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¹⁴Equations (1) and (2) are valid when $r/\lambda > 2.6\kappa^{-1}$. When r/λ is small, the superheating field decreases and the supercooling field increases with decreasing r/λ .^{3,4} As λ increases rapidly with temperature near T_c , r/λ becomes small so that values of κ calculated from (1) and (2), using the observed fields near T_c , are too large. The size effect is more marked in κ_6 than in κ_3 , because the supercooling field H_6 is characteristic of the smaller spheres, whereas the superheating field H_3 is characteristic of the larger spheres.

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THEORY OF THE SELF-CONSISTENT HARMONIC APPROXIMATION WITH APPLICATION TO SOLID NEON

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Mathematical techniques have been described^{1,2} by which one can perform an exact calculation in coordinate space of the matrix elements of a crystal Hamiltonian

$$H = -\frac{1}{2}\lambda^2 \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} V(r_{ij}), \quad (1)$$

between the eigenfunctions $|a; n\rangle$ of a harmonic Hamiltonian³

$$H^{(1)}(a) = \frac{1}{2}\lambda^2 \bar{p}\bar{p} + \frac{1}{2}a^2 \bar{q}\bar{q} \quad (2)$$

appropriate to a crystal of the same symmetry. Here a is a parameter which is essentially a scale factor for the generation of a set of harmonic Hamiltonians whose eigenfunctions and eigenvalues are simply related, $\lambda^2 = \hbar^2 / (m\sigma^2\epsilon)$, and the Mie-Lennard-Jones potential $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ has been used, with σ and ϵ as units of distance and energy, respectively. We will also use

$$V = \frac{1}{2} \sum_{i \neq j} V(r_{ij}).$$

A notation is used in which q is a supervector whose components are the vectors q_i , and the Cartesian components of q_i are denoted by q_i^α .

A similar notation is used for other vectors and matrices. The coordinate of the i th particle is given by r_i and its equilibrium position by R_i , and $q_i = r_i - R_i$.

It was found that $W(a) \equiv \langle a; 0 | H | a; 0 \rangle$ and $E_k^\alpha(a) \equiv \langle a; k | H | a; k^\alpha \rangle - W(a)$ were readily obtained, where $|a; 0\rangle$ is the ground-state eigenfunction of $H^{(1)}(a)$, and $|a; k^\alpha\rangle$ is the state with one phonon of wave vector k , belonging to the α th branch, excited. Thus, a variational calculation can be performed to determine the optimum value a_0 of a and the ground-state energy $W_0(a_0)$ of the crystal. The $E_k^\alpha \equiv E_k^\alpha(a_0)$ then give the phonon spectrum to first order.

In this Letter it will be shown that a logical extension of the calculation described above leads to the construction of a "self-consistent harmonic Hamiltonian" for a crystal, which we shall define as that Hamiltonian

$$H^{(c)} = \frac{1}{2}\lambda^2 \bar{p}\bar{p} + \frac{1}{2}\bar{q}\bar{q} \Phi^{(c)} \quad (3)$$

in which

$$\Phi_{ij}^{(c)\alpha\beta} = \left\langle c, 0 \left| \frac{\partial^2 V}{\partial r_i^\alpha \partial r_j^\beta} \right| c, 0 \right\rangle. \quad (4)$$

This intuitively appealing equation is similar to a result obtained by Nosanow and Werthamer⁴ except, here, the additional feature of self-consistency is present.

By differentiating Eq. (I-64) with respect to

$$G_{ij}^{(c)\alpha\beta} = [(\Phi^{(c)})^{1/2}]_{ij}^{\alpha\beta}$$

one can show, after some matrix manipulation, that the relationship given by Eq. (4) is sufficient to cause the right-hand side of

$$\partial W_0 / \partial G_{ij}^{(c)\alpha\beta} = \frac{1}{4} \delta_{ij}^{\alpha\beta} - \langle c, 0 | q_i^\alpha q_j^\beta V | c, 0 \rangle + \frac{1}{2} (\bar{T} \omega^{-1} T)_{ij}^{\alpha\beta} \langle c, 0 | V | c, 0 \rangle \quad (5)$$

to vanish, where T is the matrix which diagonalizes⁵ $\Phi^{(c)}$. Thus,

$$|c, 0\rangle \propto \exp\{-\frac{1}{2} \bar{q} G^{(c)} q\} \quad (6)$$

is that particular correlated Gaussian wave function which minimizes the expectation value of the true crystal Hamiltonian, and, in this sense, is the optimum harmonic wave function with which one can approximate the ground-state eigenfunction of H . In addition, if b is the nearest-neighbor distance, one can show that $\partial W_0 / \partial b = 0$ is equivalent to

$$\langle c, 0 | \partial V / \partial b | c, 0 \rangle = 0. \quad (7)$$

The approximation of a crystal Hamiltonian by a model harmonic Hamiltonian was first suggested by Born,⁶ and subsequent work along these lines was performed by Hooton.⁷ Equation (7) and a result similar to Eq. (4) but expressed in terms of normal-mode coordinates were obtained by these authors.

Here, because the calculations are performed in coordinate space, simpler expressions are obtained. In addition, straightforward modification of Eq. (I-53) shows that satisfaction of Eq. (4) is also sufficient to produce the result

$$\omega_k^{(c)\alpha} = E_k^{(c)\alpha}. \quad (8)$$

The construction of $H^{(c)}$ is a simple iterative procedure in which a matrix Φ is used in Eq. (2)

to construct $|a, 0\rangle$. Then a_0 is found and a new matrix

$$\Phi_{ij}^{(1)\alpha\beta} = \frac{1}{2} \left(\Phi_{ij}^{\alpha\beta} + \left\langle a_0, 0 \left| \frac{\partial^2 V}{\partial r_i^\alpha \partial r_j^\beta} \right| a_0, 0 \right\rangle \right)$$

is constructed and used to repeat the process.

