

Theory of Solid Neon at 0°K

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A quantum-mechanical variational calculation of the energy per particle, the equilibrium nearest-neighbor distance, and the pressure-volume relationship for solid neon at 0°K is performed. Use is made of a Jastrow-type trial wave function, a phenomenological Mie-Lennard-Jones 12-6 potential, and a cluster expansion evaluation of the energy expectation value. It is found that correlation effects are negligible at equilibrium, contrary to the speculations of some authors, and that good agreement with the experimental data can be achieved if one of the interparticle potential parameters, ϵ , is changed by a small amount from its accepted gas-phase value. This parameter change is discussed.

I. INTRODUCTION

THE atoms of the inert gases have closed electronic shells which minimize the importance of the details of their atomic structure in any discussion of the solid phase of these elements. The fact that only the gross properties are significant makes these elements ideal for testing basic principles of quantum mechanics and solid-state theory. Despite the straightforwardness of theoretical treatment, some discrepancies have been found in comparison of theory and experiment. For one, it is found that the predicted cohesive energy of solid neon at 0°K is too small.^{1,2} (One writer³ has predicted a cohesive energy which is in agreement with experiment; we will discuss this result in Sec. IV.)

Some authors^{1,2} have speculated that the disagreement of the theoretical and measured values is caused by correlation effects. We will study this conjecture by using a Jastrow-type trial wave function⁴ in a variational calculation. A cluster expansion will be used to evaluate the energy expectation value. The Mie-Lennard-Jones 12-6 potential is used to describe phenomenologically the electron interaction energy. We will show that correlation effects are negligible in solid neon near the equilibrium density and that theory and experiment can be brought into reasonable agreement by altering a Mie-Lennard-Jones potential parameter value by a small amount.

II. THE SCHRÖDINGER EQUATION AND THE TRIAL WAVE FUNCTION

The Schrödinger equation for both electrons and nuclei of the solid is

$$H\Psi(\mathbf{x}, \mathbf{x}_e) = E\Psi(\mathbf{x}, \mathbf{x}_e), \quad (1)$$

where

$$H = H(\mathbf{x}, \mathbf{p}, \mathbf{x}_e, \mathbf{p}_e) = (1/2m) \sum_i \mathbf{p}_i^2 + (1/2m_e) \sum_j \mathbf{p}_{ej}^2 + U(\mathbf{x}, \mathbf{x}_e), \quad (2)$$

with m , \mathbf{x}_i , \mathbf{p}_i , the mass, position vector, and momentum

operator of the i th nucleus, respectively; m_e , \mathbf{x}_{ej} , \mathbf{p}_{ej} , the mass, position vector, and momentum operator of the j th electron. $U(\mathbf{x}, \mathbf{x}_e)$ is the total electrostatic energy of the system, with the symbol \mathbf{x} , for example, representing the set of vectors $\mathbf{x}_1, \mathbf{x}_2, \dots$. The Born-Oppenheimer approximation⁵ can be applied to Eq. (1) to yield an equation for the nuclear motion alone,

$$[(1/2m) \sum_i \mathbf{p}_i^2 + V(\mathbf{x})]\psi(\mathbf{x}) = E\psi(\mathbf{x}). \quad (3)$$

The wave function $\psi(\mathbf{x})$ is that of the nuclei; $V(\mathbf{x})$ is the electronic energy.

The most widely used form for $V(\mathbf{x})$ is the phenomenological Mie-Lennard-Jones 12-6 potential

$$V(\mathbf{x}) = 4\epsilon \sum_{i < j} [(\sigma/x_{ij})^{12} - (\sigma/x_{ij})^6], \quad (4)$$

where $x_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$. Gas data are normally used to evaluate σ and ϵ .

If we now let

$$\lambda^2 = \hbar^2 / (2m\sigma^2\epsilon), \quad (5)$$

then the combination of Eqs. (3) and (4) gives

$$[-\lambda^2 \sum_i \nabla_i^2 + 4 \sum_{i < j} (x_{ij}^{-12} - x_{ij}^{-6})]\psi(\mathbf{x}) = E\psi(\mathbf{x}), \quad (6)$$

where x_{ij} and E are now dimensionless, i.e., we have made the substitutions $x_{ij}/\sigma \rightarrow x_{ij}$ and $E/\epsilon \rightarrow E$.

