref. 5) estimated a melting defect temperature, defined as the temperature at which the Boltzmann factor of the defect activation energy is of the order of 0.1, corresponding to the maximum volume fraction of defects that the crystal can tolerate before vacancies and interstitials spontaneously recombine. For pressures of the order of the pressure at which a phase transition from molecular to metallic hydrogen is estimated to occur, the melting defect temperatures were found to be comparable to the ordinary melting temperatures of metallic hydrogen derived from other simpler models (Refs. 41 and 42). This implies that in metallic hydrogen the defects may well constitute the primary melting mechanism.

Another aspect of finite-temperature defects is worth noticing. While solid helium is a true quantum solid, metallic hydrogen is probably halfway between a quantum and a classical solid, as noted earlier. As a result, zero-temperature defects are expected to be static, and phonons are probably the only low-temperature excitations. With increasing temperature both the number and mobility of defects increase, and it may be necessary to treat them as another type of excitation, similar to the vacancy waves (or vacancies) in solid helium (Refs. 10 through 13).

B. SUPERCONDUCTIVITY

Metallic hydrogen is believed to be a high-temperature superconductor (Refs. 3 and 4). The available estimates place the superconducting transition temperature T_c in the range 100 to 300 K. However, it should be noted that these estimates have been made on the basis of the simple BCS-type formula and McMillan's subsequent generalization (Ref. 43) for T_c and they do not take into account either finite-temperature effects or the expected modifications caused by defect excitation. Now it is quite well established that defects and impurities in ordinary superconductors often have a drastic effect on T_c , either lowering it (usually) or raising it, and sometimes even causing oscillations in T_c with increasing defect concentration. In any reliable estimate of T_c for metallic hydrogen, it is therefore essential to include the defect effects. A first guess might be that defects cause phonon softening in metallic hydrogen, thereby reducing the Debye temperature and the electron-phonon coupling constant, and thus, by the BCS formula for T_c , lead to a depressed transition temperature. With the detailed phonon spectrum to be evaluated, it will be possible to test this guess and, with the help of a theory of electron-phonon interactions for disordered structures (Ref. 44), to explicitly compute the changes of the superconducting transition temperature caused by the defects.

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APPENDIX

We provide here an integral representation for the variational thermodynamic potential, involving the full defect Hamiltonian (Eq. 37) rather than its linear approximation. Mathematically this involves replacement of the geometric series used in Eq. (39) by a sum of the form

$$\begin{aligned}
 \sum_N e^{-aN - bN^2} &= \sum_N e^{-aN} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2 - 2ibtN} dt \\
 &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dt e^{-t^2} \sum_N e^{(-a - 2i\sqrt{b}t)N} \\
 &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dt e^{-t^2} \cdot \frac{1}{1 - e^{-(a + 2i\sqrt{b}t)}}
 \end{aligned}
 \tag{A-1}$$

or, in real form

$$\frac{2}{\sqrt{\pi}} \int_0^{\infty} dt e^{-t^2} \frac{1 - e^{-a} \cos 2\sqrt{b}t}{1 + e^{-2a} - 2e^{-a} \cos 2\sqrt{b}t}
 \tag{A-2}$$

For $b = 0$ this reduces, of course, to the geometric series.

The thermodynamic potential is slightly more general, as it involves summation over the two variables $N_v = N_1$ and $N_i = N_2$. The preceding procedure can be generalized to

$$\sum_{N_1 N_2} e^{-\sum_{i=1}^2 a_i N_i - \sum_{ij=1}^2 b_{ij} N_i N_j}$$

$$= \sum_{N_1 N_2} \frac{1}{\pi} \int dt_1 dt_2 e^{-t_1^2 - t_2^2} e^{\sum (2\alpha_i t_i + c_i) N_i - 2\gamma t_1 t_2} \quad (\text{A-3a})$$

$$= \frac{1}{\pi} \int dt_1 dt_2 \frac{e^{-(t_1^2 + t_2^2 - 2\gamma t_1 t_2)}}{\left(1 - e^{2\alpha_1 t_1 + c_1}\right) \left(1 - e^{2\alpha_2 t_2 + c_2}\right)} \quad (\text{A-3b})$$

The five constants α_1 , c_1 , and γ can be determined in terms of the five a_i , b_{ij} by performing the t -integration in Eq. (A-3a) and comparing with the original equations. The calculation is straightforward, though somewhat tedious, and gives

$$c_i = -a_i, \quad \gamma = -\frac{b_{12}}{2\sqrt{b_{11}b_{22}}}$$

$$\alpha_1^2 = \frac{b_{12}^2 - 4b_{11}b_{22}}{4b_{22}}, \quad \alpha_2^2 = \frac{b_{12}^2 - 4b_{11}b_{22}}{4b_{11}}$$

Hence,

$$\sum_{N_1, N_2} e^{-\sum_i a_i N_i - \sum_{ij} b_{ij} N_i N_j} = \frac{\sqrt{1 - \frac{b_{12}^2}{4b_{11}b_{22}}}}{\pi} \int_{-\infty}^{\infty} dt_1 dt_2 \frac{e^{-\left(t_1^2 + t_2^2 + \frac{b_{12}}{\sqrt{b_{11}b_{22}}} t_1 t_2\right)}}{\left(1 - e \sqrt{\frac{b_{12}^2 - 4b_{11}b_{22}}{b_{22}}} t_1 - a_1\right) \left(1 - e \sqrt{\frac{b_{12}^2 - 4b_{11}b_{22}}{b_{11}}} t_2 - a_2\right)} \quad (\text{A-4})$$

or, in real form,

$$\frac{\sqrt{1 - \gamma^2}}{\pi} \int_0^{\infty} dt_1 dt_2 e^{-\left(t_1^2 + t_2^2\right)} \left[\frac{(1 - A_1 x_1) (1 - A_2 x_2) \cosh 2\gamma t_1 t_2 - A_1 A_2 y_1 y_2 \sinh 2\gamma t_1 t_2}{(1 - 2A_1 x_1 + A_1^2) (1 - 2A_2 x_2 + A_2^2)} \right]$$

where

$$A_i = e^{-a_i}$$

$$\begin{cases} x_i \\ y_i \end{cases} = \begin{cases} \cos \\ \sin \end{cases} \left(2 \sqrt{b_{ii}(1 - \gamma^2)} t_i \right)$$

Finally, what is the difference between the full expression Eq. (A-2) and the approximate value used in the text for $b = 0$? To answer this, we consider the difference between the two corresponding integrands

$$\frac{1 - e^{-a} \cos 2\sqrt{b} t}{1 + e^{-2a} - e^{-a} \cos 2\sqrt{b} t} - \frac{1}{1 - e^{-a}}$$

$$= \frac{1}{1 - e^{-a}} \cdot \frac{(e^{-a} + e^{-2a})(\cos 2\sqrt{b} t - 1)}{1 + e^{-2a} - 2e^{-a} \cos 2\sqrt{b} t} \equiv \frac{f}{1 - e^{-a}}$$

The approximation is justified if $f \ll 1$. For low temperatures, a (which is proportional to $1/kT$ by Eq. 39) is large and, consequently,

$$f \sim e^{-a} + e^{-2a} \ll 1$$

For high temperatures, b is small (b is obtained from the quadratic terms in the full defect Hamiltonian Eq. (37)), $\cos(2\sqrt{b} t) - 1 \approx -2bt^2$, and the contribution to the integral is again small. This brings us back to the low-defect approximation in which the b_{ij} are neglected from the beginning. If necessary, however, one can start from the more rigorous Eq. (A-4).