A calculation following the procedure outlined above has been made for solid neon at 0°K. Certain of the results are shown in Table I. The zeroth iteration results are those from the conventional harmonic approximation and are given for comparison. The self-consistent calculation begins with the first iteration, which is an energy calculation to determine the optimum uncorrelated Gaussian wave function which is then used to compute $W_0^{(1)}$ and $\Phi^{(1)}$. Next, $\Phi^{(1)}$ is used to construct the wave function from which $W_0^{(2)}$ and $\Phi^{(2)}$ are computed, etc. [In the above a superscript (n) was used to indicate values appropriate to the n th iteration.]

This calculation was performed to illustrate certain aspects of the theory and to show that the wave function selected here gives a lower value for W_0 in a variational calculation than was obtained variationally by Bernardes⁸ (-420 cal/mole), Nosanow and Shaw⁹ (-431 cal/mole), and Mullin¹⁰ (-431 cal/mole). The values of the Lennard-Jones parameter were, therefore, taken to be $\epsilon = 50.0 \times 10^{-16}$ erg and $\sigma = 2.74$ Å, in agreement with Refs. 6-8. The energy was

Table I. Results for the ground-state energy W_0 , nearest-neighbor ($\Phi_{01}^{\alpha\alpha}$) and second-nearest-neighbor ($\Phi_{02}^{\alpha\alpha}$) force constants, and longitudinal (c_l) and transverse (c_t) velocities of sound in the [111] direction for solid Ne at 0°K. Other components of the force constants for these two neighbors are easily obtained from the values given here.

Iteration	$-W_0$ (cal/mole)	Φ_{01}^{xx}	Φ_{01}^{zz} (units based on ϵ and σ)	Φ_{02}^{xx}	Φ_{02}^{zz}	c_l (10^5 cm/sec)	c_t
0	462	21.1	0.712	-2.92	0.469	0.969	0.516
1	431	40.6	-1.65	-2.96	0.481	1.48	0.673
2	438	39.8	-1.51	-2.97	0.483	1.41	0.679
3	438	39.7	-1.49	-2.97	0.483	1.41	0.678

Table II. Contributions to $\langle 0|H|0\rangle$ in cal/mole from the kinetic energy K and from terms proportional to the n th derivative of the potential V^n computed with the ground-state eigenfunctions of the self-consistent $|c, 0\rangle$ and the traditional $|h, 0\rangle$ harmonic Hamiltonians.

Term	Computed with	
	$ c, 0\rangle$	$ h, 0\rangle$
K	84.7	62.3
V^0	-586.0	-586.0
V^2	45.8	62.3
V^4	14.5	26.8
V^6	2.6	6.5
V^8	0.5	1.4

not minimized with respect to b , but rather $b = 2.74 \text{ \AA}$ was chosen to agree with the optimum value reported in Ref. 8. Thus, this theory is compared with other theories. A detailed comparison with experiment will be reported in the future. The value of $-W_0$ is in reasonable agreement with the experimental value¹¹ 450 ± 10 cal/mole.

It should be noted that the expectation value of the second derivative of the potential is quite different from the second derivative for nearest neighbors but that second-nearest-neighbor and further force constants are not altered much.

Although space limitations do not permit an adequate discussion of this point, an interesting aspect of the numerical procedure used here is that the contributions to W_0 from terms proportional to various derivatives of the potential V are obtained almost trivially. Contributions to $W_0^{(3)}$ and $W_0^{(0)}$ from these terms as well as the kinetic energy K are shown in Table II.

Note that in $W_0^{(3)}$, $K = V^2 + 2V^4 + 3V^6 + \dots$. The contributions for $W_0^{(0)}$ show clearly that solid neon cannot be treated adequately by the traditional harmonic approximation. Note that $W_0^{(0)}$ as given in Table I equals $K + V^0 + V^2$ here, and that truncation of the Hamiltonian at V^2 results in an error of approximately 35 cal/mole.

One can also show from Eq. (I-54b) that $\langle c; k^\alpha, -k^\beta | H | c, 0 \rangle = 0$. Since these matrix elements would normally give rise to the largest correction in perturbation theory, the eigenfunction of $H(c)$ appears to be a logical set with which to begin perturbation calculations.

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"s-d" EXCHANGE MODEL OF ZERO-BIAS TUNNELING ANOMALIES*

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Anomalies in the tunneling conductance centered at zero bias have been found in several experiments.¹ These studies were performed on a large class of p - n junctions, as well as on junctions composed of normal metals separated by an insulating oxide layer.

In particular, Wyatt has observed² a peak in the conductance, $G(V)$, centered at zero bias in tunneling junctions where Ta or Nb was

separated from Al by a thin oxide layer. Wyatt found that $G(V)$ could be divided into a temperature-independent part $G_0(V)$ and a strongly temperature-dependent part $\Delta G(V) = G(V) - G_0(V)$. $\Delta G(V)/G_0(V)$ varied as $\ln|eV/kT|$ for $eV > kT$, while $\Delta G(0)/G_0(0)$ varied with temperature as $\ln T$. The effect persisted both above and below the superconducting transition temperature, when care was taken to quench the