Our procedure is to solve Eq. (6) by means of a variational technique. Because of the large repulsive term, x_{ij}^{-12} , in the potential (4), a wave function for the solid must tend to zero when any two nuclei approach closely. One way to provide for this is to approximate the total wave function $\psi(\mathbf{x})$ by a product of single-particle, localized, nonoverlapping wave functions,

$$\psi(\mathbf{x}) = \prod_{i=1}^N \phi(\mathbf{x}_i - \mathbf{R}_i). \quad (7)$$

\mathbf{R}_i is the position of the i th lattice site. Bernardes^{1,3} chose $\phi(\mathbf{x}_i - \mathbf{R}_i)$ to be the wave function of a particle moving freely in a sphere centered at \mathbf{R}_i . The radius

¹ N. Bernardes, Phys. Rev. **112**, 1534 (1958).

² L. H. Nosanow and G. L. Shaw, Phys. Rev. **128**, 546 (1962).

³ N. Bernardes, Phys. Rev. **120**, 807 (1960).

⁴ R. Jastrow, Phys. Rev. **98**, 1479 (1955).

⁵ M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).

of the sphere was used as a variational parameter. In this theory an atom feels a force exerted on it by each of the other atoms, but otherwise its motion is independent or "uncorrelated" with that of the others.

A more realistic wave function is one of the Jastrow-type

$$\psi(\mathbf{x}) = \prod_{i=1}^N \phi(\mathbf{x}_i - \mathbf{R}_i) \prod_{j < k} f(x_{jk}), \quad (8)$$

where

$$\begin{aligned} f(x_{jk}) &\rightarrow 0 & \text{if } x_{jk} &\rightarrow 0 \\ f(x_{jk}) &\rightarrow 1 & \text{if } x_{jk} &\rightarrow \infty. \end{aligned} \quad (9)$$

The factor $f(x_{jk})$ is the "correlation" function. The wave function (8) gives each nucleus a larger effective potential well than (7) since it allows it to move more freely toward and in between neighboring lattice sites. Divergences in the expectation value of $V(\mathbf{x})$ are avoided, even if the $\phi(\mathbf{x}_i - \mathbf{R}_i)$ are overlapping, by the vanishing of $f(x_{jk})$ as $x_{jk} \rightarrow 0$.

As normalized single-particle wave functions we choose

$$\phi(\mathbf{x}_i - \mathbf{R}_i) = (2A/\pi)^{3/4} \exp[-A(\mathbf{x}_i - \mathbf{R}_i)^2], \quad (10)$$

where A is a constant.

We write

$$f(x_{jk}) = \exp[S(j,k)], \quad (11)$$

and take

$$S(j,k) = -\frac{1}{2}(C/x_{jk}^n), \quad (12)$$

where C , n are positive constants. It is clear that our $f(x_{jk})$ satisfies the conditions of Eqs. (9). The constants C , A , and n are variational parameters.

III. THE ENERGY EXPECTATION VALUE AND ITS CLUSTER EXPANSION

The expectation value of the energy is given by

$$E = \frac{\int e^{S\Phi} [-\lambda^2 \sum_i \nabla_i^2 + V(\mathbf{x})] e^{S\Phi} d\mathbf{x}}{\int e^{2S\Phi} d\mathbf{x}}, \quad (13)$$

where $\Phi = \prod_i \phi(\mathbf{x}_i - \mathbf{R}_i)$ is real; $S = \sum_{i < j} S(i,j)$, and $d\mathbf{x} = d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N$. If we integrate by parts we find

$$\int \Phi e^{S\Phi} \nabla_i^2 \Phi e^{S\Phi} d\mathbf{x} = \int e^{2S\Phi} \left\{ \frac{1}{4} \nabla_i^2 (\Phi^2) - (\nabla_i \Phi)^2 \right\} + \frac{1}{2} \Phi^2 \sum_{i(j \neq i)} \nabla_i^2 S(i,j) \} d\mathbf{x}. \quad (14)$$

(See Ref. 6 for details. Note the absence of three-particle terms which occur in earlier Jastrow-type calculations.⁷) For our Gaussian wave functions, the

⁶ H. W. Jackson and E. Feenberg, Ann. Phys. (N. Y.) 15, 266 (1961).

⁷ J. W. Clark and E. Feenberg, Phys. Rev. 113, 388 (1959).

term in square brackets of Eq. (14) becomes simply $(-3A\Phi^2)$. By Eq. (12)

$$\nabla_i^2 S(i,j) = -(C/2)[n(n-1)/x_{ij}^{n+2}]. \quad (15)$$

Thus Eq. (13) becomes

$$E = 3A\lambda^2 N + \frac{\sum_{i < j} \int e^{S\Phi} \tilde{V}(i,j) e^{S\Phi} d\mathbf{x}}{\int e^{2S\Phi} d\mathbf{x}}, \quad (16)$$

where the "effective" two-body potential is

$$\tilde{V}(i,j) = 4(x_{ij}^{-12} + p x_{ij}^{-(n+2)} - x_{ij}^{-6}), \quad (17)$$

with

$$p = (C/8)\lambda^2 n(n-1). \quad (18)$$

We evaluate the matrix elements of \tilde{V}_{ij} in Eq. (16) by means of the cluster expansion technique.⁶⁻⁸ Following the method of Iwamoto and Yamada⁸ we write

$$\frac{\sum_{i < j} \int e^{S\Phi} \tilde{V}(i,j) e^{S\Phi} d\mathbf{x}}{\int e^{2S\Phi} d\mathbf{x}} = \left. \frac{\partial}{\partial \beta} \ln I_N(\beta) \right|_{\beta=0}, \quad (19)$$

where the "generalized normalization integral," $I_N(\beta)$, is defined by

$$I_N(\beta) = \int \exp(2S + \beta \tilde{V}) \Phi^2 d\mathbf{x}, \quad (20)$$

and $\tilde{V} = \sum_{i < j} \tilde{V}(i,j)$. Define the "subnormalization" integrals by

$$I_i = (i|i) \equiv \int \phi^2(\mathbf{x}_1 - \mathbf{R}_i) d\mathbf{x}_1 = 1, \quad (21a)$$

$$\begin{aligned} I_{ij} &= (ij|g(1,2)|ij) \equiv \iint \phi^2(\mathbf{x}_1 - \mathbf{R}_i) \\ &\quad \times \phi^2(\mathbf{x}_2 - \mathbf{R}_j) g(1,2) d\mathbf{x}_1 d\mathbf{x}_2, \end{aligned} \quad (21b)$$

$$I_{ijk} = (ijk|g(1,2)g(2,3)g(3,1)|ijk), \quad (21c)$$

⋮

$$I_{i_1 i_2 \cdots i_m} = (i_1 i_2 \cdots i_m | \prod_{1 \leq \gamma < \delta \leq m} g(\gamma, \delta) | i_1 i_2 \cdots i_m), \quad (21d)$$

where

$$g(\gamma, \delta) = \exp[2S(\gamma, \delta) + \beta \tilde{V}(\gamma, \delta)]. \quad (22)$$

⁸ F. Iwamoto and M. Yamada, Progr. Theoret. Phys. (Kyoto) 17, 543 (1957); 18, 345 (1957).

Using the subnormalization integrals we define the cluster integrals

$$Y_i = I_i, \quad (23a)$$

$$Y_{ij} = I_{ij} - I_i I_j, \quad (23b)$$

$$Y_{ijk} = I_{ijk} - I_{ij} I_k - I_{jk} I_i - I_{ki} I_j - I_i I_j I_k, \quad (23c)$$

etc.

We find

$$Y_i = 1, \quad (24a)$$

$$Y_{ij} = (ij | h(1,2) | ij), \quad (24b)$$

$$Y_{ijk} = (ijk | [h(1,2)h(2,3)h(3,1) + h(1,2)h(3,1) + h(1,2)h(2,3) + h(2,3)h(3,1)] | ijk), \quad (24c)$$

where

$$h(\gamma, \delta) = g(\gamma, \delta) - 1. \quad (25)$$

In Ref. 8 it is shown that

$$I_N(\beta) = \prod_i Y_i e^{G}, \quad (26)$$

where

$$G = \frac{1}{2} \sum'_{i,j} y_{ij} - \frac{1}{4} \sum'_{i,j} y_{ij}^2 - \frac{1}{2} \sum'_{i,j,k} y_{ij} y_{jk} + \frac{1}{6} \sum'_{i,j,k} y_{ijk} + \dots, \quad (27)$$

and, for example, $y_{ij} = Y_{ij}/Y_i Y_j$. The prime on each of the summations of Eq. (27) means omit those terms for which two or more indices are equal. Equation (27) is an expansion in powers of the function $h(\gamma, \delta)$. We will consider only terms with two or fewer factors of $h(\gamma, \delta)$. Those terms symbolized by the dots in Eq. (27) are of higher order in $h(\gamma, \delta)$ than we wish to consider.

We find from Eqs. (16)-(27)

$$\begin{aligned} E = & 3A\lambda^2 N + \frac{1}{2} \sum'_{i,j} (ij | W(1,2) | ij) \\ & - \frac{1}{2} \sum'_{i,j} (ij | W(1,2) | ij) (ij | \eta(1,2) | ij) \\ & - \sum'_{i,j,k} (ij | \eta(1,2) | ij) (jk | W(1,2) | jk) \\ & + \sum'_{i,j,k} (ijk | W(1,2)\eta(1,3) | ijk) + \dots, \quad (28) \end{aligned}$$

where

$$W(\gamma, \delta) = e^{2S(\gamma, \delta)} \tilde{V}(\gamma, \delta), \quad (29)$$

and

$$\eta(\gamma, \delta) = h(\gamma, \delta) |_{\beta=0} = (e^{2S(\gamma, \delta)} - 1). \quad (30)$$

Equation (28) includes terms no higher than first order in the function $\eta(\gamma, \delta)$. Succeeding terms will be higher order in $\eta(\gamma, \delta)$. We will discuss the contribution of such terms later. Note that the new "effective" potential $W(\gamma, \delta)$ contains a factor

$$\exp[2S(\gamma, \delta)] = \exp[-Cx_{\gamma\delta}^{-n}],$$

which insures convergent results for the matrix elements in Eq. (28).

IV. REVIEW OF PREVIOUS THEORETICAL TREATMENTS

Bernardes has made two variational calculations, each of which involves the use of a trial wave function which is a product of single-particle wave functions each spherically symmetric around a lattice site. In his first calculation¹ he found an energy per particle of -420 cal/mole compared to the experimental value of -450 ± 10 cal/mole.⁹ His second calculation³ gave a value of -445 cal/mole in good agreement with experiment. Nosanow and Shaw,² however, have done a Hartree calculation resulting in a theoretical value of -431 cal/mole. They used the same potential parameters, σ and ϵ , in Eq. (4), as did Bernardes. The Hartree technique used by Nosanow and Shaw yields the best result in a variational computation of the energy with a trial wave function which is a product of single-particle wave functions each of which is spherically symmetric about a lattice site. We may speculate that Bernardes' first result does not agree with that of Nosanow and Shaw either because his wave function lacks sufficient variational flexibility or because an expansion he makes does not converge sufficiently rapidly. As he discounts both of these possibilities we are unable to resolve the discrepancy. Bernardes' second calculation leads to an energy which is actually lower than the result of the Hartree technique. Since our results, given in the next section, agree with those of the Hartree technique we are inclined to believe that Bernardes' agreement with experiment is fictitious. Possibly he did not keep a sufficient number of terms in an expansion made in powers of λ .

V. NUMERICAL TECHNIQUES AND RESULTS

As a first approximation we keep only the first two terms of Eq. (28), giving

$$E = 3A\lambda^2 N + \sum_{i < j} (ij | W(1,2) | ij). \quad (31)$$

We have

$$\begin{aligned} (ij | W(1,2) | ij) = & \int \int \phi^2(\mathbf{x}_1 - \mathbf{R}_i) \phi^2(\mathbf{x}_2 - \mathbf{R}_j) \\ & \times W(x_{12}) d\mathbf{x}_1 d\mathbf{x}_2 \\ = & \left(\frac{2A}{\pi}\right)^3 \int \int \exp[-2A(\mathbf{x}_1 - \mathbf{R}_i)^2] \\ & \times \exp[-2A(\mathbf{x}_2 - \mathbf{R}_j)^2] \\ & \times W(x_{12}) d\mathbf{x}_1 d\mathbf{x}_2. \quad (32) \end{aligned}$$

⁹ E. R. Dobbs and G. O. Jones, *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. 20, p. 516.

Let $\mathbf{z}_1 = \mathbf{x}_1 - \mathbf{x}_2$, $\mathbf{z}_2 = \mathbf{x}_2 - \mathbf{R}_i$. Then

$$(ij|W(1,2)|ij) = \left(\frac{2A}{\pi}\right)^3 \int d\mathbf{z}_1 W(|\mathbf{z}_1|) \\ \times \exp[-2A\mathbf{z}_1^2] \int d\mathbf{z}_2 \exp[-4A(\mathbf{z}_2 + \mathbf{R}_{ij})^2] \\ \times \exp[-2A(\mathbf{z}_2^2 + 2\mathbf{z}_1 \cdot \mathbf{z}_2)], \quad (33)$$

with $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. Carrying out the \mathbf{z}_2 integration yields

$$(ij|W(1,2)|ij) = (2A/\pi)^3 \int d\mathbf{z}_1 W(|\mathbf{z}_1|) \\ \times \exp[-A(\mathbf{z}_1 + \mathbf{R}_{ij})^2] \\ = (A/\pi)^{1/2} (1/R_{ij}) \int_0^\infty dz z W(z) \\ \times \{\exp[-A(z - R_{ij})^2] \\ - \exp[-A(z + R_{ij})^2]\}, \quad (34)$$

where $R_{ij} = |\mathbf{R}_{ij}|$ and $z = |\mathbf{z}_1|$.

Our procedure is to choose initial values for n and C and minimize E as a function of A . We then choose a new value for C and again minimize with respect to A . In this way we find the minimum of E as a function of C . The whole procedure is repeated for a second value of n , etc. All of the above is done for various values of the nearest-neighbor distance R until we find the equilibrium or zero pressure nearest-neighbor distance R_0 which is the value of R when E is an absolute minimum. The procedure is greatly simplified by the fact that the energy expectation value has a broad minimum as a function of C and n . The computations were performed numerically using an IBM-7090 computer.

In computing the lattice sums indicated in Eq. (31) we found sufficient accuracy was obtained if we summed over the first sixty "shells" of particles, all particles on a "shell" being a given distance from the particle at the origin. This involved summing over the nearest 3126 neighbors to each nucleus. Values for the numbers of particles on the shells and for the shell distances for the face-centered cubic lattice were taken from Ref. 10.

First we make use of Bernardes' potential constants $\sigma = 2.74 \text{ \AA}$ and $\epsilon = 50.0 \times 10^{-16} \text{ erg}$. (Second virial coefficient gas-phase data give $\sigma = 2.75 \text{ \AA}$, $\epsilon = 49.2 \times 10^{-16} \text{ erg}$.)¹¹ Initially we take the convenient value $n = 10$. We find that the value of C which minimizes the energy at a nearest-neighbor distance near the experimental equilibrium value is less than 10^{-4} . In fact, we find that

the lowest energy value given by Eq. (31) occurs if, in our numerical computations, we set $C = 0$ and begin our integration in Eq. (34) at that value of z for which $\exp[-A(z - R_{ij})^2]$ is negligibly small, say, less than 10^{-5} in comparison with its maximum of unity. Of course, C cannot be precisely zero since then the matrix element $(ij|W(1,2)|ij)$ would diverge. We will describe this situation by saying $C = 0+$.

A good measure of the importance of correlation is the relative size of the term $\rho x_{ij}^{-(n+2)}$ in comparison with the other potential terms in Eq. (17). For $n = 10$, the ratio of this term to x_{ij}^{-12} is $\rho = 90(\lambda^2 C/8) < 10^{-5}$. Because C is so small the result does not depend on the value of n chosen. To demonstrate this statement explicitly we consider the case $n = 4$. Again we find $C = 10^{-4}$ and the ratio of $\rho x_{ij}^{-(n+2)}$ to x_{ij}^{-6} is less than 10^{-6} . Thus we have the important result that near equilibrium correlation effects are negligible in solid neon. Table I summarizes the results.

Because the value of C minimizing the approximate E value of Eq. (31) is small, the neglected terms in the expansion, Eq. (28), do not contribute. To see this consider the matrix element $(ij|\eta(1,2)|ij)$. Using the derivation leading to Eq. (34), we can show

$$(ij|\eta(1,2)|ij) = (A/\pi)^{1/2} (1/R_{ij}) \\ \times \int_0^\infty dz z \{\exp[-Cz^{-n}] - 1\} \{\exp[-A(z - R_{ij})^2] \\ - \exp[-A(z + R_{ij})^2]\}. \quad (35)$$

The factor $\exp[-Cz^{-(n+2)}]$ is unity over the entire range of integration for which the Gaussian functions are appreciable, so that $(ij|\eta(1,2)|ij)$ is essentially zero. Similar arguments hold for the other terms first order in $\eta(\gamma, \delta)$ in Eq. (28). Other terms in the expansion are of even higher order in $\eta(\gamma, \delta)$ and also do not contribute.

TABLE I. Energy expectation value as a function of the variational parameters C and n , using Bernardes' potential constants^a $\sigma = 2.74 \text{ \AA}$, $\epsilon = 50.0 \times 10^{-16} \text{ erg}$. All quantities are expressed in reduced units, length in units of σ , energy in units of ϵ . A_0 is the value of the parameter A which yields the minimum energy per particle, E_0/N , for a given C and n , at a fixed value $R = 1.138$ of the nearest-neighbor distance near equilibrium. (For the sake of comparison we have quoted values of E_0/N to four significant figures. Although we claim only three figure absolute accuracy, the relative accuracy between the values of E_0/N for various values of C is four figures.)

| n | C | A_0 | $-E_0/N$ |
|-----|-----------------|-------|----------|
| 10 | 0+ ^b | 94.0 | 5.984 |
| | 10^{-4} | 94.0 | 5.984 |
| | 10^{-3} | 94.0 | 5.982 |
| | 10^{-2} | 93.6 | 5.968 |
| 4 | 0+ ^b | 94.0 | 5.984 |
| | 10^{-4} | 94.0 | 5.983 |
| | 10^{-3} | 94.0 | 5.980 |
| | 10^{-2} | 93.7 | 5.953 |

^a Reference 1.

^b Explained in Sec. V of text.

¹⁰ J. Hirschfelder, C. Curtis, and R. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons Inc., New York, 1954), p. 1037.

¹¹ J. de Boer, *Physica* 14, 139 (1948).

TABLE II. Comparison of various theoretical results with experiment for the energy per particle $\epsilon E_0/N$ and the equilibrium nearest-neighbor distance σR_0 .

| | Theory $\sigma=2.74 \text{ \AA},$ $\epsilon=50.0 \times 10^{-16} \text{ erg}$ | | | Theory $\sigma=2.75 \text{ \AA},$ $\epsilon=51.7 \times 10^{-16} \text{ erg}$ | | Experiment |
|---------------------------------|---|-----------------------|--------------------------|---|-----------|----------------|
| | Bernardes (Ref. 1) | Bernardes (Ref. 3) | Nosanow-Shaw (Ref. 2) | This work | This work | Refs. 9 and 12 |
| $-\epsilon E_0/N$ (cal/mole) | 420 | 445 ^a | 431 ^b | 431 | 449 | 450±10 |
| σR_0 (\AA) | 3.14 | 3.13 ^a | — | 3.12 | 3.13 | 3.13 |

^a See Sec. IV of text.
^b Computed at the experimental value of R_0 only.

If we transform from our reduced units we find the minimum energy per particle at the equilibrium density to be $\epsilon E_0/N = -431$ cal/mole, in precise agreement with the Hartree computation. This result shows that we do not need additional variational parameters in our wave function. The nearest neighbor distance at equilibrium is found to be $\sigma R_0 = 3.12 \text{ \AA}$ in comparison with the experimental values¹² of 3.13 \AA .

To find the pressure-volume relationship for the solid, we use $P = -\partial E/\partial V$, where P is the pressure, and V the volume. We analytically differentiate Eq. (31) with respect to the nearest-neighbor distance R and use

$$P = -\frac{\partial E}{\partial V} = -\frac{2^{1/2}}{3} \frac{1}{R^2} \frac{\partial E}{\partial R} \quad (36)$$

which holds for the face-centered cubic lattice. In this equation P is expressed in units of ϵ/σ^3 . We find

$$P = (8A/\pi)^{1/2} (1/3R^3) (F_0 - 2AF_1), \quad (37)$$

where

$$F_0 = \sum_{i<j} (1/R_{ij}) \int_0^\infty dz z W(z) \{ \exp[-A(z-R_{ij})^2] - \exp[-A(z+R_{ij})^2] \}, \quad (38)$$

$$F_1 = \sum_{i<j} \int_0^\infty dz z W(z) \{ (z-R_{ij}) \exp[-A(z-R_{ij})^2] - (z+R_{ij}) \exp[-A(z+R_{ij})^2] \}. \quad (39)$$

Given an R value we find that value of A , which minimizes E (with $C=0+$ and $n=10$) and compute the corresponding pressure by Eq. (37). (Note that by taking $C=0+$, we have assumed correlation to be negligible at all pressures.) Our results for Bernardes' σ and ϵ are shown as curve A in Fig. 1, where we have plotted pressure in kg/cm^2 versus V/V_0 , V_0 being the molar volume at equilibrium. The dots are the experimental data of Stewart.¹³ We note that there is some disagreement between curve A and the experimental points in contrast to the good agreement each of

Bernardes' calculations give. (Bernardes' curves are not shown in Fig. 1.)

The question arises concerning the possibility of obtaining agreement between our theory and all of the experimental data by merely adjusting the potential constants σ and ϵ by a few percent. Consider the values $\sigma=2.75 \text{ \AA}$ and $\epsilon=51.7 \times 10^{-16}$ ergs. The performance of the same operations as described above gives a value of -449 cal/mole for the energy per particle at an equilibrium distance of 3.13 \AA . Table II compares the various theoretical results with experiment. Curve B in Fig. 1 is the resulting P - V relationship which is in good agreement with the data up to about $15 \times 10^3 \text{ kg/cm}^2$. Above that pressure it is possible that correlation effects become nonnegligible. Our discussion of correlation applies only to equilibrium.

VI. DISCUSSION

Our results show that it is possible to explain the properties of solid neon on the basis of a two-body (Mie-Lennard-Jones 12-6) potential and a simple product trial wave function. Correlation effects are

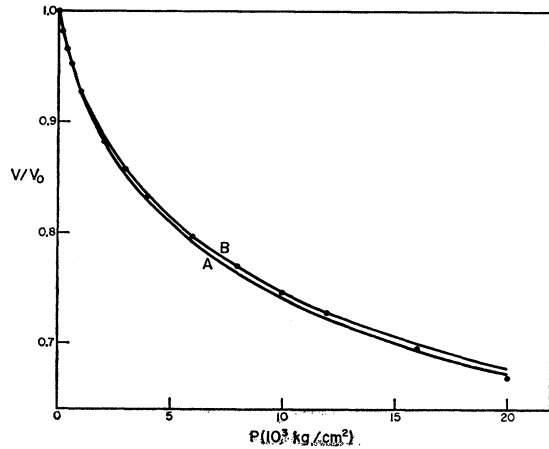


Fig. 1. Pressure-volume relationship for solid neon. The dots are the experimental values of Stewart (Ref. 13). Curves A and B are the theoretical relationships corresponding, respectively, to the potential constants of Bernardes, $\sigma=2.74 \text{ \AA}, \epsilon=50.0 \times 10^{-16} \text{ erg}$, and to those discussed in the text, $\sigma=2.75 \text{ \AA}, \epsilon=51.7 \times 10^{-16} \text{ erg}$.

¹² D. G. Henshaw, Phys. Rev. **111**, 1470 (1958).
¹³ J. W. Stewart, Phys. Chem. Solids **1**, 146 (1956).

negligible at low pressures. The values of the potential constants which give a fit to the data, $\sigma=2.75 \text{ \AA}$, $\epsilon=51.7 \times 10^{-16}$ ergs, differ at most by only a few percent from those given by gas phase data, $\sigma=2.75 \text{ \AA}$, $\epsilon=49.2 \times 10^{-16}$ ergs.

The fact that different constants are needed to explain the gas and solid-phase data of neon should not be at all surprising. The Mie-Lennard-Jones potential is a phenomenological interaction and should be expected to vary somewhat from one type of phenomenon to another.¹⁴ A similar situation occurs, for example, in the treatment of argon. Second virial coefficient data¹⁵ give, $\epsilon=165 \times 10^{-16}$ ergs, gas viscosity data¹⁶ give

¹⁴ See, for example, Ref. 10, p. 208.

¹⁵ E. Whalley and W. G. Schneider, *J. Chem. Phys.* **23**, 1644 (1955).

¹⁶ H. L. Johnston and E. R. Grilly, *J. Phys. Chem.* **46**, 938 (1942).

$\epsilon=171 \times 10^{-16}$ ergs, and crystal data¹⁷ give $\epsilon=169 \times 10^{-16}$ ergs.¹⁸

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¹⁷ C. Domb and I. J. Zucker, *Nature* **178**, 484 (1956).

¹⁸ A small change of potential parameters may not account for the experimental data of the heavier inert gas solids. See the *P-V* data and discussion of C. A. Swenson for xenon [*International Conference on the Physics and Chemistry of High Pressures* (Society of the Chemical Industry, London, June, 1962)]. It may be necessary to include the effects of many-body forces to correlate the properties of solid xenon.

Positronium in a LiH Crystal*

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The question as to whether the existence of a bound positronium-like system in an ionic crystal is energetically possible is considered with particular reference to lithium hydride. The crystal field of LiH is simulated by a potential expressed as a sum of central field potentials centered on the ion sites. An upper bound is obtained for the ground-state energy of a system of an electron and a positron in Coulomb interaction with each other and moving in the crystal potential, and comparison is made with estimates of the energies of the positron and the electron moving independently in the crystal. The result is energetically favorable to the formation and persistence of positronium in the crystal through capture by a positron of an electron from the valence band.

I. INTRODUCTION

CONSIDERATION of possible mechanisms for the annihilation of positrons in ionic crystals gives rise to the question as to whether positronium, or more precisely a positronium-like bound system, can be formed and persist for an appreciable time in such a crystal. This question has formerly, on the basis of qualitative arguments, been answered in the negative.^{1,2} It would appear desirable to reconsider the matter on a more quantitative basis.

In the following, we consider in Sec. II the simulation of the crystal field of LiH by means of a suitable potential. In Sec. III we consider the problem of a system of a positron and an electron in Coulomb interaction moving in the constant periodic potential of the crystal, the potential energy of the positron as a function of position being taken to be simply the negative of that of

the electron. By treating the effect of the crystal field as a perturbation of the Hamiltonian for free positronium, the energy shift of the ground state is calculated to second order of perturbation theory. An improved result is then obtained in the form of an upper bound to the ground-state energy by calculating the average of the Hamiltonian with the aid of a wave function given by perturbation theory. In Sec. IV the procedure used in estimating the ground-state energy of a positron in the crystal field is outlined. In Sec. V use is made of the results obtained in a discussion of the energetics of positronium formation in the crystal. Section VI contains an assessment of the results and their relation to experiment.

II. CRYSTAL POTENTIAL OF LiH

The lithium hydride crystal, being an ionic crystal, has a relatively open structure. We therefore make the approximation of treating the potential as being made up of a sum of spherically symmetric potentials centered on the ion sites. The first problem, then, is to obtain an

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¹ R. A. Ferrell, *Rev. Mod. Phys.* **28**, 308 (1956).

² P. R. Wallace, *Solid State Physics* (Academic Press Inc., New York, 1960), Vol. 10.